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Studies of the influence of physical properties, in particular particle size, on the flow behaviour of emulsions

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STUDIES OF THE INFLUENCE OF PHYSICAL PROPERTIES,
IN PARTICULAR PARTICLE SIZE, ON THE FLOW
BEHAVIOUR OF EMULSIONS.

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Submitted for the Doctor of Philosophy degree of
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SUMMARY

The physical properties of concentrated solid-liquid emulsion systems typical of materials important in the pharmaceutical and cosmetic industries are investigated.

An emulsion is defined as a heterogeneous system consisting of at least one immiscible liquid intimately dispersed in another in the form of droplets. However, it is noted that many industrial oil-in-water emulsions contain high melting point fats and waxes so that the disperse phase is liquid at elevated temperatures but solidifies on cooling. Emulsion properties are reviewed from the literature. It is concluded that emulsification is a random process so that an emulsion contains droplets of varying size. The size distribution is best described by a log-probability relationship. Previous investigators have generally relied upon light microscopy for particle size measurement but since submicron particles are known to exist in some systems this method is of limited application.

Size analysis of a model emulsion using different methods confirmed that the system contained submicron particles and demonstrated that extrapolation techniques are unreliable. It is concluded that no one method is adequate for the measurement of the wide range of particle sizes that can exist in emulsion systems and a combination of centrifugal photosedimentometer and Coulter Counter is suggested. Coulter Counter measurements are shown to be subject to flocculation effects due to the presence of electrolyte and a means of overcoming this is described. The centrifugal photosedimentometer can only be employed using a homogeneous suspension technique which is also described. Repeated analysis of the same sample using

these two instruments suggests that the two methods may be compared, at least over the common range of size. A method of building up a log-probability distribution by a normalisation process is described.

A number of oil-in-water solid-liquid emulsion systems were prepared by varying the type and concentration of the emulsifier. A simple method of ultrasonic emulsification is described which enabled the application of prolonged periods of irradiation. Some of the physical characteristics of the constituent phases of these emulsions were determined. The apparent density of every system was found to be less than the calculated density. Some of the systems contained non-spherical particles and the numbers increased with increased disperse phase ratio. This suggests that the particles are distorted by localised close packing during the solidification stage of the emulsification process.

Emulsion droplets have an interfacial film of finite thickness with properties different from the constituent phases. These properties are probably influenced by the presence of impurities and for this reason materials of commercial grades of purity are employed in this investigation. Concentrated emulsions exhibit complex or non-Newtonian flow behaviour. There is only qualitative agreement on the implied relationship between the disperse phase particle size and the flow behaviour of an emulsion system.

Flow behaviour was measured using a Ferranti-Shirley cone-and-plate viscometer. Most of the flow curves of the emulsion systems exhibited hysteresis. The down curves were fitted in a number of cases by the Williamson equation of pseudoplastic

(iii)

flow but none were fitted by the so-called structure equation of Shangraw, Grim and Mattocks. Using an interactive method of least squares the Williamson equation constants were calculated for the systems under investigation.

Formulation factors are shown to influence the particle size and the flow behaviour of the emulsion systems, in particular the disperse phase ratio and the concentration of the emulsifier. Differences between otherwise similar systems appear to be due to the nature of the emulsifier. The anomaly between apparent and calculated emulsion densities is shown to be consistent with the presence of an interfacial layer which may also account for non-spherical particles occurring in systems of disperse phase ratio well below the theoretical close-packing limit. A simple consideration of flow in terms of mass transfer enabled a relationship between the viscosity at infinite shear rates and particle size parameters to be derived. This appears to be broadly consistent with the experimental data. Alternative theories are considered and particle size, and distribution of size, are shown to be among the most important factors controlling the flow behaviour of emulsions. Some possible future investigations of this problem are outlined.

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CHAPTER ONE

GENERAL INTRODUCTION AND BACKGROUND TO THE STUDY

An emulsion is defined as a heterogeneous system consisting of at least one immiscible liquid intimately dispersed in another in the form of droplets, and is prepared by applying shear to the system in order to reduce the size of the dispersed droplets. There are many characteristics of an emulsion, which differ from those of its individual constituents. For example, mixing two liquids which individually exhibit simple or Newtonian flow behaviour will often result in a product with marked non-Newtonian properties. It is also widely recognised that applying high shear rates to an emulsion product will increase its viscosity. However, the relationship which may exist between droplet size on one hand and flow characteristics on the other is imperfectly understood at present and largely remains at a qualitative level.

Emulsions occur widely in industry, have a variety of industrial applications and often form the desired end-product of a process. Familiar examples are the edible salad dressings and dairy products, cutting oils, insecticidal and pesticidal products, rubber and polymer latices, textile and paper finishes, polishes, paints and the various pharmaceutical creams and lotions. These exemplify the wide variety of types that can exist but it is the pharmaceutical emulsions which are of particular interest since many of them contain high melting point fats or waxes so that the disperse phase is liquid at elevated temperatures but solid at ambient conditions. These preparations are true liquid-liquid emulsions at elevated temperatures when the two phases are mixed and emulsified but cool to solid-liquid dispersions; they therefore combine properties associated with emulsions and with suspensions. To illustrate the frequency of occurrence of this type of preparation, nine of the twelve emulsions in the 1963 British Pharmaceutical Codex fall into this category,

as do forty of the fifty preparations described in a cosmetic formulary issued in 1960 by the Atlas Powder Company. Inevitably each industry has its own specialised requirements but materials as varied as rubber latices, some milk products and wax polishes could also be classified as solid-liquid dispersions although they are **usually regarded as** emulsions in the widest sense.

Industrially, practical problems occur at all stages during the development of an emulsion product. For example, the viscosity of a given formulation may change following the translation of a manufacturing process from a pilot scale batch to a factory batch. Subtle changes in the state of the dispersed phase may also occur on storage and render a product unsatisfactory for use. Certain types of equipment or certain formulation features are recognised as yielding satisfactory products whereas others do not; the exact reasons are less clearly understood.

This present study is concerned with the relationship between the droplet size and the flow behaviour of simple emulsion systems such as are found in the pharmaceutical industry. This may not only lead to a better understanding of the factors that influence emulsion behaviour in general but also indicate possible solutions to practical problems which are applicable to other industrial fields.

CHAPTER TWO

REVIEW OF THE LITERATURE: THE PROPERTIES OF EMULSIONS
AND THE INFLUENCE OF PARTICLE SIZE

- 2.1 Definition of emulsions, their preparation and theories of emulsification
- 2.2 The properties of emulsions
- 2.3 The rheology of emulsions and methods of measurement
- 2.4 The meaning of particle size and methods of measurement
- 2.5 The influence of particle size on viscosity of emulsions and suspensions
- 2.6 Conclusions
- 2.7 Lines of enquiry followed in this study.

2.1 Definition of emulsions, their preparation and theories of emulsification

2.1.1 Definitions and terminology

Becher (23) reviewed the definitions of an emulsion and suggested the following as a basis for discussion:-

"An emulsion is a heterogeneous system, consisting of at least one immiscible liquid intimately dispersed in another in the form of droplets, whose diameters, in general, exceed 0.1 μ . Such systems possess a minimal stability, which may be accentuated by such additives as surface active agents, finely divided solids, etc."

In this present work it is necessary to accept the qualification suggested by McLachlan (303), since one phase can be solid at ambient temperatures although at the time of emulsification the two immiscible phases are liquid. This will be discussed later but Becher's definition is satisfactory on most counts. His limitation on the lower size of the disperse phase particles is clearly not intended to be anything other

than a broad generalisation. Indeed, Becher himself recognised this since in a later section (p. 44) he stated that: "Emulsions are essentially unstable heterogeneous systems; they are partly dispersions, partly colloids"; the use of the term, colloid, inferring sub-micron sizes.

When discussing emulsions it is necessary to clearly distinguish each of the phases present. The phase present in the form of finely divided droplets is called the disperse phase; the phase forming the matrix in which the droplets are suspended, the continuous phase.

Since two immiscible liquids are required to form an emulsion it is generally understood to refer to oil and water; for this reason two distinct emulsion types can be shown to exist depending on which component is the continuous phase. These are by convention oil-in-water (oil the disperse phase) or water-in-oil (water the disperse phase) emulsions, conveniently abbreviated to o/w and w/o respectively. The terminology is often extended to systems in which the phases are not, strictly speaking, either oil or water and becomes inexact when considering multiple emulsions. In this present work, confined to a solid "oil" phase dispersed in an aqueous system, ambiguity cannot arise and the o/w convention will be retained.

Although the systems under investigation are stabilised by surface active agents it is not proposed to discuss these materials in detail since they are adequately dealt with in standard texts (157, 284, 391, 392, 420, 513). A surface active agent will be simply defined as a substance which preferentially migrates to an interface between two phases. Other properties of surface active agents will be discussed where relevant to an understanding of the properties of emulsions or dispersions.

For out of olde felde, as men seith,
Cometh al this newe corn froe yeer to yere;
And out of olde bokes, in good feith,
Cometh al this newe science that men lere.

Chaucer, G.

The Parlement of Foules, 1, 22 (1380)

2.1.2 The preparation of emulsions

Becher (23), Sumner (451) and others (143, 262) have reviewed the types and operation of emulsifying equipment currently available. The types can be classified into those which introduce one liquid into another by means of orifices, by high shear, by ultrasonic techniques or by simple agitation.

(a) Simple agitation

Direct mixing of the two phases is often satisfactory for preparation of emulsions. The equipment is generally of the propeller-type (373) or the paddle and whisk type widely used in the food industry. In many situations simple mixing is also used to prepare crude emulsions before final homogenisation by a high shear method.

(b) High shear methods

These methods include the so-called colloid mills in which the dispersion is sheared between a stator and high-speed rotors of various designs. The rotor, revolving at speeds from 1,000 to 20,000 r.p.m., fits closely to the stator face so that the emulsion must pass through a gap as small as 0.001 inch. The opposing faces may be completely smooth or roughened by a series of concentric or radial corrugations.

(c) Orifice homogenisers

In this type of emulsifier the mixture to be emulsified is forced through a small orifice under very high pressure. Hand operated homogenisers are used in the laboratory and are claimed (322) to be useful for the preparation of standard emulsions. Industrially such homogenisers are used with pumps and have one or two stage valves arranged in tandem. A simple orifice homogeniser consists of two hypodermic syringes connected by a double-hubbed needle, through which the liquids are passed back and forth. This type has a number of advantages for the preparation of small quantities of emulsions under controlled conditions. Some of the factors involved when using

a low pressure capillary homogeniser were investigated by Fox & Shangraw (115).

(d) Ultrasonic emulsifiers

Ultrasonic energy is applied to emulsion systems by means of piezo-electric or magnetostrictive devices. The magnetostrictive transducers overcome the difficulty of obtaining large piezo crystals, thereby enabling application on a larger scale. The best-known example of an industrial ultrasonic emulsifier uses the principle of the organ pipe, the so-called Pohlman "liquid whistle" (263).

2.1.3 Theories of emulsification

All emulsification equipment employs a means of increasing the shear or applying cavitation to a system in turbulent flow. Accordingly it is necessary to consider the fragmentation of liquid droplets under a shear flow, and the break-up of liquid jets. Sir Geoffrey Taylor, in his classical investigations into the formation of emulsions in definable fields of flow, showed clearly that under shear a droplet undergoes distortion, elongates into thread-like filaments and subsequently breaks up into smaller droplets (460, 461). The following figure is typical of a drop breaking up under shear stress.

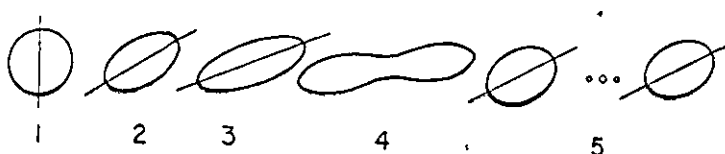


Fig. 2.1 The break-up of a droplet under increasing rates of shear (371)

Rumscheidt & Mason (371) emphasised the fact that simple binary breakage did not always occur so that the breakage mode and, therefore, the size distribution of the daughter droplets are the result of a random process.

Thus, it would seem unlikely that any emulsification process will produce a monosize disperse phase and, indeed, a range of particle sizes must occur.

Stamm (447) suggested that the method of preparation was a primary factor in determining emulsion dispersancy. However, Clay (63) appears to be the first to have drawn attention to another factor influencing the state of dispersion, the growth of particles in an emulsion. In a thorough investigation of the factors involved in the genesis of an emulsion size distribution Clay showed that particles could coalesce by either direct impaction in turbulent flow or by cohesive forces of the type later discussed by Cockbain (65). Vermeulen et al. (383) correlated average droplet size with stirring speed, geometry of the vessel and physical properties utilising this principle. Church & Shinnar (62, 418, 419) demonstrated the coalescence effect, and evaluated various emulsifying machines. Rajagopal (340) proposed a hydrodynamic mechanism for the disruption of the interface between two liquids leading to the basic formation of the disperse phase droplets. Valentas et al. (469, 470) investigated the theoretical aspects of the breakage and coalescence and proposed a mathematical model.

It is therefore surprising to find in the literature statements such as that of Jürgen-Lohmann (202) who claimed that his laboratory homogeniser would prepare essentially mono-disperse emulsions. Martynov (268) showed that a limiting droplet size was achieved after a long period of stirring, an implicit recognition of an equilibrium between the rate of breakage and coalescence. Hüttig (190, 191) recognised that in grinding or emulsification an equilibrium was produced which was independent of the initial particle size. Rodger et al. (364) related the interfacial area of droplets formed by turbulent fluid motion with equipment size. Similarly, Cockton & Wynn (68) evaluated emulsifying equipment and emulsifying agents by determining the number of droplets a unit volume of

oil had been broken into. Marshall & Taylor (264) compared the emulsifying efficiency of a number of machines by assessment of the particle size distribution of the disperse phase.

It is generally agreed that emulsification processes will yield a product with a spread of particle sizes. This was noted by Clayton & Morse (64) and extensively confirmed (62, 331, 348, 393, 418, 448, 449).

2.1.4 Electrostatic emulsification

Although it has been shown that the majority of emulsification methods yield a spread of droplet sizes, a method which could produce a substantially monosize product would have a considerable advantage from the investigational standpoint. This resulted in the suggestion by Nawab & Mason (304) of electrostatic emulsification for experimental purposes.

When a high electrical potential is applied to certain liquids contained in a glass tube ending in a capillary, the liquid issues from the capillary in the form of threads and, under certain conditions, as a highly dispersed aerosol consisting of drops of relatively uniform size. The formation of threads, apparently discovered by George Mathias Bose in 1745, was investigated further by Burton & Hegand (50), Zeleny (520 - 522) and Macky (523). Vonnegut & Neubauer (307, 493) produced streams of uniform droplets about 0.1 mm diameter with potentials of 5 - 10 kv, a.c or d.c. With liquids of low electrical conductivity issuing from a positively charged capillary mono-disperse aerosols with particle radii of 1 μ or less were obtained. Drozin (97) reported that non-polar organic liquids with small electric constants could not be dispersed. However, Nawab & Mason (304) found that a metal capillary enabled a wide variety of non-polar liquids to be dispersed. The technique was claimed to have many advantages for preparing emulsions for research purposes.

Denier, in a French patent (86) issued some nine years prior to Nawab & Mason (loc. cit.), claimed an emulsification process in which oil was passed through hollow needles under a 30 - 200 kv potential; this device does not appear to have been exploited commercially.

Some groups of workers, notably those associated with Higuchi (179, 241) appear to have accepted Nawab & Mason's method uncritically. Wachtel & La Mer (494, 495) stated frankly that it did not work and **produced** charged oil aerosols by means of a Sinclair-La Mer generator. **These** were dispersed in the aqueous phase. The resulting emulsions were claimed to be mono-disperse although the evidence for this claim must be viewed with caution. The method also produces a thoroughly aerated product or foam, a disadvantage for most investigational purposes.

Hendricks (171) and Ryce (375) have continued these investigations. Lindblad & Schneider (346) proposed an alternative method in which a steel capillary tube is tapped with a transducer to set up instabilities in the liquid stream, and produced drops down to 50 μ in diameter. The main problem when preparing an emulsion is that of dispersing the droplets in the continuous phase. Experimentally this has been confirmed by other workers in the field, notably Swift & Friedlander (455). Electrostatic emulsification is not at present a useful experimental technique for preparing mono-size emulsions although this might offer a topic for later investigation.

2.1.5 Ultrasonic emulsification

Using piezo-crystals oscillating at 300,000 cycles/sec Wood & Loomis (517) were the first to show that stable emulsions could be formed when ultrasonic waves passed across an oil/water interface although Richards (345) considered that the action of emulsification was mainly at the walls of the containing vessel. Rogowski & Söllner (365) showed that the appearance of a paraffin oil/water emulsion depended upon the

presence of air as a third component. Later, Söllner & Bondy (31, 32, 445) demonstrated that the mechanism was due to cavitation of dissolved gas bubbles in the system, particles of disperse phase being disrupted when the cavities collapsed, a fact confirmed by Kruger (229).

Morozov (389) stabilised paraffin oil droplets without the use of surface active agents, Bondy & Söllner (31) having earlier suggested that dissolved gases could also act as stabilisers. Freundlich & Gillings (118) used ultrasonics for degassing liquids. Auerbach (11) extended this observation by suggesting that emulsification could be achieved by pumping two liquids through a venturi tube, improving stability by adding surface active agents. He further suggested that high speed impellers also produced emulsification by a cavitation process, a suggestion which seems reasonable following section 2.1.2.

Beal & Skauen (22) investigated the effects of ultrasonic irradiation of an emulsion by a piezo-electric quartz crystal generator and found there was a marked tendency to cause coagulation on prolonged exposure. Singiser & Beal (433) evaluated two other ultrasonic devices, the Pohlmarb "liquid whistle" device noted earlier and a barium titanate tank-type transducer. The former, known as the Minisonic or Rapisonic homogeniser, reviewed by Marshall (262) and McCarthy (295), was extremely efficient (155). The tank-type transducer was less efficient and required gentle stirring to keep the emulsion components in contact.

Ostroski & Stambaugh (318) also considered ultrasonic polymer emulsification to be an improvement over other emulsification procedures although no size analyses were provided in support of this.

Rajagopal (335, 336) studied the particle size distributions of emulsions prepared by ultrasonic emulsification and showed that they were of the same order ($\sim 1 \mu$) as those obtained in colloid mills. He also demonstrated that the effect of continued irradiation was to

increase the mean size of the particles and to broaden the size distribution, presumably due to coalescence following droplet collisions. The situation is probably even more complex. For example, Allinson found (4, 5) that there was a discrepancy between theory and practice when considering the particle size, especially with smaller particles. He suggested that this was due to pulsation of globules which deformed to an ellipsoidal shape but did not disrupt.

From a consideration of the work referred to in the foregoing section it was proposed to utilise ultrasonic irradiation to broaden the shape of the size distribution in emulsions prepared by simple mixing.

2.2 The properties of emulsions

2.2.1 The interface

Since an emulsion is a two-phase system the nature of the interface and adsorbed materials have a considerable influence upon its behaviour.

Hatschek (163) speculated on the presence of an adsorbed layer at the interface and the effect of the thickness of this layer on the viscosity of the dispersion. Later Sibree (424, 425) found he had to increase the allowance for an adsorbed layer, and suggested the presence of a hydrated layer of emulsifier. Sheppard (400) reported that emulsion stability was favoured by the presence of interfacial films. The existence of the interfacial film and its importance in stabilising emulsion systems has been confirmed by others (52, 77, 78, 93, 113, 213, 216, 255, 258, 316, 360).

Some properties of the interfacial film forming between aqueous sodium oleate solution and various oils were investigated by Serrallach & Jones (396) who later (397) made quantitative measurements on the strength of interfacial films by pulling a platinum ring through the oil/water interface. Shotton & White (421, 422) and Münzel & Zwicky (292) extended these investigations to paraffin or olive oil emulsified with acacia or a number of surface active agents.

Accepting for the moment the point made by Osipow et al. (316) that the interfacial film does exist and that it is the principle energy barrier to the coalescence of emulsion droplets, it is useful to enquire into the nature of the film and its thickness.

Stamm (447) and Fischer & Harkins (113) concluded that an expanded monomolecular layer of soap was formed which in time condensed to a rigid condensed layer.

King (213), considering stabilised emulsions, felt that the strength and compactness of the film were the most important factors favouring

stability, a conclusion supported by others (238, 458, 459). The investigations of Schulman and co-workers using monomolecular films spread on the Langmuir balance provided quantitative evidence (388). Water-insoluble materials were spread on solutions of surface active agents and it was noted that some of the substrate solute penetrated into the monolayer. Schulman & Friend (389, 390) found that a definite molecular complex was formed between the insoluble material of the monolayer and the penetrating molecules. When this occurred the complex film withstood greater pressure than either component alone. Pilpel (326) later showed that interaction, and hence some sort of complex formation, occurred between water and any third component normally regarded as an emulsifying agent. Delgado (85) used X-ray methods to investigate the structure of the interfacial emulsion films found with olive and soya bean oils and showed them to be of a complex lipoprotein nature. The significance of the interfacial complexes for emulsion formation was clarified by the work of Schulman & Cockbain (388) who reasoned that if complexes could form at air-water interfaces they could also form at o/w interfaces. They concluded that the conditions for maximum stability of a o/w emulsion were satisfied if the interfacial film was charged, was completely covered with charged molecules and was stable enough to keep the interfacial tension at a minimum. The packing at an interface was found to be densest when a distinct complex film was formed. Mixtures of surface active agents evidently form complexes and much of the confusion apparent in the early literature may well have been due to the presence of trace quantities of impurity which complexed with one or more of the components (for example, free fatty acids and long-chain alcohols in oils from natural sources). Alexander (1, 2) pointed out that adsorption and desorption of stabiliser is much slower than would be predicted from diffusion considerations and this in itself is

indication of complex formation or steric hindrance at the interface.

The viscosities of interfacial films have been measured directly. Using highly purified materials Cockbain & McMullen (66) found that there was no evidence of enhanced viscosity due to molecular interaction between anionic, cationic or non-ionic detergents and oil-soluble surface active materials. Davies & Mayers (84), using an interfacial viscometer, found a very high interfacial viscosity of a mixed film of adsorbed sodium lauryl sulphate and cetyl alcohol. Using essentially the same apparatus as Davies & Mayers, Carless & Hallworth (52) were unable to confirm this result with purified sodium lauryl sulphate, in agreement with Cockbain & McMullen, **but** found an extremely rigid interface with an impure surface active agent and octadecanol. These conclusions all suggest that purified materials may yield different results from the less pure commercial products. Accordingly the materials selected in this present investigation were taken from commercial sources to ensure that the results had some relevance to industrial products.

2.2.2 The thickness of the interfacial film

It was suggested in 1957 that maximum stability was obtained if equimolecular concentrations of surface active agent were present in the oil and water phases and sited at the interface (238, 274, 283), preferably (283) above its critical micelle concentration (CMC). It follows that the interfacial film must have a finite thickness. Hatschek (loc. cit.) included a factor for the thickness of this layer without giving dimensions. van der Waarden (479) concluded that during flow of emulsions all oil droplets, irrespective of size, behave as if they were enveloped by a rigid layer of 30 - 35 Å thickness. van den Tempel (476), investigating the distance between emulsified droplets upon coalescence, found that the droplets were always separated by a water film of at least 100 Å thickness. This film was reduced in thickness by the presence of

electrolytes but the results suggested that other repulsive forces of a steric nature were operative at distances between interfaces of less than 125 \AA . This observation is consistent with the suggestion of Sherman (410) that adsorption of the emulsifying agent occurs at the water-oil interface, resulting in the development of poly-molecular layers when the surface active agent concentration is in excess of its CMC. He also postulated that the disperse phase particles may be linked together by orientated multilayers of emulsifier in concentrated emulsions.

However, experimental investigations of the dimensions of the interfacial film indicate thicknesses sometimes in excess of those suggested above. Kremner & Soskin (227) obtained values in the range of $0.01 - 0.024 \mu$ ($100 - 240 \text{ \AA}$). Figurovskii & Futran (110, 111) found the effective thickness of emulsifier layer in the presence of 0.1% sodium oleate to be $0.25 - 0.3 \mu$, increasing to $0.5 - 0.55 \mu$ with 0.82% sodium oleate. From geometrical considerations Martynov (269) deduced that the thickness of a gelatin film around heptane droplets was between 0.106 and 0.108μ . Rajagopal (334) calculated that an interfacial film up to 100 \AA thick could account for the increased viscosity of small droplets, with a film thickness of up to 2000 \AA for larger sizes. Shotton & White (423) deduced that the film in their acacia-stabilised systems was elastic and up to 0.1μ thick. In the subsequent discussion of this paper Janus mentioned gelatin films of up to 0.17μ thickness which he suggested were highly hydrated. Sherman, in the same discussion, also gives examples of monoglyceride-milk protein complexes of 0.3μ thickness.

Commenting on theoretical approaches to the flow behaviour of suspensions of spherical particles, Mooney & Hermenat (286) found that it was necessary to include a factor for an increase of hydrodynamic volume due to the presence of an adsorbed layer, the nature of which was

not specified. Saunders (379) had to make the same correction when measuring the rheological properties of monodisperse latex systems. Whitmore (507) found that a layer of dispersing agent of at least 100 - 200 Å was necessary to prevent coagulation of polymethyl methacrylate spheres suspended in aqueous solutions, the thickness increasing for smaller particles.

It must therefore be concluded that in most emulsion systems there is a rigid (or almost so) film about 100 Å thick at the oil-water interface which can in some cases make a significant contribution to the behaviour of the emulsions.

2.2.3 The rigidity of emulsion droplets

Emulsions are generally regarded as suspensions of deformable liquid droplets. Many people have found it necessary to take into consideration the viscosity of the internal oil phase, the interfacial film merely transmitting tangential stress from one phase to another. However, this view appears, in practice, to be unrealistic. In 1927 Bond (29) showed that fluid spheres should rise at a velocity $1\frac{1}{2}$ times that of a solid sphere of the same diameter and density according to Stokes' Law. Bond & Newton (30) showed experimentally that drops and bubbles below a certain critical size behaved like rigid spheres. Richardson (347) and Broughton & Squires (43) concluded from viscosity data on stable emulsions that the particles were small enough to behave as rigid spheres. Taylor (460) showed theoretically that circulation patterns would be detectable inside a fluid droplet and this has been confirmed by Mason and his co-workers (20). However, Mason (273) also reported that the presence of an interfacial film induced by impurities or added surface active agents instantly stops internal circulation. Thus, when an interfacial film is present droplets behave as rigid spheres (compare the significance of impurities on the interfacial film,

noted in Section 2.2.1). Nawab & Mason (305), investigating the viscosity of dilute emulsions, found that the behaviour of some systems could be satisfactorily explained if internal circulation existed. Many of their systems, however, behaved like suspensions of rigid spheres. Leviton & Leighton (242) found that Taylor's work could be extended to the viscosity of emulsions of milk fat in skim milk. On the other hand, Sherman (405), investigating concentrated emulsions of various types, concluded that the viscosity of the internal phase was of no significance in most cases.

Sherman (410) summarized the situation by pointing out that if emulsion droplets do behave as rigid spheres, the viscosity (and constitution) of the internal phase does not require consideration. Thus, equations developed for the flow properties of solid suspensions of spherical particles in liquid media (of which there are many) should also be applicable to emulsions.

2.2.4 The shape of emulsion particles

Taylor (460) showed that above a certain size liquid spherical droplets would deform under shear. Swift & Friedlander (455) calculated from Taylor's results that 1 μ droplets of Unity Oil (paraffin oil) would only deform from sphericity at a shear rate in excess of 10^6 sec.^{-1} , concluding that the drops remained spherical for all practical purposes.

The implicit assumption that the disperse phase particles of an emulsion are spherical droplets has been a convenient starting point for many investigations of emulsion systems, such as those of Lawrence & Mills (237). This assumption is not always justified. Axon, in the discussion to his paper (14) suggested that emulsions containing cetylalcohol (similar to those investigated in the current work) tended to have a crystalline appearance if the ratio of cetylalcohol to liquid paraffin was greater than 8 : 5. Winsor (513), describing an emulsion as a dispersion of spherical droplets of one isotropic liquid in another,

extended the definition to include a dispersion of an isotropic liquid in a liquid crystal, or vice versa, and noted that the equilibrium form of the droplets may not always be spherical. Phipps (324), investigating the supercooling behaviour of dispersions of hydrocarbons of high molecular weight, found that the particles were sometimes slightly irregular in shape, whereas glyceride particles were usually uniformly spherical. Similarly Simpson & Cavanagh (431) reported that some of their nitrocellulose lacquer emulsion particles had a wrinkled appearance owing to the rigid nature of the interfacial films. Schulman & Cockbain (388) noted that the water envelopes in w/o emulsions were frequently irregular.

Martynov (271) pointed out that a non-spherical surface may have a lower surface energy than a spherical surface enclosing an equal volume and found that a dodecahedron has a lower energy than spheres of equivalent volume below about 10^{-6} cm radius. An alternative explanation is required to explain the presence of larger polyhedra in concentrated emulsions. This appears to be provided in terms of the "polyhedral drop foams", or honeycombs, described by Manegold (256) in unstable close-packed emulsions with disperse phase ratios in excess of 0.74, the theoretical limiting value for close packing rigid spheres of equal diameter. Lissant (247) extended this idea to a consideration of the geometrical shapes produced by close packing of initially spherical liquid drops in very concentrated systems.

2.2.5 The size of emulsion droplets

From hydrodynamic considerations such as those of Taylor (460) it would be anticipated that there was an upper limit to the size of an emulsion droplet which is imposed by the flow pattern around it, a conclusion drawn by Troesch (466) and confirmed by Hinze (185a). Both these authors gave theoretical formulae for the maximum size likely to

be encountered under a given set of conditions. Kaufman (203a) extended these observations and showed that there are two hydrodynamic regions, from R_e 2000 - 17,600 and 18,000 - 53,000, which yield different values for particle size of various oils in water.

There is however some difficulty when considering the lower limit of particle size which could be encountered in an emulsion system. Part of this difficulty is philosophical in nature and is imposed by, for example, the definition of Becher (23) noted in 2.1.1. To overcome this difficulty it is necessary to agree with the views of Sennett & Olivier (395) who discussed this precise point. They pointed out that the classical, and to some extent current, definition of the colloidal state is in terms of size alone; a lower limit of 10 - 50 Å and an upper of 0.1 - 0.2 μ being generally accepted. The upper limit is arbitrary, as is Becher's lower limit for emulsions, in that it was chosen to coincide with the smallest particles visible with the light microscope. Dispersions smaller than about 1.0 μ are generally considered to be sols and those in excess of this value, suspensions. Whereas these terms are useful for conveying an idea of the particle size, emulsions and suspensions can exhibit colloid properties and should be so treated. Many of the properties associated with colloids such as Brownian movement, diffusion rates and light scattering phenomena are associated with particle size. Other factors such as rheology and stability are a function of the nature and the extent of the surface or fluid interface. The size of colloidal particles is therefore largely an incidental quality except insofar as it affects the degree to which the surface forces are manifested. There is therefore no reason why an emulsion particle should not be small enough to be considered a colloid in classical terminology.

What then is the smallest particle size which is likely to be

encountered in an emulsion system? The ultimate limitation was discussed by Gogoberidze (128) in terms of the dispersed phase vapour pressure. The limiting vapour pressure of a curved surface from the Gibbs-Kelvin Law is that of the atmospheric pressure, and the limiting size of a water droplet was shown to be of the order of 10^{-8} cm. Lewis (244) and others (112, 159, 160) related surface tension and droplet radius of curvature. Cassel (55), discussing thermodynamic adsorption on to curved surfaces, derived an expression similar to that of Gibbs-Kelvin and proposed the idea that emulsions are only stable if the interfacial density of the emulsifying film is greater for larger drops than for those of smaller curvature, suggesting that small particles were unlikely to exist. However, Martynov (269) showed that, because the surface tension of a droplet increases when the radius decreases, the vapour pressure of small droplets must be greater than that calculated from the Kelvin equation. A likely limiting value is therefore between 10^{-6} and 10^{-8} cm radius. Although these relationships apply to spherical particles, i.e., curved surfaces, Walton (51) reported that the Gibbs-Kelvin equation can be applied to polyhedral particles.

From a practical standpoint it should be pointed out that emulsion droplet sizes well below Becher's limit of 0.1μ have been reported in the literature. Droplet diameters in the transparent emulsions investigated by Bowcott & Schulman (33) were of the order of $100 - 500 \text{ \AA}$. Emulsions prepared by van der Waarden (479) had diameters varying between 250 and 900 \AA . Kiyama et al. (217, 218) reported particle sizes in ranges between 80 and $200 \mu\mu$, finding up to 30% w/w below $80 \mu\mu$ in some instances. Lucas (251) found that rubber latex particles were generally below 0.1μ , and chylomicrons have a size range extending down to 150 \AA (26). Schoenholz & Kimball (383) showed that bright-drying wax polish emulsions had particles in the range of $0.05 - 0.1 \mu$, the particle size decreasing

if the emulsifier/wax ratio was increased.

2.2.6 Electrical effects at the oil/water interface

Although evidence for the existence of an interfacial film has been reviewed it is also necessary to consider the presence of an electrical charge on the oil droplet interface. The existence of a surface charge was recognised by Lewis (244) and can arise by ionisation, adsorption or frictional contact. The distinction between ionisation and adsorption becomes blurred when discussing emulsions stabilised by ionisable surface active agents. Although there is little experimental evidence, Becher (23) considered it likely that the charge on non-ionic emulsions arises from frictional contact between the disperse phase and continuous medium. As a rule of thumb measurement, the charge at the particle interface with a cationic emulsifier is positive and with an anionic emulsifier, negative. Nevertheless, as recognised by Helmholtz and modified by others, the layer of charges at the interface must be balanced by others of opposite sign. Stern (450) postulated that the layer was in two parts: one, approximately one ion in thickness, remains fixed to the interfacial surface. In this layer, therefore, there is a sharp drop in potential. The second layer extends some distance into the liquid disperse phase and is diffuse, with a gradual fall off in potential into the bulk of the liquid. The potential at the shear plane, the so-called zeta potential, can be measured by electrophoretic techniques which, in themselves, provide good evidence for the presence and magnitude of the interfacial charge. van den Tempel (475) reported an experimental determination of the Stern layer potential and demonstrated that it was lowered by an increased salt concentration. The magnitude of the charge has considerable influence on aggregation and this observation is important when considering the use of the Coulter Counter. The charge clearly prevents particles of like charge approaching closely

and, although an exact quantitative treatment has proved difficult, Verwey & Overbeek (486), preceded by Derjaguin (87), analysed the problem of the interaction of two double layers. They showed that the total interaction between droplets is the sum of the repulsive electrostatic force and the attractive van der Waals forces. These latter forces, dependent on the polarisability of the molecules comprising the droplet, are only effective over a short distance whereas the electrostatic repulsion has a much longer range effect. A modern picture of the situation taken from one of van den Tempel's recent papers (478) is as follows:-

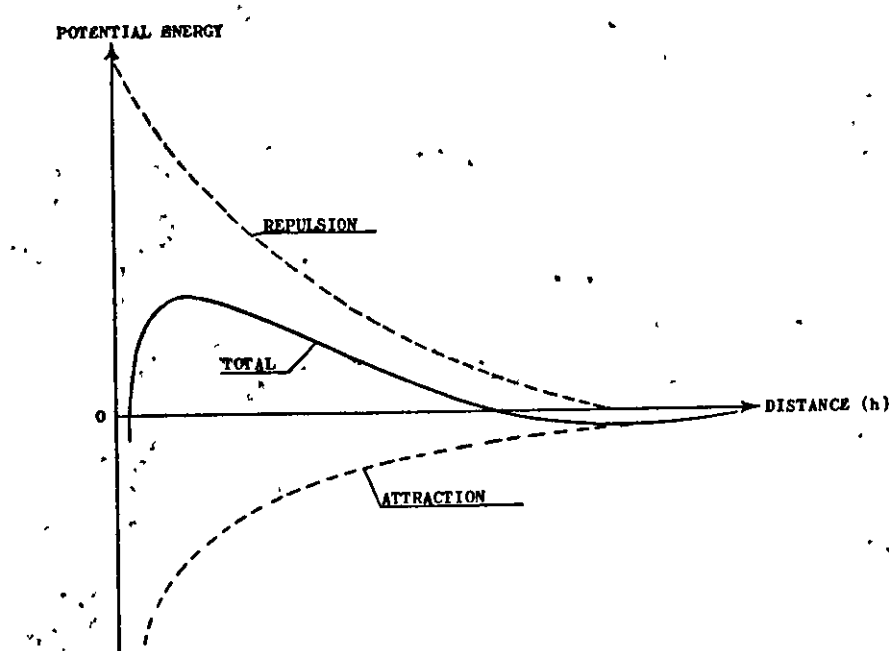


Fig. 2.2 Showing how interaction energy depends on distance between dispersed particles

A shallow minimum in the potential energy curve is generally present at particle separations of the order of several times 10^{-6} cm; this is called the "secondary" minimum to distinguish it from the primary minimum of the potential energy where the distance between the particles

is of atomic dimensions. The depth and position of the secondary minimum are determined by the types of forces operating between the particles. The attraction, determined by the depth of this minimum, results in reversible aggregation where particles in an aggregate are still separated by a thin layer of the continuous phase, and can clearly affect the viscosity of the dispersion.

2.2.7 Coalescence, aggregation and flocculation in emulsions

Although emulsions are inherently thermodynamically unstable systems they can be "stabilised".

The subject of emulsion stability has been reviewed by Becher (23), Garrett (121) and Griffin (143) amongst others. Instability is characterised by droplets coalescing into bigger droplets until, ultimately, the emulsion has separated completely into two phases with a minimum interfacial area between them. During the coalescence process two particles must come sufficiently close for them to cohere, the two interfacial films must rupture and the two oil droplets combine to form a single entity, a process studied by Cockbain & McRoberts (67) and Hill & Knight (185). Brown & Hanson (44) reviewed coalescence during extraction procedures, and drew attention to the formation of secondary droplets during the coalescence process.

Particles may grow bigger by collision-induced coalescence but there is another growth process by diffusive aging. This was considered in detail by Ravdel & Kremnev (341) and Higuchi (177, 178). The process is obviously dependant upon the diffusion coefficient of the solute in the continuous phase. In the case of insoluble non-polar materials such as paraffin oil it is clearly very low but for the volatile materials such as benzene or dibutylphthalate on which the theory has been tested the diffusion coefficient is much higher. This mechanism is emphasised because solid disperse phase emulsions cannot coalesce in the same way

as liquid-liquid systems. The only way the particle size distribution can change, therefore, is by a diffusion process which in the present case must be very slow.

The difference between flocculation and aggregation must be considered to be one of degree, the former being at long interparticle distances (secondary minimum) and the latter being due to van der Waals and London forces. Hence floccules are much more readily broken up by shear forces (344). It seems likely that flocculation is, in fact, the initial stage of "creaming", the particles being drawn together by Brownian movement until they are more tightly packed into aggregates. It could be argued that emulsion systems, especially those showing non-Newtonian flow behaviour, are already flocculated, the measurement of viscosity at low shear rates being an indirect measurement of the strength of the links involved in the formation of floccules (487, 452). Axon (13) maintained that the effect of the emulsifier was simply to cause a difference in the aggregated state of the globules. The idea has been explored by Sherman (410), and investigated in detail for kaolin suspensions by Michaels & Bolger (280, 231).

Mima & Kitamori (282) reported that oil droplets stabilised with acacia were flocculated even in dilute concentrations. The phenomenon was reversible and reached equilibrium floc size distribution rapidly. The flocculation depended on the drop concentration, the size distribution of the primary droplets and the amount of salts present. As might be anticipated from the above consideration, a relationship was found between floc-size and the emulsion stability.

2.2.8 Solid-liquid dispersions

Mention of solid-liquid dispersions has been made previously. It is the term preferred by Phipps (324) to distinguish them from true emulsions, or liquid-liquid dispersions. Discussing emulsions stabilised

by solids, Verwey (484) pointed out that emulsions stabilised by surface active agents tend to become more stable as the interfacial properties of the dispersed droplet approach those of a solid. Many emulsions in modern formularies and pharmacopoeias are, strictly speaking, solid-liquid dispersions. The formulae often contain high melting point fats and waxes such as the long-chain fatty alcohols or paraffin waxes which solidify the oil phase, thereby preventing the droplets from coalescing. Such preparations may still flocculate, aggregate and "cream" but these properties are reversible and may be slowed by increasing the viscosity of the continuous phase or adding suitable surface active agents. However, the fundamental studies of such systems are relatively few at present. Phipps (loc. cit.) studied the supercooling of solid-liquid dispersion systems such as glycerides and higher paraffins and later (325) reported the nucleation behaviour of such systems. The only strictly fundamental study has been that of Hollingshead, Johnson & Pethica (183) who investigated the electrophoretic mobility of octadecanol dispersions in water as a function of pH, salt concentration and temperature. van den Tempel (477) published a theoretical account of the mechanical properties of triglyceride particles dispersed in vegetable oils but this is outside the scope of the present enquiry. Vol'fenzon (492) investigated a w/o system in which the oil phase was solidified with high melting point waxes but this too is not strictly relevant. Griffin (143) gives an account of the practical aspects of solid-liquid dispersions but is mainly empirical in his approach.

However, other solid-liquid dispersions are also considered as emulsions in practice. Bitumens (464), rubber latex (251, 474), wax polishes (383) and polymer emulsions (157, 449) have all received attention.

2.3 The rheology of emulsions and methods of measurement

2.3.1 Newtonian and non-Newtonian flow

Viscosity is defined as the tangential shearing force per unit area that will produce a unit velocity gradient, i.e.,

$$F = \eta \frac{dv}{dr}$$

where F is the shear stress (dynes/cm²) and $\frac{dv}{dr}$ the rate of shear in sec.⁻¹; the proportionality constant η is the coefficient of viscosity in poises (dimensions $ML^{-1}T^{-1}$). A plot of stress vs strain (rate of shear) for a Newtonian material is therefore linear, passing through the origin, with slope = η , as shown in Fig. 2.3 (a). Concentrated dispersions do not obey this simple Newtonian relationship. Characteristic forms of the stress-strain curve are shown in Fig. 2.3 (a) as follows:-

(a) Bingham flow (Plastic flow)

The flow curve is linear but does not pass through the origin, the intercept on the stress axis being known as the yield point. This is considered (265) to result mainly from a network of floccules which requires a definite shearing stress before it can begin to move. Such materials are rare.

(b) Pseudoplastic flow

Unlike Bingham bodies the flow diagrams of pseudoplastic materials show no yield value but pass through the origin. The curve is non-linear and the viscosity is not constant at different rates of shear. Materials characterised by this type of flow are common and it is generally considered to be due to alignment of particles resulting in continuous phase being squeezed out at high shear so that the systems are sometimes called "shear (rate) thinning" (265).

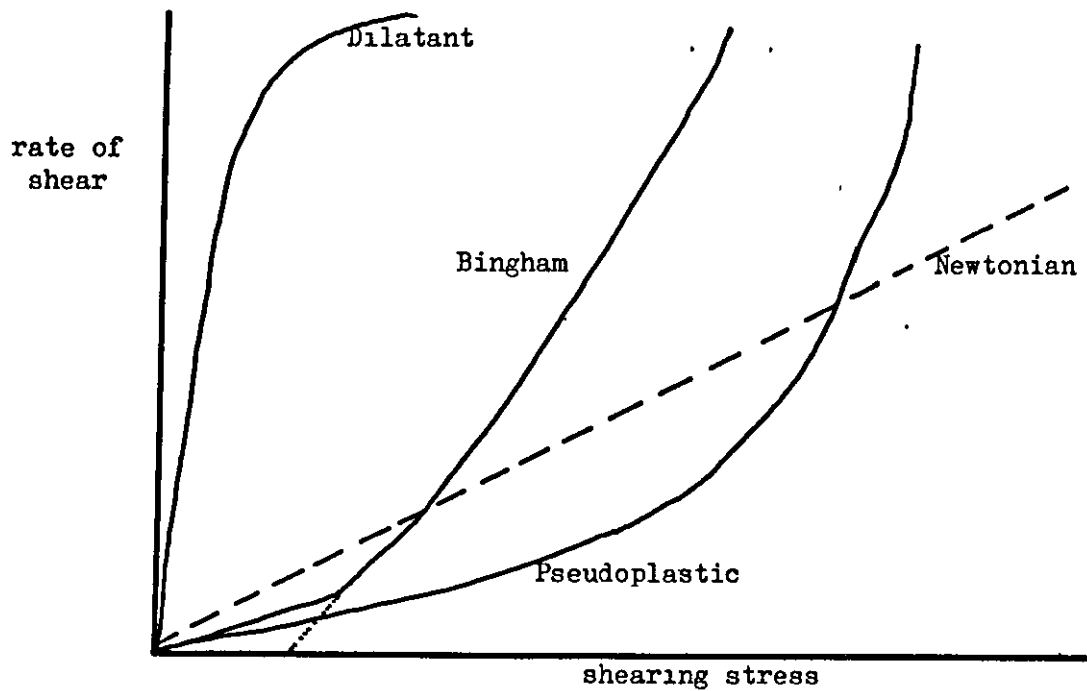


Fig 2.3 (a) TYPES OF FLOW CURVE

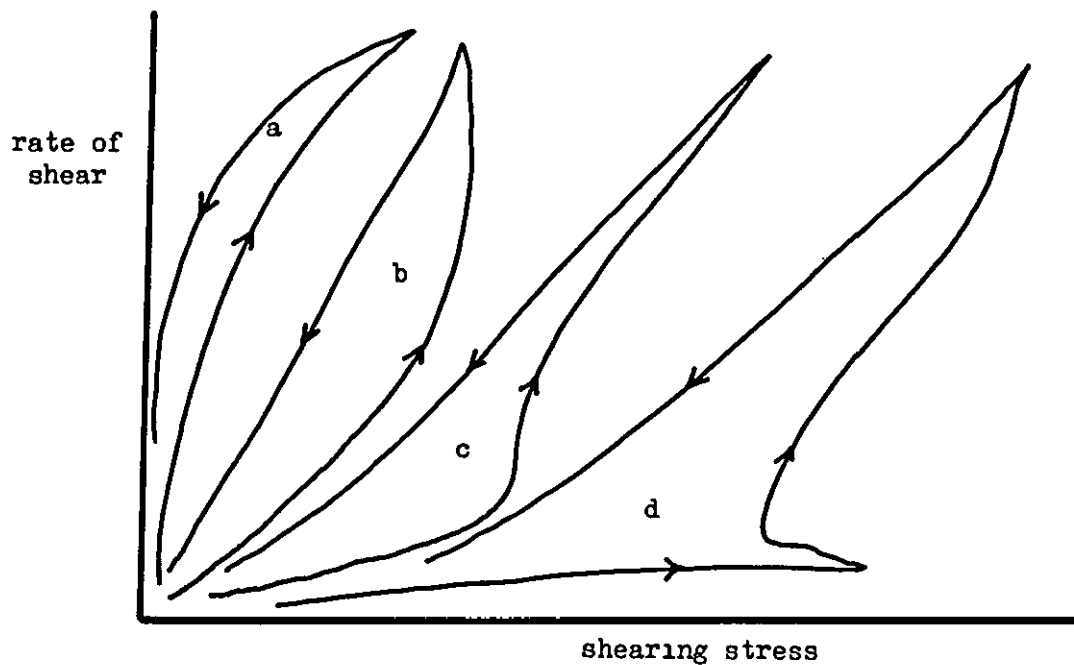


Fig 2.3 (b) FORMS OF HYSTERESIS LOOP OBSERVED

- a. Dilatant material
- b. Bingham body
- c. Upcurve loop shown by 12% aqueous bentonite
- d. Loop and spur shown by 2% aqueous carboxymethylcellulose

(c) Dilatant flow

Dilatant materials exhibit an increase in resistance to flow with increasing shear rate, i.e., "shear thickening". It is demonstrated in concentrated suspensions, especially with large numbers of very fine particles which are deflocculated but tightly packed. It is probably due to the initial expansion of a tightly packed bed which must first take place before movement under stress can occur. Becher (23) observed that this behaviour is apparently rare in emulsions.

2.3.2 Thixotropy

Green (141) described the hysteresis loop occasionally observed in the flow diagram of non-Newtonian materials as thixotropy. Thus the curve of strain vs stress obtained by progressively increasing the stress does not coincide when the stress is gradually decreased, as shown in Fig. 2.3 (b). The hysteresis loop results from a progressive breakdown of a gel-like structure under stress and is sometimes described as a reversible isothermal sol-gel transformation. It is a dynamic process and there seems little doubt that the viscosity relationships for thixotropic materials should be plotted on a three dimensional axis with ordinates of stress, strain and time. Green (loc. cit.) discusses various means of giving a quantitative expression to thixotropy, the most favoured of which is the area of the hysteresis loop (332, 333). However in 1947 Carver & van Wazer (54) described a concentric cylinder viscometer which could be made to suddenly rotate at a constant speed. The photographic traces of time vs force for an aluminium soap solution in petroleum produced a characteristic maximum just after rotation was commenced. From these traces it was deduced that the material had a cross bonded structure which was partially destroyed under shear. van Wazer et al. (481), in a textbook discussed this phenomenon in a qualitative fashion. The following diagram is taken from their book to

show the type of representation which it is felt is more realistic, if a method of measurement could be found:-

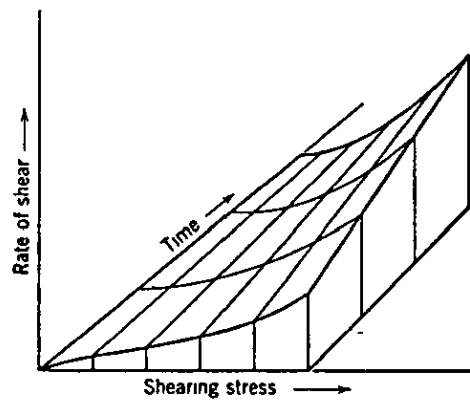


Fig 2.4 A complete flow curve for a rheopectic pseudoplastic liquid at a given temperature and hydrostatic pressure (481)

Cheng (58, 59) investigated the phenomenological characterisation of the rheological behaviour and presented a mathematical definition of thixotropy.

2.3.3 Equations for the characterisation of non-Newtonian flow

In order to treat and investigate non-Newtonian flow it is desirable to be able to reduce the flow curves to mathematical terms.

It is likely that a concentrated emulsion system can be regarded as completely flocculated at rest. As shear forces increase the system is progressively broken down into smaller and smaller floccules until ultimately, at an infinite rate of shear, the primary particles of the system are behaving as individual entities. At each point on the up-curve the floccule size, the number of particles constituting the floccules and the proportion of continuous phase locked away in the centre of the floccule must vary. The down-curve is drawn after the floccule size has been reduced to a minimum and should be amenable to mathematical treatment since many of the variables have been overcome, the system behaving as if it is constituted of individual particles.

The viscosity at infinite shear rates is relevant to direct

particle-particle interactions and will be influenced by the particle size distribution. It is difficult to define infinite shear rates and attempts at direct measurement might also involve breakage of the primary particles. The viscosity at infinite shear rates requires to be calculated by extrapolation of data obtained at lower shear rates using the down-curve as a representative pseudoplastic curve.

A number of empirical equations and several with a theoretical basis have been proposed to describe non-Newtonian flow. Shangraw (398) examined the applicability of these to several sets of shear-stress data and concluded that the Williamson equation (510) provided the best fit of experimental and theoretical data. This equation in linear form is written as:-

$$F = f + \eta_0 \dot{\gamma} + \eta_0 S - sF/S \quad (1)$$

where η_0 is the slope of the tangent, f the intercept on the stress axis, F is the total shearing stress, S the rate of shear and s is a constant which determines the degree of curvature. The constants in this equation, f , s and η_0 have physical meaning. Despite the excellence of fit of the Williamson equation Sheth (416) noted that there were some objections, mainly that the asymptote to the curve appeared to be too far removed from the curve when compared with actual flow curves. Shangraw, Grinn & Mattocks (399) modified Williamson's equation and proposed the so-called Structure Equation:-

$$F = f + b - b_v e^{-as} \quad (2)$$

where b_v = a coefficient of viscoelastic resistance and a is a constant to which the arbitrary value of 0.001 was assigned in order that values of e^{-as} should have a useful magnitude. This relationship was derived from a consideration of data obtained with a suspension of solid

materials in aqueous methylcellulose; its wider applicability does not appear to have been explored further than Sheth's investigation (loc. cit.) into corn oil emulsions in the same vehicle. It will therefore be necessary in this present investigation to determine the applicability of both these equations.

2.3.4 Theories of emulsion structure

Discussing a new method of measuring thixotropy Goodeve & Whitfield (131) advanced the concept of friable links existing between particles of a thixotropic system; links which broke under shear and reformed in the steady state. This theory was developed more fully by Goodeve (129), non-Newtonian viscosity behaviour being considered to consist of two parts, one Newtonian and the other attributed to interference between particles and the formation of links. The particles were considered to be in layers so that when links were stretched and broken a series of impulses (a transfer of momentum) occurred between stationary and mobile layers. The amount of each pulse was shown to be inversely proportional to the rate of shear and the number of impulses (per second) proportional to the rate of shear. The product, the total force due to the links, is therefore independent of the shear rate. There were obvious difficulties with this picture, assuming flow to occur in layers being one, and it takes no account of the heterogeneity of particle size. Goodeve visualised the presence of links of different length and strength but, again, no account of the time factor was attempted.

Williamson (510) anticipated some of the features of Goodeve's theory and his paper makes the first mention of flocculation as a contributory factor. As noted previously, Carver & van Wazer (54) found that they had in part a means of measuring the breakage rate of the particles. van Wazer et al. (481) proposed an equation for pseudoplastic

flow based on these considerations and Cross (81) modified this equation on the assumption that pseudoplastic flow is associated with the formation and rupture of structural linkages. This was also an empirical equation but resembles the theoretical one derived by Oldroyd (313). Gillespie (124, 125) re-examined Goodeve's theory by calculating from kinetic considerations the number of elementary particles in a representative aggregate at a given concentration and found the concept useful. One other useful concept, due to Gillespie (126), which requires mention is that the emulsifier layer must enter into the interaction. Since the distance of separation is small even with spherical particles there must be a definite area of contact, not the point contacts visualised by Goodeve (loc. cit.).

Rebinder (1954) considered thixotropic structures and distinguished between irreversible condensation structures and those which are perfectly reversible to form a thixotropic network.

Takano (1963) has also used a network model in which particles are linked at random by thermal and mechanical links. These were distinguished into two types in the stationary state: the primary links which are elongated without the separation of neighbouring particles in an instant, and the secondary links, which are broken and reformed reversibly in an instant. He took into consideration particle size and the mean free energy of activation for breaking links to calculate the number of interparticle links. The theory, applicable for only very low shear rates ($< 10 \text{ sec}^{-1}$), was explored by Takano & Kimbe (1963) for suspensions of barium sulphate in oils. The value of this otherwise interesting approach was diminished by a failure to define particle size or distribution of size.

Various qualitative expressions of the same theory have been published in recent years. Ford (114), Williams (508, 509), Moore (287), Matsumoto (275 - 278), Vol'fenzon (492) and Bujake (47) have all

interpreted flow curves on emulsions and suspensions in terms of a network structure with reversible time dependent bonds.

2.3.5 The measurement of flow properties

In recent years the methods available for the measurement of viscosity and related flow properties have been reviewed extensively (265, 300, 412, 481).

(a) Types of viscometer

McKennell (481) classified viscometers according to the type of physical measurement employed, the commonest types being as follows:-

- I Measurement of the rate of flow in a capillary or tube
(Ostwald)
- II The rate of motion of a solid through the sample fluid
(Hoeppler)
- III Rotational viscometers
 - (i) Measurement of the torsional couple on a suspended solid element due to the viscous force transmitted through the subject medium by a second element in motion (e.g., coaxial cylinder of Couette type).
 - (ii) Measurement of the rotational velocity of a cylinder or similar element immersed in the fluid (e.g., Stormer viscometer).
 - (iii) Measurement of the reaction torque due to viscous traction on a solid element rotating at a known rate in the fluid. The Ferranti-Shirley and Weissenberg cone-plate viscometers operate on this principle, the rotating element being a disc with a slightly conical face.
- IV Measurement of the damping of a vibrating element immersed in the fluid.

The Bendix Ultraviscoson measures the decrement of free vibrations of a reed oscillating at ultrasonic frequency in the longitudinal mode.

(b) Selection of a viscometer for emulsion systems

As discussed in Sections 2.3.1 and 2.3.2, emulsion systems,

especially when concentrated, demonstrate complex or non-Newtonian flow behaviour. The choice of viscometer is thus limited by this consideration alone since many types such as the falling-sphere and ultrasonic reed viscometers are not suitable for demonstrating pseudoplasticity or thixotropy. Of the other types only the cone-plate viscometer provides uniform shearing conditions throughout the sample. As noted by Sherman (412), the principal practical disadvantage of capillary instruments is their unsuitability for studying the effect of time of shear on viscosity at any given rate of shear, and hysteresis effects, since the sample in the capillary is changing all the time. These criticisms, themselves sufficient to discount use of capillary instruments, are to some extent off-set by the fact that end-effects do not occur; there is no Weissenberg effect (due to normal components of stress) and there are no temperature fluctuations or structure changes brought about by shearing. Sherman's investigations (401 - 411) were, initially at least, carried out on capillary viscometers, mainly because higher shear rates can be achieved than with coaxial instruments, thus extending application to a wider range of flow behaviour.

The measurement of viscosity in a coaxial cylinder instrument results in a torque being transmitted through the test sample to an inner or outer cylinder. The rate of shear therefore varies from a maximum at the rotating cylinder surface to a minimum at the surface of the other cylinder. The rate of shear gradient can be minimised by a suitable design in which the thickness of the sample layer is small. The difficulties have been described by McKennell (481) who also discussed the influence of shear induced heating brought about by shear in the sample fluid. These considerations resulted in the development of cone-plate instruments, typified by the Ferranti-Shirley viscometer and the Weissenberg rheogoniometer.

The essential elements of the cone-plate viscometer are shown in the following

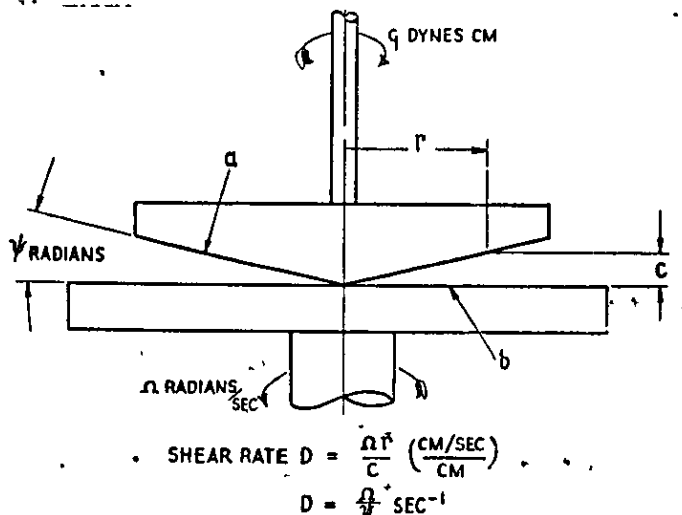


Fig. 2.5 Elements of the cone-plate viscometer (481)

The cone, a, is a slightly conical disc, the apex of which just touches the surface of the flat plate, b. The sample is contained in the narrow gap between the cone and plate (the angle ψ being exaggerated for clarity). The cone is driven at a known speed and, in the case of the Ferranti-Shirley instrument, the torque on the cone is measured by means of a dynamometer. Cone angles down to 0.3° have been used, the smaller angles being preferable since end effects (akin to end effects in the coaxial cylinder viscometer) are reduced to negligible proportions. In addition, shear induced heat is rapidly dissipated and the volume of sample is extremely small, as little as 0.1 ml being required.

(c) Methods of rotating cone-plate viscometers

The means by which the cone is rotated is important when considering the application of a cone-plate viscometer, in particular the meaning of the results obtained from it.

Green (140) was the first to point out that investigations upon time dependent flow properties such as thixotropy required viscosity measurements at smoothly increasing rates of shear. Green noted that the necessity of a gear change whilst increasing the rate of shear could

produce anomalous results for a thixotropic system. He therefore designed a concentric viscometer which McKennel (298) criticised but acknowledged that the drive of the Ferranti-Shirley instrument was designed with Green's comments in mind.

In two current commercial instruments of the cone-plate type (Weissenberg rheogoniometer, Haake Rotavisko) the cone is driven through gears by a motor whereas on the Ferranti instrument the drive is by an electronically controlled motor, providing continuously variable cone speeds up to 1000 r.p.m. With this instrument there is a flat load-torque/speed characteristic; that is, the cone speed is substantially independent of load changes due to variations in viscosity of the sample under shear. There is therefore no necessity to stop the rotation of the cone whilst changing speed and the speed of rotation can be accurately determined from a potentiometer. On the Weissenberg instrument there are small but finite steps in the speed range whilst changing gear and in the Haake viscometer the steps are somewhat greater.

To summarise, from the foregoing considerations the optimum type of design for the investigation of concentrated emulsions would appear to be a shallow cone-plate viscometer, preferably one in which the cone speed is increased by a continuously variable speed drive without the steps associated with the use of a gear box. The only commercial instrument at present available which fits these criteria is the Ferranti-Shirley cone-plate viscometer. This instrument, critically reviewed by Slattery (437) and by van 'tazer et al. (481) although not ideal (176) appears to be better suited for measuring flow properties than other instruments previously employed in this type of investigation.

2.4 The meaning of particle size, and methods of measurement

2.4.1 Particle size distributions

In practice it is rarely found that all the particles in a system under examination have the same size parameter. Accordingly, size measurements on polydisperse particle systems indicate the probability that a given particle picked at random has a specified size. Thus the particle sizes reported for any material are associated with their frequency of occurrence; being the number of particles, or the weight greater or smaller than a stated size, or range of sizes. The purpose of a particle size measurement technique is to discover the true frequency distribution of particle size, either as a number distribution or a weight distribution.

2.4.2 The form of size distribution for emulsion systems

Jellinek (1933) suggested that it was unlikely that emulsions prepared by different methods and with different materials would have similar mathematical forms of distribution. Nevertheless, Herdan (1972) noted that many systems appeared to obey some standard forms of distribution function such as arithmetical or logarithmic forms of normal (Gaussian) distribution, or exponential distributions of the Boltzmann Law type.

The earliest attempt to derive a statistical function of this type was by Rossi (1933) who considered the mechanism of subdivision as a random process. Rossi's model had certain deficiencies which Dobrowsky (94), van den Tempel (474) and Lederer (240) attempted to overcome. Jellinek (1933), however, found that Rossi's equation fitted experimental data for homogenised bitumen except for the largest particles present.

Troesch (466) applied statistical theory to the breakdown of droplets under turbulent flow conditions, and deduced that the droplet size frequency followed a normal Gaussian distribution. Brodnyan (42),

considering emulsion polymerisation processes, found that in some cases radii were distributed normally although in other examples a log normal distribution occurred.

However, a Gaussian distribution is absurd in many ways since it implies that a fraction of the particles, even though a small one, has to be expressed as having negative diameters (449). Cooper (70, 71) found that the Rossi equation (vide supra) appeared to apply only to the main drops in the emulsion. The presence of small daughter droplets always means that the size distribution is skewed and this also applies to a Gaussian plot. However, empirically, one method of removing this skewness (that is, make the distribution more evenly spaced out) is to plot it as a function of the logarithm of the particle size. Kottler (222), in 1952 reviewed the use of a logarithmico-normal distribution and cites examples back to 1924. Although Kottler's analysis of the statistical aspect of the log normal distribution was confined to photographic emulsions, he demonstrated that if a distribution was not linear when plotted on log-probability paper it was an indication that the sample contained at least two different populations.

Mugale & Evans (291) critically compared Rossin-Rammler and Nukiyama-Tanasawa distributions with log-probability plots and showed that the first two were largely unsatisfactory. They found that the log-probability equation predicted the general distribution trend correctly for most data and gave good results for the mean diameter calculations. These authors showed that the emulsion data of Harkins & Beeman (15.) and of Cooper (loc. cit.) fitted this presentation satisfactorily despite the extremely small size of the emulsion particles.

Gwyn, Crosby & Marshall (154) considered bias in particle size analyses resulting from the use of a log normal distribution. Many analyses indicate the existence of maximum size classes but the log normal

distribution is in fact infinite in extent. Thus the results tend to be biased, an occurrence implicitly recognised by Mugele & Evans. Gwyn et al. assumed that the sample was taken from a population with a true log normal distribution and adjusted the data for bias. Relevant to the results in this present investigation was the suggestion that the analysis could be carried out in two parts, a few particles being first counted to establish the central portion of the distribution, and a larger number of particles falling above, say, 5% of the total distribution based on the central portion. As noted by Gwyn et al., if a single distribution applies over the entire range of sizes the curve for the upper range will exactly, or very nearly, coincide with the extension of the curve for the central portion of the distribution.

Rajagopal (337) derived a rigorous proof of the log normal distribution by considering the randomness due to violent breakup of the interface during cavitation, the formation of daughter droplets, the disruption due to collisions and coalescence due to the same cause. The process was considered as a Markoff chain and the empirical applicability of a log-probability law to emulsion particle size distribution was placed on a firm theoretical basis.

Schwarz (393) introduced a so-called universal distribution law and this was later amplified and confirmed in two papers by Schwarz & Bezemer (25, 394). However, this equation, derived on statistical grounds, is also a variation upon the log normal distribution. From the data supplied by these authors the equation appears to be less universal in application than their claims suggest, and the law does not appear to have been applied by other workers.

There are a number of advantages in utilising a distribution law of the log normal type to describe a particle size distribution, as discussed by Smith & Jordan (440). Thus, on a number basis a particle

size distribution is defined uniquely by two parameters, M , the geometric mean particle diameter, and σ_g , the geometric standard deviation. Both these parameters can be readily obtained by plotting the size distribution data as a cumulative undersize curve on log-probability paper, a point also brought out by Koller (223). In establishing line of best fit Kottler pointed out that preference should be given to those points lying closest to the mid-value of 50 cumulative per cent. Due to the distortion of the probability axis the distance by which points are displaced from a straight line becomes increasingly significant as one considers points progressively closer to the 50% mark. For this reason some investigators such as Drinker & Hatch (96) fit the best line to those points within the 20% to 80% limits, ignoring points outside these marks.

Espenscheid et al. (104) criticised the use of log normal distribution functions obtained from light scattering data. They suggested that this was a new distribution function with different parameters and physical properties, and coined the term zeroth-order logarithmic distribution. However, Honig (189) pointed out that the suggested distribution function was readily reduced to the usual log-normal distribution function and this was the only one which could be determined experimentally.

One other approach deserved mention since the method of presenting the size analysis is unique. Broadbent & Callcott (39) suggested that a size analysis could be presented in the form of a matrix, leading to the derivation of a single parameter, the breakage function, (π), which was defined as the proportion of particles **that** are broken during a grinding process. This approach, developed in a series of papers (40, 41, 46) in the context of coal grinding is interesting although it does assume that the chance of breakage is the same irrespective of the particle

size. Furthermore, in its suggested form it could not be applied to emulsion systems since no account is taken of coalescence, a necessary feature of emulsification processes. Nevertheless, the concept of presenting the size analysis as a matrix is an attractive mathematical model since it is not necessary to assume any "law" controlling the emulsification process and it might be possible to derive a single parameter to describe any one distribution. Arbiter & Harris (7) extended the concept to include a time relationship in grinding but the approach does not appear to have been used in the context of emulsions and might be a fruitful approach for a future investigation.

To summarise, there is considerable agreement that a size distribution follows a logarithmic-normal distribution, being characterised by the mean size and the slope, or standard deviation. This distribution can be plotted on log-probability paper and, although a relatively insensitive method of presenting results, it must be regarded as satisfactory when considering such factors as sampling error and repeatability of a particular size analytical method.

2.4.3 Methods of particle size analysis

The Society for Analytical Chemistry published in 1963 a classification of methods for determining particle size (376). This, supplemented by the standard textbooks on the subject by Herdan (172), Orr & Dallavalle (315), Rose (367) and Cadle (51) and **review articles** such as that by Scarlett (381) are sufficient background. It is not therefore proposed to discuss the methods in general but rather select certain aspects for comment and deal with two methods, the Coulter Counter and the centrifugal photosedimentometer, in detail.

(a) Microscope measurement of emulsion particles

Most of the work carried out on correlation of properties of emulsions to the particle size of the disperse phase has relied upon

optical microscopy for the particle size measurement (Table 2.2).

The microscope has the advantage that it is direct and inexpensive but the measurements in themselves may be extremely lengthy and tedious.

Mounting techniques for emulsions have been discussed and described by Simmonite (428). The emulsion under examination must first be diluted before mounting and various dilution media have been proposed including aqueous gelatin, acacia solution and diluted polyols such as glycerol or propylene glycol (243). Various techniques have been described for examining the particles and classifying into size groups. The simplest form utilising a micrometer eyepiece or calibrated graticule has been widely employed (115). Harkins & Beeman (158) used a projection microscope, thereby reducing eye strain and improving the accuracy of the method. Smith & Grinling (439) introduced a counting technique using a haemocytometer slide and Cockton & Wynn (68) improved this by using a shallow Helber counting chamber. Levius & Drommond (243) criticised the previous papers and suggested a camera lucida method which they found to be an improvement over the counting techniques. Photographic methods were employed by, for example, Cooper (70) who measured the particle size from prints. Photomicrography of emulsions is difficult since particles in the micron range exhibit Brownian movement, necessitating very short exposure times with subsequent loss of contrast.

The necessity of sizing large numbers of particles to obtain meaningful results has received some attention, the most serious attempt being probably that of Fischer & Harkins (113) who counted 50,000 particles in each of their systems. However, as discussed by Becher (23), statistically significant counts can be obtained with only 300 particles. A count of 300 particles will result in a cumulative distribution in which the error at any value will be less than 8% ($P = 0.95$) and to lower this to 5% would require a count of 2960 particles. Kaye (205)

also discussed this point and showed that errors arising from sampling were such that a tenfold increase in count only produced a slight increase of accuracy.

Cooper (70, 71) carried out the classical critical evaluation of microscope sizing methods for emulsions. He pointed out that photographic methods were limited by the depth of focus since no lens is available which can give a clear image of particles of $1\ \mu$ or less and yet have a depth of focus of $20\ \mu$, the thickness of a haemocytometer cell. Direct visual counting, in which the focus of the microscope can be continually varied, was found always to show a higher value for the number of particles in the smallest size range, confirmed by van Kreveld (480). As the particle approaches the wavelength of the incident light the resultant halo makes estimation of the actual particle diameter extremely difficult so that sizing of particles below, say, $2\ \mu$ cannot be carried out with 100% efficiency, a point also confirmed by Saylor (380). Lucas (251) noting that rubber lattices contained particles well below $0.5\ \mu$, attempted to improve the light microscope by reducing the wavelength of the radiation to the ultraviolet range ($\lambda = 2573\ \text{\AA}$). The technique was extremely difficult since the source was not stable. van den Tempel (474) showed from Lucas's data that there was a considerable number of particles present in his system below the visibility limit of $0.12\ \mu$, probably more than 60% being below the limit. van den Tempel considered the use of the light microscope for such small particles to be meaningless and favoured the ultramicroscope which can be used to detect and count particles down to $0.02\ \mu$ diameter but is unable to differentiate particle sizes.

Although Cooper showed that microscope measurement of particles below $2\ \mu$ was of limited value the method has continued to be used up to the present. King (213) implied that misleading results were occasionally

obtained when correlating emulsion stability with particle sizes of 0.5 - 1 μ diameter. Knoechel (219) and Knoechel & Jurster (220), investigating o/w emulsion stability, discussed the inability of the microscope to take into account sub-micron particles, concluding:-

"The experimental evidence indicates that the presence of sub-visual particles could lead to unreliable values for various diameters and interfacial areas during the period in which minute globules coalesce to a visible size." This conclusion was echoed by Sherman (411, 412) and he proposed that the only way out of this dilemma was to allow all the minute particles to coalesce until they could be measured microscopically. The value of this suggestion for unstable systems may be doubted but the idea clearly cannot be applied to those which are stable or in which the particles do not coalesce. Sherman pointed out in the discussion to a paper (415) that submicroscopic particles are "cancelled out" when determining a mean size. He made a tentative proposal for utilising a reciprocal mean diameter, thereby bringing out the importance of submicron particles in a system. The method of measurement was not mentioned although a microscope method has been employed in all this author's previous work.

Thus, even if one accepts Becher's definition of an emulsion (Section 2.1.1), and his arbitrary limitation to particles exceeding 0.1 μ diameter, the accuracy of measurement of the smaller particles and the assessment of the significance of the results must at least remain suspect when using a microscopical measuring technique.

(b) The Electron Microscope

The early development of electron microscopy and its application to the investigation of materials below the limits of light microscope discrimination was reviewed by Anderson (6). Walton (502) and Watson (503) reviewed the application of the instrument to particle size measurement

and described some of the limitations of the technique. The method has some advantages compared with light scattering, sedimentation and other methods. In particular the exact size distribution can be determined and any peculiarities in shape observed directly (482). As noted by Walton (loc. cit.), major difficulties are sampling and the effects of drying under vacuum. Local heating in the electron beam are often important when examining soft materials such as emulsion particles. Cravath et al. (80) improved the sampling of suspensions by depositing small droplets of the suspension from a mist (aerosol) onto a specimen film treated to promote wetting. The entire residue left by a single droplet could then be examined. Nixon & Fisher (312) used an Aerograph gun to produce droplets and dispersed their material in bovine serum albumin which dried out to yield a transparent matrix supporting the particles. The basic technique of Nixon & Fisher was later improved by Craik who used a more concentrated albumin solution and stained the protein with osmium to improve contrast at the edges of the particles where the matrix was thickest (Chapter Three).

Other methods of supporting suspensions for examination have been reported (8, 384). Soft polymeric materials which distort in vacuum have been hardened before examination by bromination (385), or cross-linking with hard polymers using high energy irradiation (34, 482). However, in general these hardening techniques have not been applied to the electron microscopy of liquid-liquid emulsion systems. Indeed, studies of emulsions by this method appear to have been confined to wax dispersions similar to those of the present investigation (383).

Particle size analysis using the electron microscope requires the measurement of a large number (at least 3000) of particles by a photographic method since the image is often not sufficiently stable for more than a few minutes. The problems associated with this aspect

of the method were described by Crowl (82) who proposed a mechanical method for sizing from photographic plates. The alternative approach of image-shearing proposed by Rippon (361) may also offer a solution for future development.

However, the use of electron microscopy for measuring the particle size of emulsion particles below about $1\ \mu$ diameter would appear to be the only direct method at present available.

(c) Ultramicroscope and light scattering methods

Recent work on ultramicroscope methods has been devoted to either counting particles in a flow cell (319) or using a flow method to separate particles out according to their size and counting in a flow ultramicroscope (89, 90, 512).

Particle sizes can also be measured in principle by optical methods depending on the measurement of the reduction of light directly transmitted through a dispersion (turbidimetric or nephelometric methods) or by light scattered at some definite angle (usually 90°) from the light path.

Krishnan (228) appears to have been one of the first workers to investigate the light scattering in dilute emulsion systems and Sing (432) showed that for small particles secondary scattering could no longer be neglected. This author utilised Mie theory and the approach was investigated theoretically by van der Hulst (472). Two regions can be distinguished: for particles below about $100\ m\mu$ (Rayleigh scattering) and for particles in the micron range (Mie scattering) (165, 197). The relationship between obscuration of a beam of light and the concentration of particles is by no means simple, especially as the particles approach the wavelength of the incident light. The extinction coefficient K is defined as the ratio of light obscured by a particle to the light which it would have obscured if the laws of

geometric optics were valid for the system under consideration. If, for a given system, the ratio of the particle diameter 'd' to the incident wavelength, λ , is greater than 100, the value of K is constant and can be taken as unity. For smaller ratios K becomes a complex function of d/λ , the relative refractive index with respect to that of the supporting medium and the shape of the particle (472). Gumprecht & Sliepcevich (152) considered the problem and proposed a quantitative relationship between Mie theory and K which enabled them to obtain a size frequency distribution. The approach was over-simplified and does not appear to have gained wide acceptance.

Lothian & Chappel (250) discussed the fractional loss of intensity of a beam of light passing through a layer of emulsion and showed that the optical density of a dilute suspension of spheres was a function of their particle size.

Goulden (133) used scattering coefficient data calculated by van der Hulst (loc. cit.) to apply this equation to determining the particle size of emulsions and extended the method to controlling the particle size of homogenised milks (134 - 138). However, the method can only yield a mean particle size and although useful for control purposes cannot be employed for any other than a mono-disperse system.

After strong criticisms of turbidimetric methods by Skinner & Boas-Traube (435) an improved instrument was described by Branson & Dunning (35). This device was developed by Rose (367) who narrowed the angle of acceptance to reduce forward scattering, and other investigations were carried out by Kaye (205) and Hodgkinson (186). The latter found that Mie theory was not applicable to irregular particles and the value of the extinction coefficient (K) was found to rise slowly from 0 - 2, an effect confirmed experimentally with a number of materials. Kaye, and later Kaye & Allen (206), investigated

the optical scattering cross-sections of small particles. Using white light and a wide angle of acceptance they showed that the fluctuations of K were much reduced under these conditions and for many purposes it was sufficient to take it as unity. Without the benefit of these investigations Bolton & Marshall (28) claimed that a simple turbidimeter could be used to measure wax particles down to 0.06μ . **This claim** must be viewed with caution. It is not clear if the authors used white light but they found values for K as low as 0.04 for their smallest particles.

Trice & Rodger (465) measured interfacial areas using a light transmission method similar to that used earlier by Langlois et al. (236) for coarse, unstable emulsions.

Reflectance relationships for emulsions are, if anything, more complex. This was noted by Lloyd (248) who incorporated a red dye in the oil phase and found that the reflectance at wavelengths at which the coloured interval phase partially absorbed the incident light was inversely proportional to a power of the surface area particle diameter. This relationship was claimed to be independent of the particle size distribution. Schulman & Friend (384) and van der Waarden (479) both used the Rayleigh formula to calculate the mean size of very small droplets (up to 400 \AA diameter). La Mer (234) investigated monodisperse aerosols using the higher order Tyndall spectra method. Heller et al. (166) verified experimentally that the theory was applicable to light scattering methods and tabulated the data required to transform light scattering measurements into particle size distributions (451, 499, 500). Although initially confined to relatively monodisperse polymer latices, Wallach (499) claimed that the method was applicable to the study of size distributions of dimethylnaphthalene water emulsions.

Gledhill (127), Wales (496) and Weber (504) have all described

methods for measuring particle size distributions by measurement of turbidity spectra using similar methods to Heller. La Mer & Plesner (235) described a rapid method of sizing a monodisperse suspension by measuring the light scattering as a function of the angle between the incident beam and scattered light and the method was extended by Deželić & Kratochvíl (91, 92). Kratochvíl & Wallace (226) re-examined the claims made by Heller & Tabibian (169) and by Wales (loc. cit.), and found them unreliable.

To summarise, there is general agreement that light scattering and turbidity methods can give a measure of the mean particle size present in a system although there is some disagreement on the means by which the size distribution can be determined. Simplified techniques, making a number of assumptions, have been applied to determining particle size distributions by a combination of sedimentation methods and turbidity measurements.

2.4.4 The Centrifugal Photosedimentometer

(a) Centrifugal sizing techniques

Most existing sedimentation techniques for particle size analysis have severe shortcomings for particles below about 10 μ . Below this size particles sediment too slowly for practical purposes. In addition, convection and displacement currents as well as Brownian movement all tend to disturb the sedimentation process. One obvious way to increase the settling rate is to centrifuge the suspension. Orr & Dallavalle (315) described a number of centrifugal sedimentation techniques and other devices have been developed in recent years.

The first attempt to use a centrifuge to obtain a size distribution was that of Dumonskii, Zabolotskii & Evseyev (98). Using an ordinary centrifuge they determined the amount sedimented by ultramicroscope counts before and after centrifuging but obtained poor agreement with

the ultramicroscope method. Svedberg & Pederson (453) suggested that this was probably due to convection currents caused by serious deviation from ideal sedimentation conditions. As described in this book, Svedberg himself was intimately involved in the initial development of the ultracentrifuge. With Nichols he developed a centrifugal densitometer, a two-arm centrifuge in which the boundary of particles was observed by taking photographs at different stages of the analysis. Nichols & Liebe (310) used a much improved version of this early instrument which rotated at 20,000 r.p.m. and had better balancing and freedom from vibration. The obscuring power, related to the cross-sectional surface diameter of the particles, was measured for six colloidal lithopone samples by measuring the optical density from light absorption measurements. The method was described in detail later by Bailey, Nichols & Kraemer (16) and by Bailey (15), the former group showing how it could be applied to the particle size of emulsions. Nichols & Bailey (309) gave a worked example of how to calculate a size distribution of an emulsion using the so-called "low-speed Svedberg ultracentrifuge".

Nichols & Liebe (loc. cit.) equated the viscous force due to Stokes' Law with centrifugal force, ignoring the Coriolis force or accelerating force which is also present. Robison & Martin (362) were able to demonstrate that this assumption would not lead to any significant error. Cheng & Schachman (61), after an intensive investigation of the ultracentrifugal sedimentation behaviour of polymer latices, concluded that Stokes' Law was valid under these conditions.

Marshall (259 - 261) suggested a two-layer technique in which particles are considered to start from substantially the same position. This technique has a superficial attraction but is fraught with many difficulties, including that of irregular sedimentation, a point noted by Keen & Schofield as early as 1930 (210). This technique and methods for

overcoming the problems have been discussed (17, 201, 261, 282) and the streaming problem for particulate solids subjected to a two-layer sedimentation technique has been effectively overcome. However, the approach is only applicable to materials which are denser than the sedimentation liquid, i.e., the particles are thrown to the outer periphery of the sedimenting vessel. Since emulsion particles are usually less dense than water and soluble in organic liquids which have a lower density, the use of a centrifugal sedimentation method is confined to a homogeneous technique. Thus emulsion particles move inwards from the outer periphery towards the centre of the sedimentation vessel. It is therefore necessary to consider in more detail homogeneous centrifugation techniques and methods for their solution.

(b) Homogeneous centrifugal techniques

The early techniques as noted above used centrifugal tubes. Martin (267), and later Robison & Martin (362), reviewed beaker-type centrifugal sedimentation and concluded that it had advantages, not the least being that collisions between the particles and the walls of the vessel are minimised. Robison & Martin developed the theoretical approach and described the application of a modified beaker or sector shaped centrifuge cell from which samples were withdrawn at the end of a variable time at a fixed depth (363). Brodnyan (42) used a similar method for polymer latices but with an ultracentrifuge. Karnack (203) improved the theoretical method and described a similar sector-shaped cell to which was attached a sampling device that removed a sample at a fixed depth whilst the centrifuge was still running, thereby removing the danger of stirring the suspension during the slowing down phase. Karnack had to use concentrated suspensions of the order of 1% and only one point on the distribution curve could be obtained from each run. Owing to hindered settling (198, 207) the method was also probably inaccurate. Nevertheless

the method of calculating the experimental results was retained when Donoghue & Bostock (95) introduced the complete disc centrifuge. This particular instrument resulted in the introduction of a centrifugal analogue of the Andreasen pipette by Slater & Cohen (436), the Simcar Centrifuge. Gupta (153) also described a version of a centrifugal Andreasen pipette technique.

Moser & Schmidt (290) described a centrifugal photosedimentometer using a shallow cylindrical tank or disc rotating in the horizontal plane. The optical density of the suspension was followed as a function of time by passing a thin beam of light through a fixed point on the tank onto a photoelectric cell. The authors used a nomograph to relate the recorder curve to the percentage of particles of a given size calculated from Stokes' Law and stress was laid on the fact that an instrument of this type must first be calibrated by some other method owing to variable factors such as particle shape and opacity. Moser (private communication) stated that the instrument was a prototype which was not developed further.

Later Kaye patented a photosedimentometer which was essentially similar to that of Moser & Schmidt (204). The new instrument used a servo-system which compared the attenuated light beam with the unattenuated beam, using the difference signal to rotate an optical wedge to cancel the difference. A potentiometer attached to the optical wedge was used to control the recorder so the instrument plotted out the optical density of the suspension. The instrument was described in more detail (205) by Kaye and evaluated with Burt (48, 49). A simplified instrument, omitting the servo unit, was described and evaluated by Groves, Kaye & Scarlett (149). The light beam was allowed to fall onto an unbalanced photocell after passing through the centrifugal disc. The instrument was used with the two-layer technique and was insufficiently sensitive

to detect the streaming later investigated by Rippon (361). Nevertheless these results were sufficiently interesting to result in the production of the commercial prototype utilised in this current work (17, 116, 117).

Other disc centrifuges have also been described. Martin, Brown & de Bruyn (266) used a hollow aluminium disc centrifuge similar to Kaye's design to size analyse submicron powders containing elements of high atomic density such as lead glass, an X-ray beam passing through it and onto a proportional counter.

Hildreth (183, 184) described a simple photo-extinction type of disc sedimentometer, similar in principle to that described by Groves, Kaye & Scarlett (loc. cit.). An initially homogeneous suspension was used on the variable time system (vide infra), the transmission versus time curve being related to transmission weight curve by obscuration factors. As noted by Rippon (361), this is an over-simplification of the theory and is not a tenable method.

Atherton, Cooper & Fox (9), Atherton & Tough (10) and Jones (201) described a small diameter disc centrifuge in which the two-layer technique is used in conjunction with a rotating probe sampling device. Thus, liquid and suspended contents are removed for subsequent analysis after pre-determined centrifugation times at a known radius while the centrifuge is still rotating.

(c) The theory of homogeneous suspension methods

When the material to be analysed is dispersed in the sedimentation liquid to produce a homogeneous dispersion, three main modes of operation are possible as noted by Murley (293):-

- (1) The inner radius of the liquid surface and the outer radius of collection are kept constant, samples being collected after varying running times of the centrifuge.

- (2) The running time of the centrifuge is kept constant, as is the inner radius of liquid and the outer collection radius is varied.
- (3) The running time of the centrifuge is kept constant as before, but the outer collection radius is kept constant for successive measurements, while the inner liquid surface radius is varied.

In all cases the centrifuge speed is kept constant. Donoghue & Bostock (95) gave solutions for solving methods (2) and (3), to which Hurley added another proof. However, Donoghue & Bostock also stated that no analytical proof exists for the derivation of the particle size distribution of a sample when time is varied, unfortunately the precise situation relevant to the centrifugal photosedimentometer. Hurley agreed that this was correct but pointed out that iterative methods could now be developed for calculating the required results using modern computer techniques at relatively low cost. The variable time mode of operation offers a number of important experimental advantages and as a result many attempts have been made to find a solution, or the best approximation.

Although the position of a particle relative to its initial position can be described mathematically, it still remains difficult for a distribution function to be derived from the experimental information. This is complicated by the fact that, from the initially homogeneously dispersed particulate system, particles are accelerated proportionally to their position from the axis of rotation. At any given reference or sampling zone, after a certain time 't' it can be said that all particles greater than a certain size ' d_t ' will have passed, where ' d_t ' is the Stokes' diameter of the particle which started from the free surface and in time t had transversed to the sampling zone. Subsequently the theory was

developed for a disc centrifuge which is an ideal form of a sector-shaped cell since wall collisions are reduced to a minimum. The size distribution is considered to be continuous, containing in an infinitesimal range of diameters a fraction of $F(y)dy$.

Referring to the sector of the disc centrifuge, the distance from the axis to the free surface is 'S'; that to the sampling zone, 'R'.

Hence a particle of diameter 'd' is defined as that particle which will just travel from the surface at S to R during the centrifuging.

From a consideration of the centrifugal forces:-

$$\ln \frac{R}{S} = \frac{(Q - \sigma) \omega^2 d^2 t}{18 \eta} \quad (1)$$

where ω = angular velocity, Q = density of particle, σ = density of sedimentation liquid and η = the viscosity of the liquid.

Thus

$$\ln \frac{R}{S} = k d^2 t, \quad \text{where } k = \frac{(Q - \sigma) \omega^2}{18 \eta} \quad (2)$$

These particles, of diameter 'd' and all larger particles will have been sedimented as well as a fraction of the particles smaller than 'd' (i.e., those which were nearer to the sampling zone than those at the surface) in time 't'.

If 'p' is the total fraction of material deposited, then 'p' is given by the equation

$$p = \int_d^\infty Fy(dy) + \int_0^d \frac{R^2}{(R^2 - S^2)} \left[1 - e^{-2ky^2 t} \right] Fy \cdot dy \quad (3)$$

Differentiating equation (3) with respect to time gives:-

$$\frac{\partial p}{\partial t} = \int_0^d \frac{R^2}{(R^2 - s^2)} - 2ky^2 e^{-2ky^2 t} F_y dy \quad (4)$$

This equation is not capable of analytical solution although Romvalter & Vendl (366) obtained equation (3) and invalidated their solution by an error. This error was detected by Brown (451) who obtained equation (3) but solved it by making (R-S) variable. Robison & Martin (362) used an iterative method to produce a set of approximate solutions which were claimed to give better accuracy than that due to normal experimental errors. Kamack (203) improved the iterative technique to give an approximate general solution to equation (4) in recursive form:-

$$F_i = \frac{1}{2} (S + S_{i-1,1}) C_1 + \sum_{j=1}^{i-1} \left[\frac{S + S_{i-1,i}}{S_{j+1,1} + S_{j,1}} - \frac{S + S_{i-1,i}}{S_{j,1} + S_{j-1,i}} \right] F_j \quad (5)$$

$$i = 1, 2, \dots, n$$

where $F = F(D)$ = fraction by weight of particles smaller than diameter D .

C = concentration of suspended solids, as a fraction of the concentration of uniform suspension prior to settling, and

$$S = \left(\frac{R}{S} \right)^2$$

Others have attempted to obtain a solution of the variable time equation. Nichols & Liebe (310) published a result which would not however give a weight distribution function. Parkinson (321) overcame the variation due to the centrifugal field by the simple process of ignoring it. More practically, Jacobsen & Sullivan (192) employed a very low value of R/S (1.05) but this was experimentally difficult since only small volumes of material were available for analysis. Dana (83) employed a pipette method

using an inclined-tube centrifuge for which mathematical analysis was found to be inapplicable. Other attempts were critically reviewed by Robison & Martin (362). It must be concluded that an exact solution of the theory for deriving a distribution function from an initially homogeneous dispersion centrifuged for various time intervals is not possible. As noted by Murley (loc. cit.) approximate methods of an order of accuracy better than that due to experimental techniques are, however, available.

(d) Light scattering as applied to centrifugal techniques

The use of a beam of radiation to measure the concentration of particles in a centrifugal cell has many attractions, especially as it is not necessary to disturb the sedimenting system in order to obtain an analysis which can be made continuous. The pioneer investigations of Svedberg & Nichols, Nichols & Liebe, and Nichols & Bailey have been mentioned. However, it is usual to employ Schlieren techniques to follow boundary changes in analytical ultracentrifugation, the boundary being detected by changes of refractive index between solvent and suspension. This method was used by Hermans & Ryke (174) to determine the particle size of colloidal silica particles. Biermann et al. (26) used the technique to measure the particle size distributions of chylomicrons, the submicron lipoprotein particles found in plasma after meals of fat, and found that the turbidity of their suspensions sometimes interfered with observation of the boundary. McCormick (296) noted that by increasing the intensity of the light beam with a mercury arc lamp the Schlieren patterns could still be obtained for concentrations up to 0.05% polystyrene latex particles with diameters of 2500 Å. He was therefore able to adapt conventional analytical ultra-centrifugal techniques for the size analysis of a number of polymeric emulsions. Averink et al. (12) criticised McCormick's method since the turbidity forced him to use such

low concentrations that the Schlieren peaks were very small, leading to poor accuracy. Averink et al. showed that the applicability of Schlieren optics was restricted to a range of particle diameters ranging from 200 - 2400 Å. They concluded that with absorption optics the range could be greatly extended and described a method for achieving this. A graphical method was used to relate optical density to concentration in order to calculate the size distribution. Using monochromatic light this method would appear to be the most satisfactory currently available.

Using a sample beam of light of mixed wavelengths Groves, Kaye & Scarlett (149) emphasised that their method (loc. cit.) could not be absolute for particles whose diameter approximates to the wavelength of the incident light but was useful for the detection of differences between samples. Kaye & Jackson (209) applied a modified centrifuge developed from the earlier models to the size analysis of polymer emulsions of narrow size range, and were able to deduce that these materials had a wider range than that claimed by the manufacturers, a conclusion adequately supported by other workers at the same meeting (226).

Thus, although the technique is relatively unsophisticated it may have some use where the particles are still big enough to cause interference with a light beam ($> 0.01\mu$) since these particles are separated according to Stokes' Law. The quantitative expression of the actual particle concentration may not be exact and may result in an overemphasis of the fines. The relationship between this effect and errors due to, for example, inadequate dispersion of the fine particles remains to be established.

(e) Other centrifugal techniques for sizing emulsion particles

The ultracentrifuge has been used to determine emulsion stability, measuring the free oil and compacted emulsion boundaries as a function of time (120, 343, 488 - 491). By analogy with gravity sedimentation

methods this technique could be applied to particle size determinations. Pinter & Zilversmit (327) and Zilversmit (523) described a density gradient method for the ultracentrifugal size measurement of chylomicrons. This technique is used in studies on living materials (317) and the approach might well be applicable to other emulsion systems.

2.4.5 The Coulter Counter

Coulter described his instrument in 1956 (75) and the device has come to be widely accepted as a convenient and valid method of size analysis. The Coulter Counter (Ljungberg, Toa and Sansar are alternative makes of instrument utilising a similar principle) determines the number and size of particles suspended in an electrically conductive liquid. This is done by forcing the suspension to flow through a small aperture having an immersed electrode on either side. As a particle passes through the aperture, it changes the resistance between the electrodes. This produces a voltage pulse of short duration having a magnitude proportional to the volume of electrolyte displaced, and hence to the particle volume (size). The series of pulses is then electronically scaled and counted. Detailed descriptions of the apparatus and its operation have appeared in the literature (21, 24, 53, 75, 76, 320, 231, 308, 377, 455, 468, 495) and it is not proposed to repeat them here.

Critical evaluations such as those by Cooper & Parfitt (72), Samyn & McGee (378), Jales & Wilson (497, 498), Kubitschek (232) and Allen (3) have to some extent been answered by Princen (329), Edmundson (100), Barnes et al. (19) and Mercer (279). To date, however, no fundamental flaw in the principle or mode of operation has been detected and it is generally agreed that the instrument serves a useful function. Coulter's Laboratory Manual (1966) claims that, with a 20 μ nominal diameter orifice, the instrument will detect particles of 0.4 μ equivalent sphere diameter. Kubitschek (230) claimed to reach a size of 0.2 μ with a resolution of

0.04 - 0.06 μ^3 . This must be viewed with considerable caution although Princen (private communication) has confirmed the claim and suggests that it may be due to instrument idiosyncrasy. It is widely believed (Coulter, private communication) that the instrument is useful down to diameters of 1.0 μ and will detect particles down to 0.5 μ diameter. However, in this range the instrument background caused by electrical effects, especially electrical 'heating' within the orifice, and cavitation by the passage of material through the small orifices which are required for these sizes make actual detection of submicron particles less certain. Practical difficulties in obtaining electrolyte free from particulate contamination are also considerable. The instrument is therefore limited to approximately the same size range as optical microscope methods and it does require dispersion of the material in electrolyte, itself a source of trouble due to flocculation effects (147, 434). Nevertheless, the instrument has an overwhelming advantage in that a vastly greater number of particles is actually counted for any one size distribution, thereby greatly increasing the accuracy and the speed of a size analysis.

The use of the Coulter Counter for sizing emulsion systems

Wachtel (495) employed the Counter to size o/w emulsion systems, using the method to examine the degree of dispersion achieved by the use of the Sinclair aerosol generator for making 'monodisperse' emulsions. Higuchi (179, 180) investigated factors influencing the aggregation of emulsions, followed by Lemberger & Mourad (241) and Swift & Friedlander (455). Rowe (370) and Mima & Kitamori (282) investigated emulsion stability parameters as reflected in changes in particle size distribution. Singleton & Brown (434) used the device whilst investigating the formulation of intravenous fat emulsions. Princen, Kudeck & Stolp (331) investigated the factors controlling the emulsion of linseed oil and Marshall & Taylor

(264) described the use of the Coulter for following changes produced in an emulsion during the evaluation of different homogenisers. Schrenzel (386, 387) discussed the use of the Coulter Counter for the size analysis of pharmaceutical emulsions. The instrument has therefore received considerable attention in this application.

2.5 The influence of particle size on the viscosity of emulsions and suspensions

2.5.1 Introduction

Since the scope of this enquiry has been broadened to include emulsion behaviour with that of suspensions, it is of interest to compare the properties which are claimed to influence their respective flow behaviour.

Table 2.1 Properties claimed to influence the flow of emulsions and suspensions

Emulsions (405)	Suspensions (119)
1. Viscosity of the external phase (η_o)	(a) Relative volume fraction of particles
2. Volume concentration of the disperse phase (ϕ)	(b) Internal flexibility and ease of deformation of particles
3. Viscosity of the internal phase (η_i)	(c) Thermodynamic condition of system (lowered by the presence of surface active agents)
4. Nature of the emulsifying agent and the interfacial film formed at the interface	(d) Presence of electrical charges
5. Electroviscous effect	(e) Shape, size and mass of suspended particles
6. Particle size and size distribution	(f) Size distribution of the particles
	(g) Concentration of the system

There are obvious similarities between the two although it is strange that Frisch & Simha (119) did not consider the viscosity of the continuous phase to be important. In addition, the factors (a) and (g) must obviously be closely interrelated, referring to the presence or otherwise of an

adsorbed layer on the particles. In a later review Sherman elaborated on the above scheme but retained its essential elements (412).

2.5.2 Viscosity relationships for suspensions of spherical particles

It is clear that the presence of a set of rigid spherical particles in a Newtonian liquid will raise the viscosity of the liquid to a value η which is higher than the viscosity η_0 of the liquid itself. The dimensionless ratio η/η_0 , the relative viscosity (η_r), is likely to be a function of the total volume fraction (ϕ) of the suspension.

The most widely known expression for η_r was derived by Einstein (103):-

$$\eta_r = \eta/\eta_0 = 1 + \alpha_0 \phi \dots\dots\dots (1)$$

where α_0 = a constant; for spheres = 5/2

This requires that there is no interaction between the particles, and their distance of separation greatly exceeds their diameter.

As discussed by Hawab & Mason (305), this is, in fact, a power series in the form:-

$$\eta_r = 1 + \alpha_0 \phi + \alpha_1 \phi^2 + \alpha_2 \phi^3 \dots\dots\dots (2)$$

Porter (328) showed that a simple power law was inadequate to represent the change of η over all possible rates of shear. A large number of theoretical and empirical attempts have been made to stretch the equation to fit the properties of more concentrated systems (294). Rutgers (374) reviewed 97 of these attempts (up to 1962) and it is interesting to note that not one of them contains a term to describe mean particle size or particle size distribution. Despite this, Rutgers mentioned as a fact that viscosity increased with smaller particle sizes, and that absolute particle size was important. Sherman (412) reviewed the same field as Rutgers, with reference to concentrated emulsions. He pointed

out that η increased with increased ϕ and when $\phi > 0.4 - 0.5$ the emulsions became pseudoplastic in flow properties, in some cases plastic with a definite yield value. At this point small increases in ϕ can produce profound increases in η , and above a critical value, often, but not always, in the region of 0.74 the emulsion will crack.

Richardson (346) calculated a compressibility factor for an emulsion when ϕ is increased by $\delta\phi$. Broughton & Squires (43) empirically amended his equation which Simpson (430) found to hold for nitrocellulose lacquers. Sherman (401) was unable to confirm the proposed relationship for concentrated ($\phi > 0.5$) emulsions.

Hatschek (163) proposed an equation for flow behaviour and noted that it required correction for an adsorbed layer. Sibree (424, 425) made allowance for an increase (h) in the effective volume due to hydration of the emulsifier layer around the particles. However Broughton & Squires (43) and Toms (463) found considerable variation in values of h. Brinkman (38), Gillespie (125) and Ehlers (101, 102) all considered the flow behaviour in a similar manner and introduced other forms of correction for the increase of volume of a particle. Saunders (379) also found that the measured volume fraction required correction and noted that there was an increased interaction as the particle diameter decreased. Sweeney & Geckler (454) came to a similar conclusion but the importance of the effect of particle size on flow remained on this semi-qualitative level until recently.

2.5.3 The influence of particle size and size distribution on viscosity

From packing considerations Traxler (464) reasoned that particle size distribution must influence viscosity. Lyttleton & Traxler (252) separated bituminous emulsions into fractions of graded size and showed that different viscosities were obtained which could only be accounted for on the basis of a changed size distribution. Orr & Blocker (314) and

Hermans (173) went so far as to deny that particle size mattered, considering the particle size distribution as measured by the standard deviation to be important. However, Sherman (412) noted that the bulk of the published literature contained little or no reference to the state of dispersion other than generalised statements such as "fine" emulsions gave higher viscosities than "coarse" emulsions of the same constitution. The papers of Leviton & Leighton (242), Richardson (348, 349) and of Rajagopal (339) made limited attempts to investigate the relationship. Richardson's work, devoted to a consideration of concentrated ($\phi \sim 0.75$) o/w emulsions that showed non-Newtonian flow, is in fact the only investigation up to that time relevant to the present enquiry. Empirically he found that η_{∞} was proportional to the reciprocal of D_m , the mean particle diameter, and the product, $D_m \eta_{\infty}$, was constant if the spread of size around D_m was narrow, a conclusion supported by Lawrence & Rothwell (238).

Since particles in a suspension at high rates of shear are equidistant from each other and provided they behave as rigid spheres the mean distance of separation (a_m) is given by

$$a_m = D_m \left[\left(\frac{\phi_{\max}}{\phi} \right)^{\frac{1}{3}} - 1 \right] \quad (1)$$

Sherman (407) showed that when a_m fell below a critical value ($\sim 0.5 \mu$) the ratio η_{∞}/η_0 increased very rapidly when D_m does not exceed 2 - 3 μ . The physical meaning of the critical value of a_m remains obscure at present but must be related to the hydrodynamic factors, the thickness of the surface film and the distance of the secondary minimum from the particle surface. As he pointed out in this paper, the calculated values of a_m do not allow for an increase in D_m due to adsorption of emulsifying agent at the interface or to solvation effects. Consequently

the true values of a_m would be greater than those calculated. For very low values of a_m the discrepancies must be very large.

Sherman (414) extended this idea and, by drawing regression lines between published data for the viscosity and values of a_m , derived the following semi-empirical equation:-

$$\text{Log. } \eta_r = C(1/a_m) + X \quad (2)$$

where C and X are constants.

He suggested that the form of this equation may vary with the degree of inhomogeneity of the system, the dependence of C on D_m decreasing as the particle size becomes broader and concluded that a study is required of well defined dispersions of solid spheres in which the inhomogeneity can be adjusted to any desired level.

Other workers are also active in this field. Johnson & Kelsey (200), noting that the viscosity of a latex could be changed by changing the particle size, found there was a relationship between the mass of large and small particles present. In a later paper (211) they analysed the situation and proposed the following formula (retaining the previous notation).

$$\frac{\eta}{\eta_0} = k \frac{(\bar{r}_v + \lambda)^2}{(a_m - 2\lambda)^2} + \eta_0 \quad (3)$$

where k = a constant, \bar{r}_v = volume mean radius = $\left(\frac{\sum n r^3}{\sum n} \right)^{1/3}$ and λ = a factor added for the adsorbed layer, here presumed to be the length of a soap molecule or ion (the oleate ion being taken as 27.5 Å long). Kelsey & Johnson considered the effect of adding mixtures of known particle size to each other in known ratios. Unfortunately only two different monosize components were considered. Mooney (285) and Williams (509) have also proposed equations. Cogill (69) reported an

iterative method for fitting the viscosity of a system to its disperse volume, essentially in the form

$$\phi \propto \frac{1}{(C + \log. \eta)} \quad (4)$$

The quantity C, determined by iteration, was shown to be about 1 - 6 for narrow size range material but, with an "anionic emulsion" (no details) having a size range of 1 - 10 μ , C rose to a value of 20. This was thought to be because only some of the particles in the system took any part in resisting the applied shear stress. Cogill supposed these to be the large particles, small ones merely occupying the interstices.

Thomas (462) also made a critical analysis of the experimental data on the relative viscosity of suspensions of uniform spherical particles based on the packing cell concept of Simha (426). He deliberately attempted to diminish effects due to non-Newtonian behaviour or non-homogeneity of size distribution. Simha & Somcynsky (427) accepted this approach which, from the previous discussion, would appear to be too restricted to be of use.

To summarise, there is general agreement that the particle size or distribution of size is important when considering the flow behaviour of suspensions of spherical particles. There appears to be a lack of agreement on the form of this relationship although many authors agree that it is necessary to correct for a hydrodynamic interaction due to an adsorbed layer on the particle interface.

The theories discussed on this section should be compared with theories of emulsion structure (2.3.4). It will be noted that one group of workers consider emulsions (and suspensions) as **inert** spheres so that their properties are controlled mainly by particle mechanics. On the

Table 2.2 Authors who have examined the relationship between emulsion and suspension properties and particle size, showing the method of particle size analysis (papers not necessarily discussed in the text)

Authors	Reference	Particle size analysis method
Axon	14	microscope
Bredée & de Booy	36, 37	microscope
Cheesman & King	57	microscope
Eilers	101	microscope
Eveson	105 - 107	microscope
Gillespie	123 - 125	{ microscope, electronmicroscope
Johnson & Kelsey	200	electronmicroscope
Kelsey & Johnson	211	electronmicroscope
Knoechel	219	microscope
Knoechel & Wurster	220	microscope
Lawrence & Rothwell	238	microscope
Leviton & Leighton	242	microscope
Lyttleton & Traxler	252	microscope
Manley & Mason	257	microscope
Matsumoto	275 - 278	sedimentation
Mima & Kitamori	282	Coulter Counter
Mawab & Mason	304	microscope
Orr & Blocker	314	microscope
Rajagopal	339	microscope
Richardson	348, 349	microscope
Rowe	370	Coulter Counter
Saunders	379	electronmicroscope
Sherman	401 - 415	microscope
Sheth	416	microscope
Sheth, McVean & Mattocks	417	microscope
Shotton & White	421	microscope
Sibree	424, 425	microscope
Simpson	430	microscope
Srivastava	446	microscope
Sweeney & Geckler	454	microscope
Takano & Kambe	457	electronmicroscope
Taylor	461	microscope
Traxler	464	microscope
Vand	471	microscope
van den Tempel	477, 478	microscope
Wachtel & La Mer	495	Coulter Counter
Williams	508, 509	{ microscope centrifuge
Wilson & Parke	511	microscope

other hand, the other group consider surfaces and the formation of interactions or links between the surfaces. They are therefore able to consider effects such as thixotropy but tend to take less account of particle size; a possible combination of certain features of both theories may be advantageous.

Finally, it was noted during the reading of the papers discussed in this section that the majority of the workers employed microscope size analysis methods; the situation is summarised in Table 2.2.

2.6 Conclusions

1. An emulsion is defined as a heterogenous system, consisting of at least one immiscible liquid intimately dispersed in another in the form of droplets. - 2.1.1
2. Emulsification involves shearing the heterogenous system to reduce the droplet size. - 2.1.2
3. Emulsion droplets may be non-spherical, especially in concentrated systems. - 2.2.4
4. Emulsion droplets have an interfacial film with properties different from either of the two immiscible liquids. - 2.2.1,2
5. The properties of interfacial films are influenced by the presence of impurities. Emulsions prepared with materials of commercial quality would be anticipated to differ from those made with purified materials. - 2.2.3
6. There is likely to be a spread of droplet sizes around a mean value and the particle size distribution will tend to obey a logarithmico-probability law. - 2.4.2
7. The light microscope has been employed by many workers for measuring the particle size distribution of emulsion systems. - Table 2.2
8. Light microscope methods of particle size measurement are not reliable for particles smaller than 2 μ . - 2.4.3(a)

9. Sub-micron particles can be detected in emulsions by light scattering methods. At present there is no reliable method for measuring particle size distributions by this means. - 2.4.3(c)
10. Centrifugal sedimentation methods may be used for the measurement of sub-micron particles, and for the determination of the particle size distribution. - 2.4.4
11. The Coulter Counter is a more accurate method than the light microscope for the measurement of particles larger than 1 μ . - 2.4.5
12. The flow properties of concentrated emulsions are non-Newtonian. 2.3.1,2
13. A number of factors influence emulsion flow behaviour including particle size and particle size distribution. - Table 2.1
14. There is only qualitative agreement on the nature of the relationship between particle size and emulsion behaviour. - 2.5.3
15. Two theories which attempt to explain the complex flow behaviour of emulsions may be distinguished, based on consideration of:-
- (a) links formed between particle surfaces. - 2.3.4
 - (b) mechanical interactions of spherical particles. - 2.5.2
16. The measurement of complex flow behaviour is difficult. The Ferranti-Shirley viscometer has a number of desirable features. - 2.3.5

2.7 Lines of enquiry followed in this study

In broad terms this investigation is concerned with the relationship between the particle size of the disperse phase of solid-liquid dispersions or emulsions of a type common in the pharmaceutical and cosmetic industries, and their flow behaviour under stress. Following considerations discussed in this Chapter the investigation was carried out in stages.

(1) Using a simple model system a comparative examination of some available particle sizing methods was carried out in order to determine

the best method, or combination of methods, for assessing the size distribution.

(2) Other model systems were then prepared to enable particle size (and distribution of size) and flow behaviour to be varied over the widest practicable limits. This was achieved by varying:-

- (a) emulsion concentration
- (b) type and concentration of emulsifier
- (c) method of emulsification
- (d) constitution of the disperse phase

Some other properties of the disperse phase which could affect the flow properties were also considered, including the particle shape and the presence of an interfacial film.

(3) The particle sizes of the preparations were measured using a combination of Coulter Counter and centrifugal photosedimentometer.

(4) The flow curves of the preparations were measured using a Ferranti-Shirley cone-plate viscometer.

(5) From a consideration of the experimental data an attempt was made to relate emulsion flow behaviour to the size of the disperse phase particles.

CHAPTER THREE

METHODS OF PARTICLE SIZE ANALYSIS

3.1 Introduction

3.2 Preliminary experiments

3.3 The Coulter Counter

3.4 The centrifugal photosedimentometer

3.5 Discussion and conclusions

3.6 Summary

3.1 Introduction

Much of the previous work on the correlation between physical properties and particle size or size distribution has been carried out on materials whose particles have been measured using light microscopy. This cannot adequately differentiate between particles of less than 2 μ , yet it is well known that sub-micron particles do exist in many emulsions. Hence the assessment of the significance of the results must remain a suspect feature of earlier investigations.

3.2 Preliminary experiments

The model emulsion was a single 500 g batch of a system similar to CTAB/B/120 (Table 4.1).

An electron photomicrograph of this preparation is shown in Fig 3.1. The material was examined by light microscopy, Coulter Counter, centrifugal photosedimentometer and electron microscopy. Details and results have been described elsewhere (116, 117, 151), but the results are summarized in Fig 3.2. As noted (151), extrapolation techniques suggested by Rajagopal (336), and others (99, 161, 162, 233) yield a marked underestimate of the size of the smallest particle present in the system

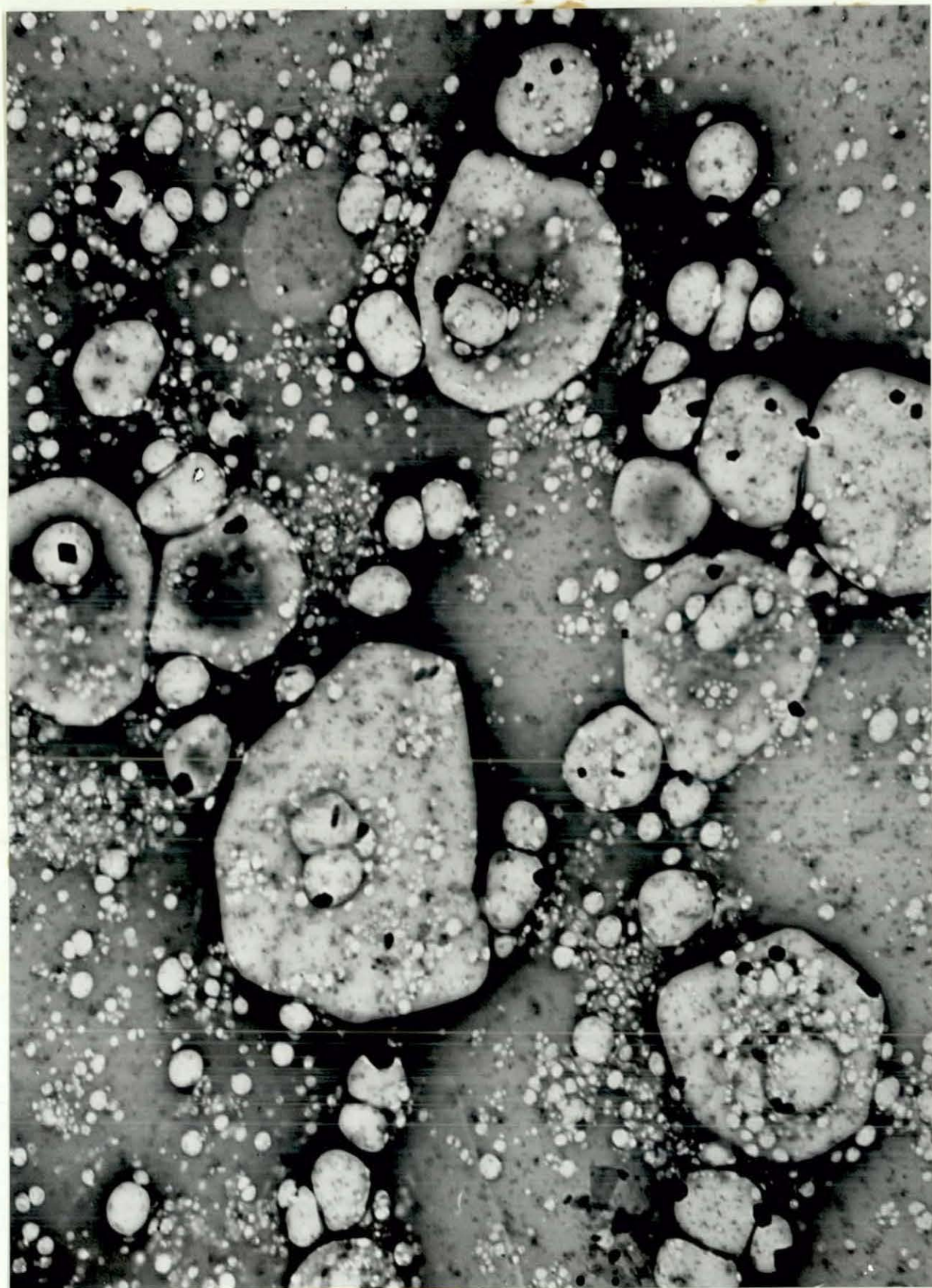
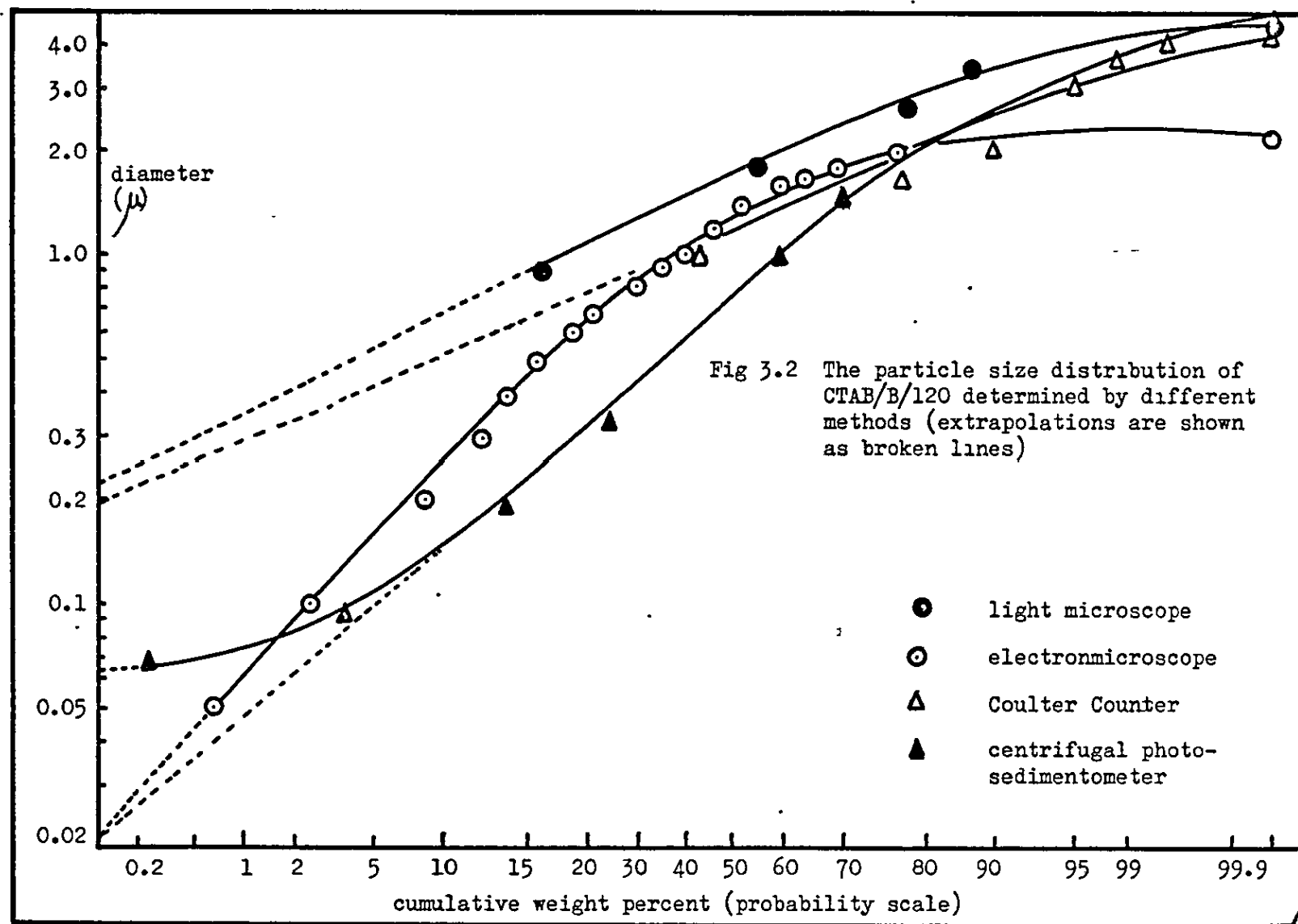


Fig 3.1 Electronphotomicrograph of CTAB/B/120 mounted using Craik's technique. x 20,000



when using light microscopy and the Coulter Counter. It was concluded that a combination of the centrifugal photosedimentometer and the Coulter Counter together offered the best means at present available for carrying out any adequate measurement of the relatively wide size distribution that can exist in some emulsion systems. These two methods were therefore employed in subsequent investigations of other models.

3.3 The Coulter Counter

3.3.1 Instrumentation

All particle counts were made on a Coulter Counter Model A (Industrial) fitted with either a 30 μ or a 70 μ orifice tube. The instrument was calibrated using a monosize polystyrene latex of 1.305 μ mean diameter, a polyvinyltoluene latex of 2.05 μ diameter (both supplied by courtesy of the Dow Chemical Company, Midland, Michigan, U.S.A.) and a mulberry pollen (13.59 μ diameter) obtained from Coulter Electronics Limited. The instrument calibration was checked for drift at monthly intervals using at least two monosize materials.

3.3.2 Dispersion media

Any sample for particle size analysis by this method has first to be diluted with electrolyte. Preliminary investigations showed that dilutions of the system in a wide range of concentrations and type of electrolyte showed considerable flocculation. The rate of flocculation appeared to be related to the concentration of electrolyte present, Table 3.1. The addition of cetrimide to 0.154 M sodium chloride (physiological saline) gave the least flocculated dilution but as the investigation progressed it became clear that, under some conditions, flocculation or aggregation could still take place. It was,

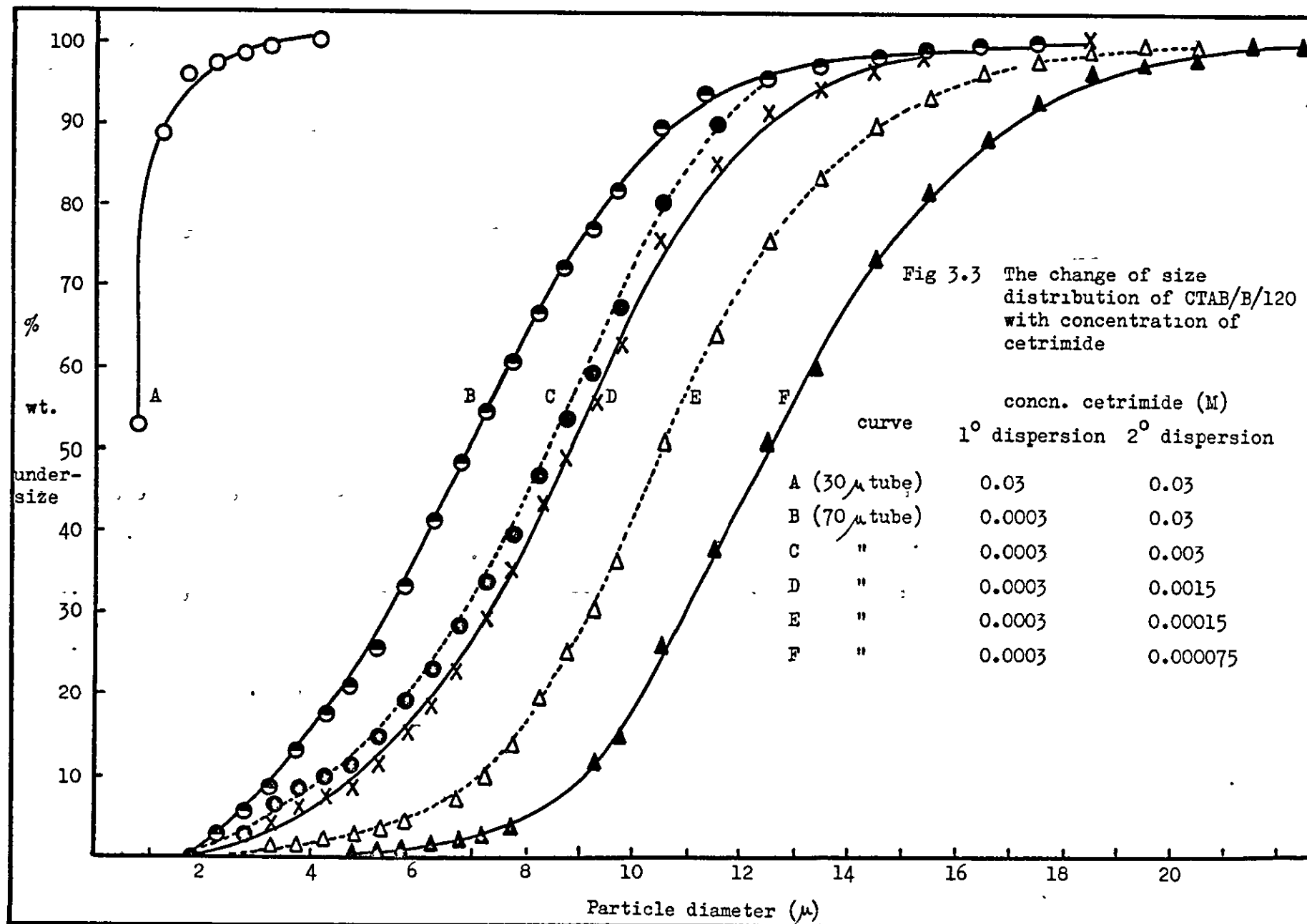
Table 3.1 The effect of electrolyte on dilute dispersions of CTAB/B/120

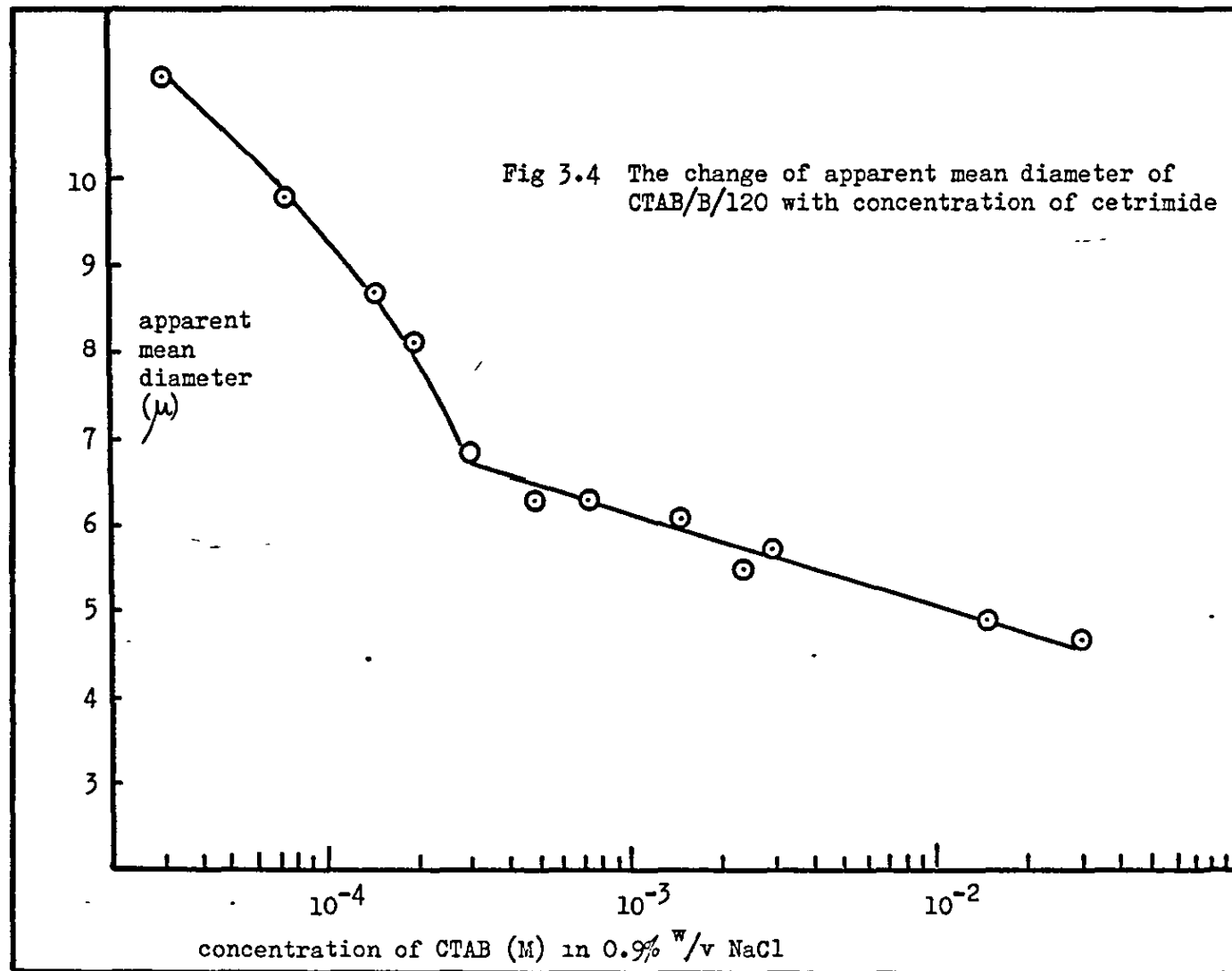
Electrolyte	Concentration % w/v	Flocculation (+ marked) (- none)
Cetrimide	0.02	-
Sodium acid phosphate	2.0	++
Sodium citrate	2.0	++
Sodium acid citrate	2.0	++
Sodium chloride	0.9	+
Sodium chloride and cetrimide	0.9 + 0.005	(+)
Sodium chloride and cetrimide	0.9 + 0.01	(-)
Sodium chloride and cetrimide	0.9 + 0.02	-

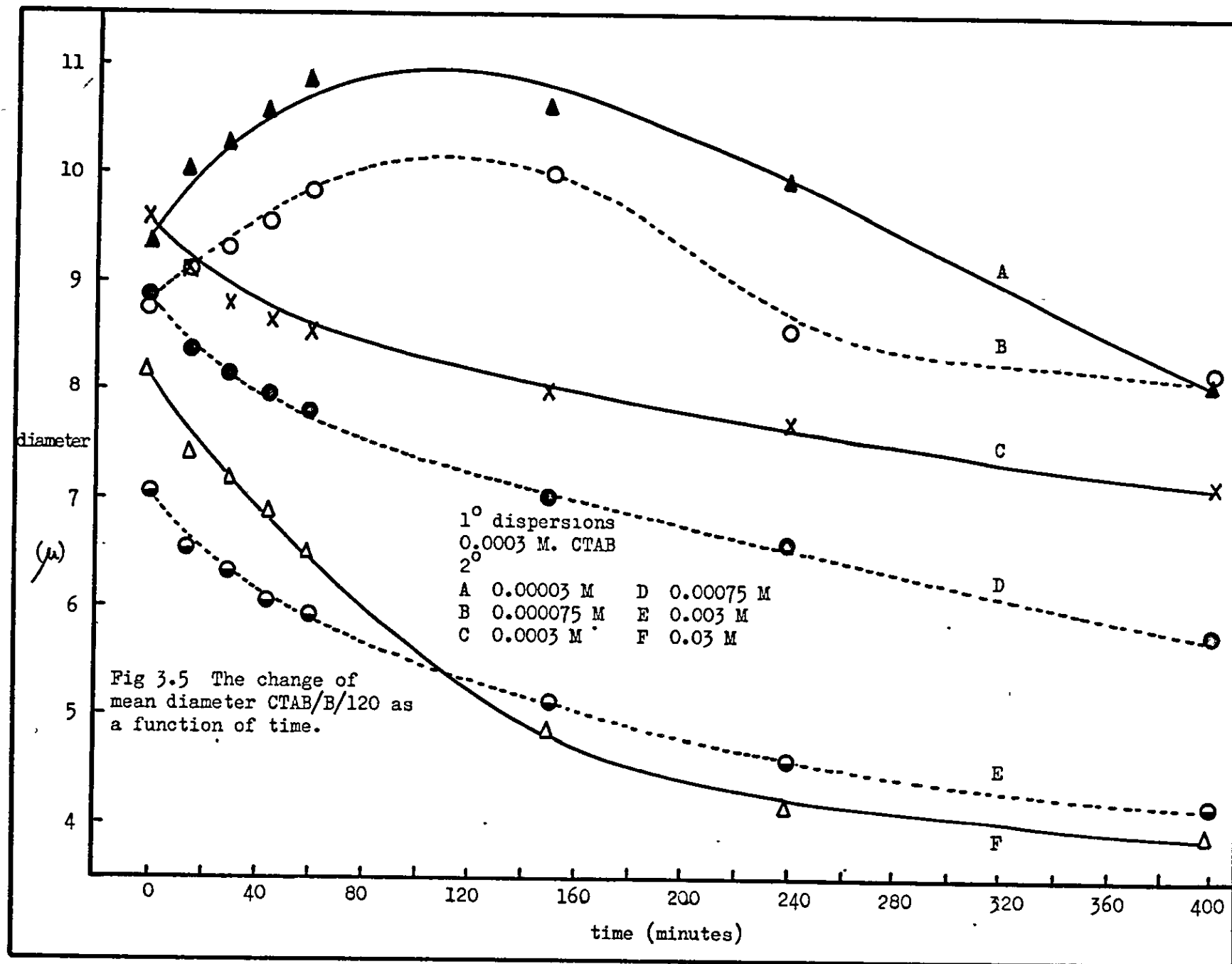
therefore, necessary to investigate these conditions more fully in order to enable the Counter to be applied to this and other systems used in the study. Most of this work has been carried out on cetrimide emulsified formulations but it was later shown that the same effect could be demonstrated in systems containing other emulsifiers.

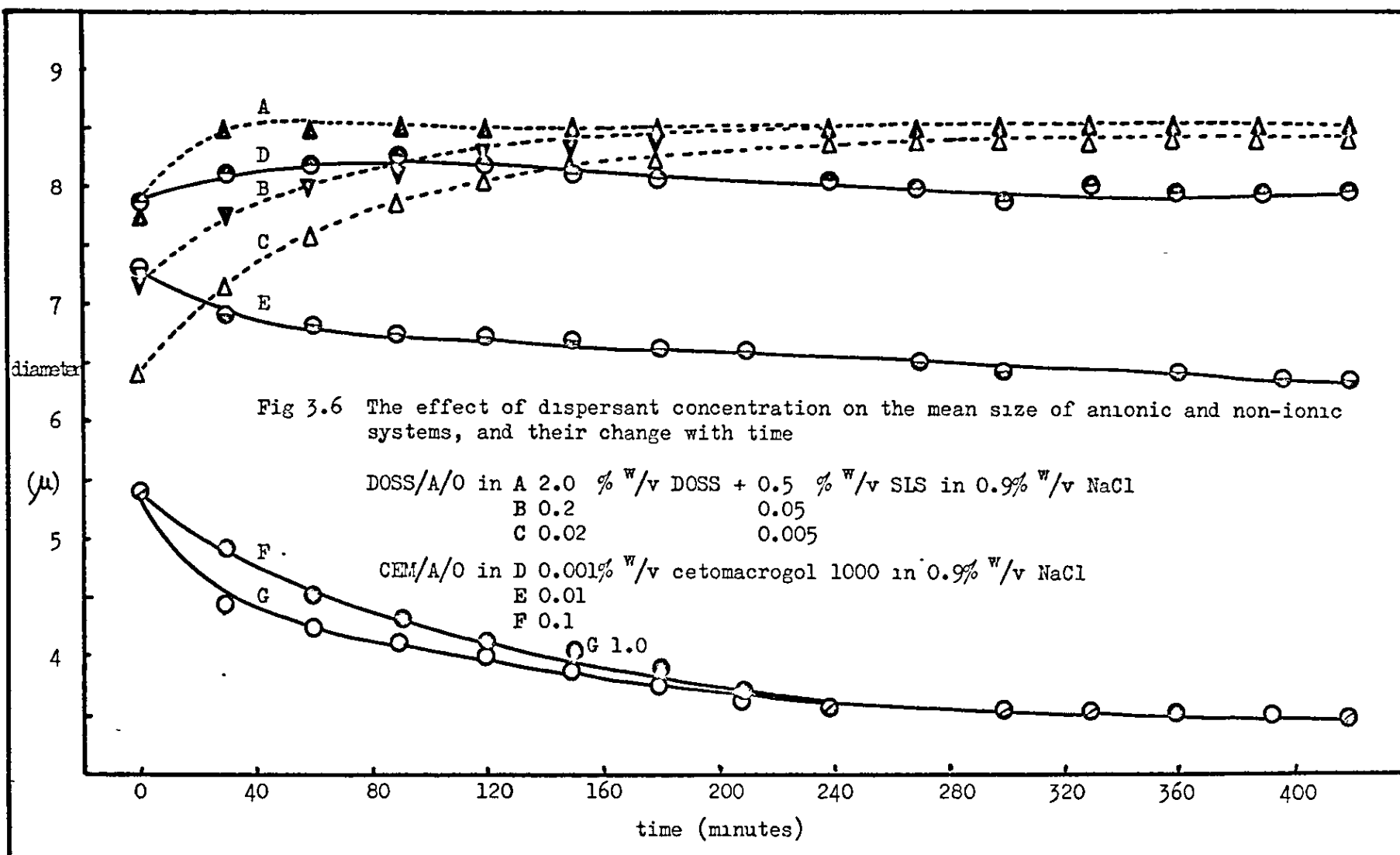
(a) Cationic systems

Since dilution media for use with the Counter require to be substantially free of extraneous particulate contamination it was convenient to employ a commercially-available, physiological saline solution for injection (Polyfusor, Boots - 145, 146, 148). A 10.0% w/v solution of cetrimide in 0.9 w/v sodium chloride was passed repeatedly through a 0.22 μ Millipore membrane filter until the background count was close to that









of the diluent saline (146). Quantitative dilutions were prepared and stored in polypropylene-stoppered glass containers (E-Mil) until required.

As noted by Higuchi et al (179) and Rowe(370) it is necessary to reduce the particle concentration of an emulsion to a suitable level for counting by diluting in at least two stages. The critical micelle concentration (CMC) of cetrimide in 0.154 M sodium chloride was shown to be approximately 0.003 M (147). Accordingly 1 : 1000 dilutions of the system under examination were prepared in saline containing either 0.03 M or 0.0003 M cetrimide. These primary dilutions were kept in plastic stoppered tubes on a slowly rocking table at ambient room temperature (24° to 28°) until required for analysis. This technique was found to be sufficient to prevent creaming of a diluted preparation without undue aeration.

Secondary dilutions were prepared and stirred with a constant speed stirrer rotating at 187.5 r.p.m. for a known time before counting.

When the primary dilution was made in 0.3 M cetrimide-saline the size analysis obtained was in reasonable agreement with that obtained from other methods (3.2); the concentration of cetrimide in the secondary dilution apparently having little effect on the state of dispersion.

However, experimentally it was found that aggregation occurred in secondary dilutions prepared from 0.0003 M cetrimide-saline, i.e., below the CMC. A series of size analyses was obtained under closely controlled conditions of time, temperature and stirring rate to investigate the influence of cetrimide concentration on the apparent size of the aggregates, Fig 3.3. On a logarithmic scale there is a linear correlation between

the apparent mean "particle" (or aggregate) size and cetrimide concentration over three orders of magnitude, Fig 3.4. The inflexion point corresponds to the concentration of the primary dilution, there being no evidence of an inflexion at the CMC (0.003 M).

Since this technique required about 30 minutes for completion it was not suited to a study of the aggregation rate. Accordingly, the procedure was abbreviated by counting at wider threshold intervals to enable an analysis to be made in 4 to 5 minutes. The results of this experiment are shown in Fig 3.5. This procedure was adopted for the subsequent investigations of flocculation effects in other emulsion systems.

This part of the investigation has been reported in detail elsewhere (147) but it can be concluded that a valid estimate of the size distribution of cetrimide emulsion systems can be obtained if the primary dilution is made in saline containing the emulsifier above its critical micelle concentration (130, 131). Cetrimide was also found to be suitable for dispersing the cetylpyridinium chloride and benzalkonium chloride systems.

(b) Anionic systems

The anionic system investigated (Table 4.1) contained both dioctyl sodium sulphosuccinate (DOSS) and sodium lauryl sulphate (SLS) as emulsifiers. Dispersion of this system in 0.9% w/v sodium chloride solution alone proved difficult and the addition of emulsifiers was again examined.

Using the same experimental technique as that used to obtain the data shown in Fig 3.5, dispersions of DOSS/A/O were made in saline containing the emulsifiers at, (a), the same concentrations and (b), one tenth and (c), one hundredth of the initial concentration. The change of mean size is shown as a function

of time in Fig 3.6, curves A, B and C. It will be seen that there is an apparent initial increase in size but all the dispersions ultimately gave the same final mean size. For this reason it was considered that the conditions were likely to be less critical. The dispersion medium was therefore standardized as 0.9% sodium chloride containing the emulsifiers at the same concentration as in the original preparations.

A practical point of interest concerns filtration of the dispersion medium. Clarification of the solution using Millipore (cellulose acetate) membrane filters proved impossible, background counts increasing after each passage through the filter until eventually the solution appeared to be turbid. No effect on the membrane could be detected although it is possible that this solution is capable of detaching small particles from the back of the cellulose acetate pad, a possibility confirmed by Millipore Inc. (personal communication). However, clarification was achieved using a bacteria-proof Seitz pad and solutions were eventually obtained with background particle counts comparable to those of other materials passed through membrane filters.

(c) Nonionic systems

The effect of electrolyte would appear to be general since it was also noted for the cetomacrogol 1000 preparations. Accordingly the addition of cetomacrogol 1000 to sodium chloride solution was again investigated. The same experimental technique was employed, the change of mean size being followed as a function of time. The results of this experiment are shown in Fig 3.6, curves D, E, F and G. The results clearly indicate that there is an effect due to the concentration of

emulsifier. The decrease in mean size and the fact that dispersions containing 0.1% and 1.0% cetomacrogol 1000 gave substantially the same result after about four hours suggested that above 0.1% dispersant the system was no longer aggregated. This concentration was therefore selected as the dispersion medium for Coulter Counter size analyses of the CEH series (Table 4.1).

5.3.3 Standard technique with the Coulter Counter

(a) Initial Dispersion

Microscopic examination confirmed that trituration with anhydrous glycerol was a satisfactory means of dispersing all the semisolids investigated in this work.

A 50 mg sample was taken from the material using a probe and accurately weighed on a watch glass. The sample was slowly triturated with 100 mg glycerol using a camel hair brush or flat bladed spatula and the dispersant-saline added before making up to a 50 ml volume. The dilution was shaken and subjected to a 15 sec. burst of ultrasonic radiation before placing the plastic stoppered tube on a slowly rocking table. Repeat analyses showed that for continuous periods of up to 10 minutes the ultrasonic treatment had no detectable effect on the size distribution of the sample and any effect thereafter was only slight. The restriction of the ultrasonic dispersion irradiation to 15 seconds only was felt to be unlikely to affect the measured size distribution and appeared to be useful in that it dispersed small, visible, aggregates which were occasionally noticed.

The primary dilution was maintained on the rocking table at ambient room temperature (24° to 28°) for at least three days before analysis.

(b) Secondary dilution

This was prepared by slowly pipetting the primary dilution into 100 ml of the dispersant in a beaker on the Counter orifice stand. The dispersion was added until the count approached the instrument coincidence level at the lowest threshold ($\sim 1.5 \mu$ diam.). The secondary dilution was kept stirred with a constant speed stirrer rotating at 187.5 r.p.m. for 30 minutes (cationic and anionic systems) or 1 hour for the non-ionic system.

After this stabilisation period the dilution was counted, starting at the highest instrument threshold and reducing this by 0.5μ intervals until the complete size range had been covered. Background counts were taken using the same procedure.

All counts were taken on volumes of 0.05 ml, in replicates of four. The results were converted to a cumulative weight size distribution by the method described in the Coulter handbook.

3.4 The centrifugal photosedimentometer

3.4.1 Description

The instrument is shown in Figs 3.7, a and b, and as a diagrammatic section in Fig. 3.8. It consists of a hollow rotating perspex disc containing a dilute suspension of the emulsion. The disperse phase particles, being less dense than the continuous phase, move radially inwards according to Stokes' Law. The concentration of particles is measured at a fixed depth by measuring the attenuation of a beam of parallel light.

The disc has an internal radius of 11.6 cm and a depth of 1.6 cm with a total liquid capacity of 650 ml. It is attached

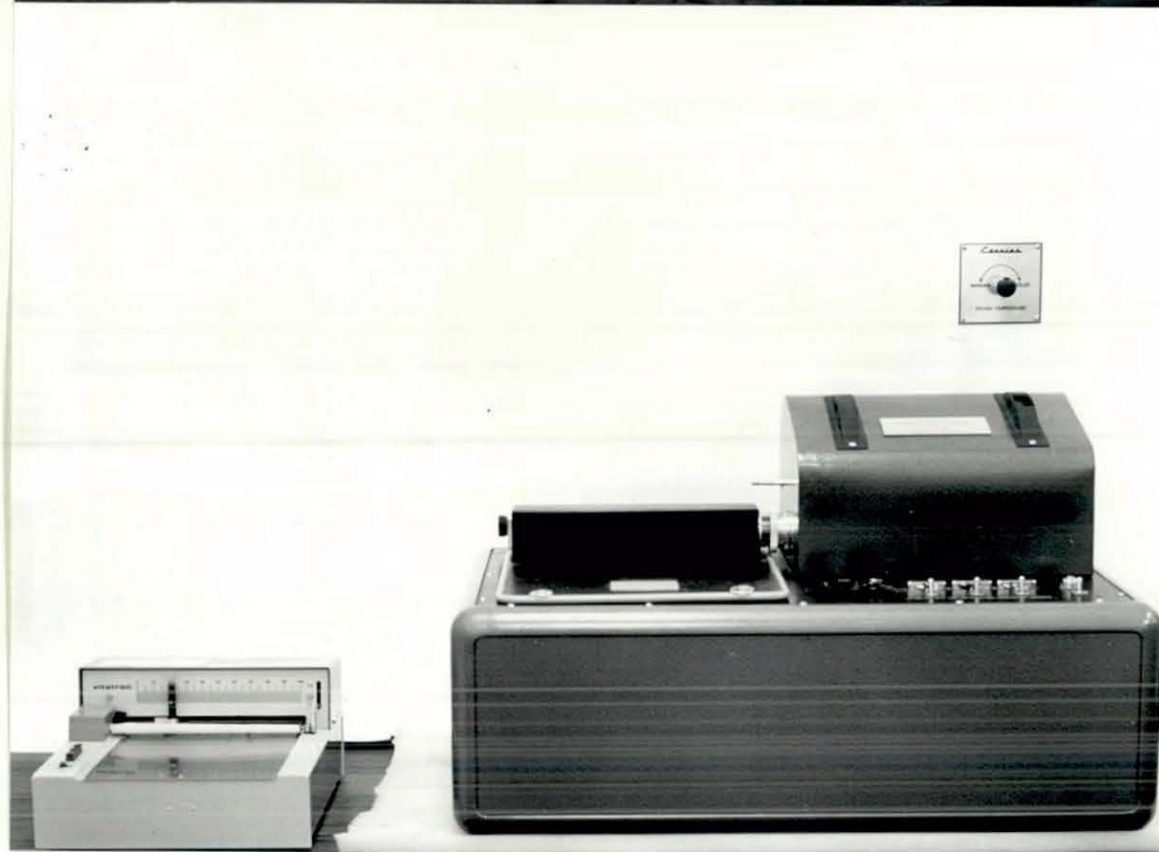


Fig 3.7 The centrifugal photosedimentometer

- (a) with lid up showing disc
- (b) in operating condition

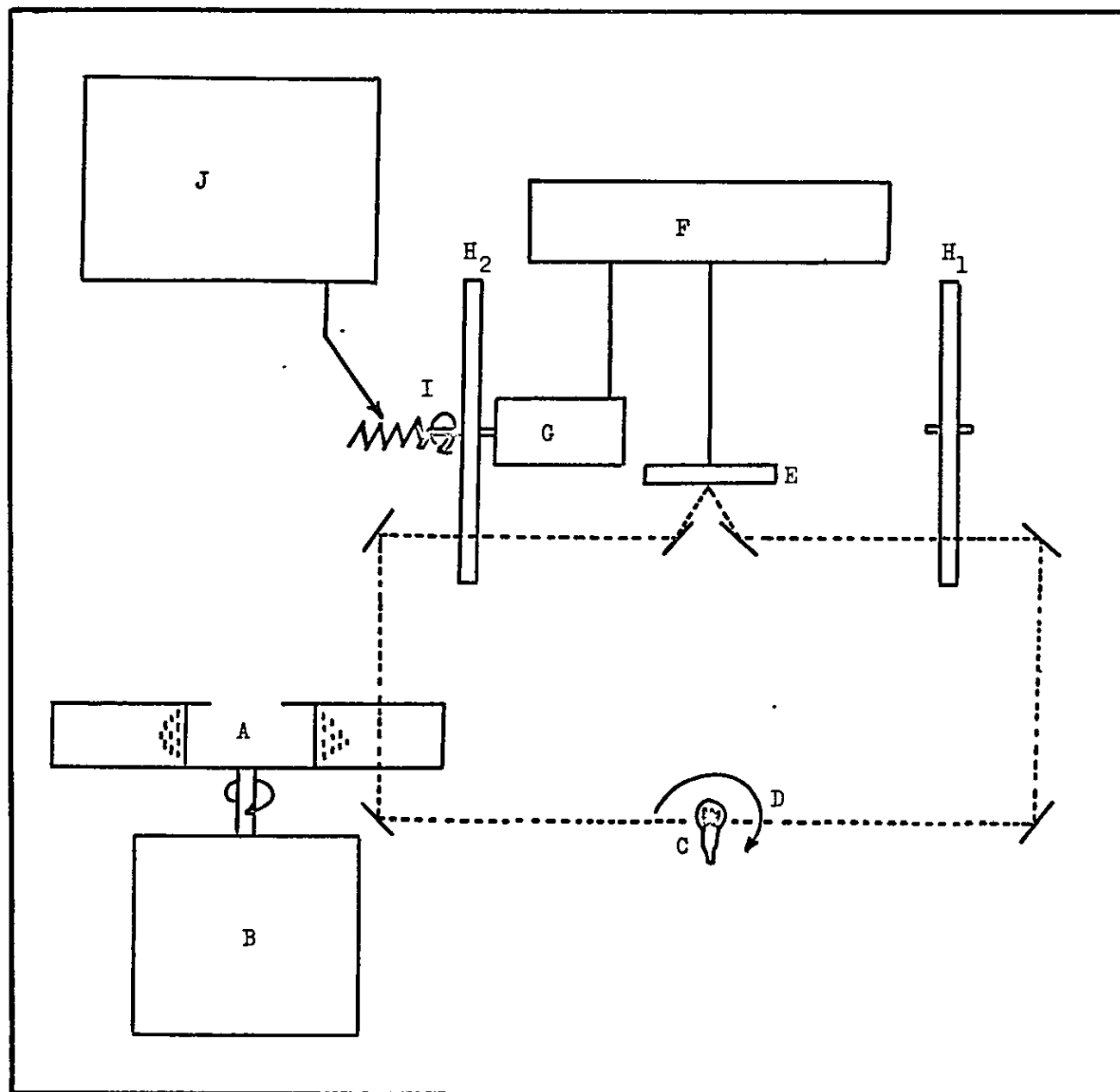


Fig 3.8 Diagrammatic section of centrifugal photosedimentometer

- A disc
- B motor
- C light source
- D chopper
- E photoelectric cell
- F amplifier
- G servo motor
- H₁ optical wedge, balancing
- H₂ optical wedge, recording
- I potentiometer
- J recorder

The optical path is shown as a broken line

directly to a $\frac{1}{4}$ h.p. synchronous motor wired for three speeds, 750, 1500 and 3000 r.p.m. Since instabilities in the tank liquid were prone to develop at 750 r.p.m. and mechanical failures did not allow the motor to operate at 3000 r.p.m. the use of this instrument was confined to 1500 r.p.m. Stroboscopic examination showed that at this setting the tank speed was extremely steady.

The beam of parallel white light (from a 12 v 24 w axial filament car bulb) is chopped at a frequency of 50 cycles/sec. to enable it to impinge onto a cadmium sulphide photo-electric cell after passage through the tank or through a hand adjusted optical wedge. The photo-electric cell is connected, via an amplifier, to a servo motor which drives a second optical wedge (H_2) on the tank side of the light circuit. Thus, once the system is in balance there is no change of resistance of the cell and the wedge H_2 remains stationary. However, if the system is unbalanced by obscuration of the light beam (by material in the rotating tank) the resistance changes and the servo-controlled wedge moves to admit more light to restore the balance. Movement of this wedge is monitored by a potentiometer on its axis which in turn is connected to a chart pen recorder. The recorder, a Vitatron 10 mv full scale deflection with variable chart speeds, has a response time of 0.5 secs. The chart is therefore a direct record of the change in optical density of the sedimenting system at a fixed point within the tank with respect to time.

3.4.2 Filling technique

Preliminary experiments failed to reveal a practicable method for injection of a thin layer of a diluted emulsion at

the periphery of the tank. Accordingly, it became necessary to utilise an homogenous suspension technique although the theoretical treatment of results is more difficult. Two methods of filling the empty tank with diluted suspension were therefore considered. Stroboscopic examination (with an E.M.I. Model 6, Xenon flash unit) showed that the tank required some 30 to 45 seconds to accelerate to speed from a stationary position, and liquid inside the tank continued to swirl for approximately 10 to 15 seconds thereafter. The visual observation of swirling was confirmed by placing thin white rayon fibres in the centre lumen of the tank, both close to the surface of the tank and suspended midway between the two surfaces. Whilst swirling was taking place the fibres were bent almost parallel to the inner meniscus of the tank liquid. The transition to a non-swirling state was marked by a rapid movement to a radial position, normal to the meniscus.

On the other hand, pouring 650 ml of liquid from a beaker into the tank rotating at 1500 r.p.m. occupied approximately 4 seconds and there was only a slight, almost imperceptible, change in the speed during that time. Repeated observations showed that the time between commencement of pouring and the movement of the suspended fibres to a radial position covered a range of 6 to 12 seconds. This technique had the advantage that commencement of streamline flow centrifuging conditions was defined more precisely than with the stationary-start method. The greater speed with which the liquid can be accelerated to the same radial velocity of the tank was probably due to the fact that the falling stream of liquid was broken into drops in the centre bowl of the tank. These drops were then thrown to the periphery at a tangent from the bowl gaining momentum

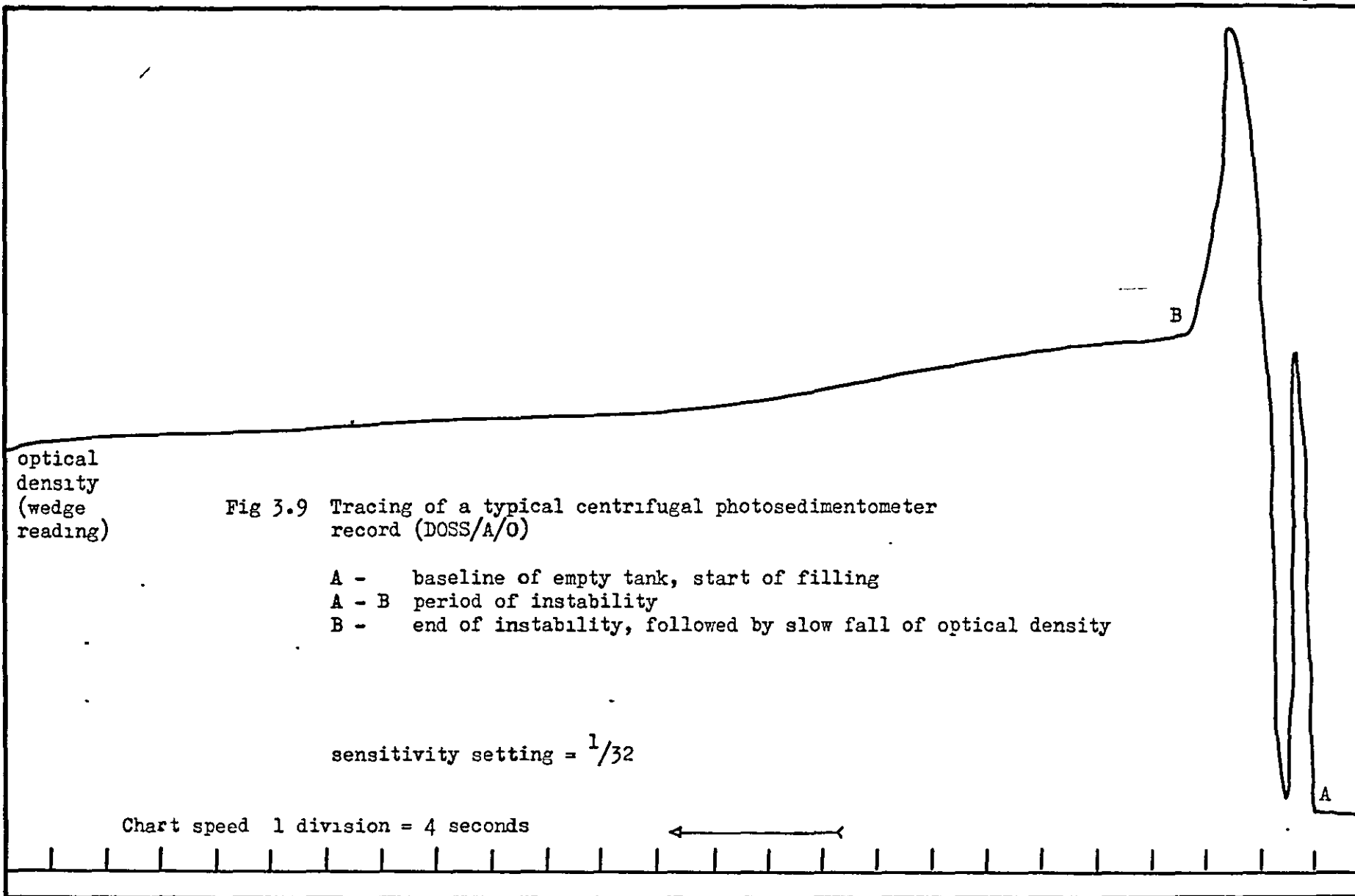
optical
density
(wedge
reading)

Fig 3.9 Tracing of a typical centrifugal photosedimentometer
record (DOSS/A/O)

- A - baseline of empty tank, start of filling
- A - B period of instability
- B - end of instability, followed by slow fall of optical density

sensitivity setting = $1/32$

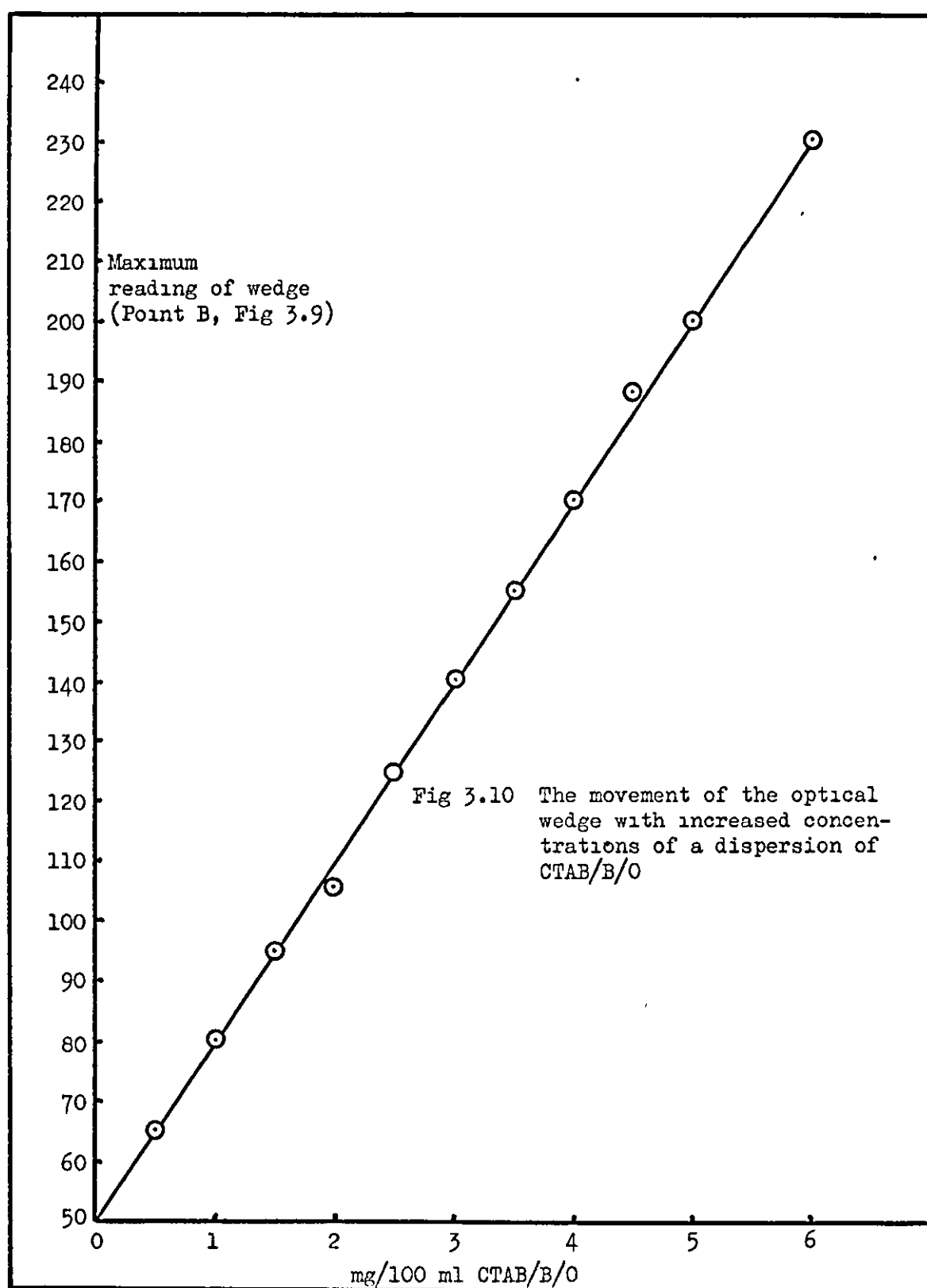
Chart speed 1 division = 4 seconds



in the desired direction of movement.

There was also circumstantial evidence for the suggested initial lag of 6 to 12 seconds from the start of filling the rotating tank. The optical density/time trace of an added suspension showed, characteristically, an increased optical density immediately after the start of filling. There followed a rapid period of decline, after which the decline became slower. The change from the rapid to a slow decline of optical density was marked and, once again, occurred between 6 to 12 seconds after starting to fill the tank. A typical trace is shown in Fig 3.9. The upsurge in optical density may well be due to swirling in the tank and displacement of air bubbles. However, it seemed reasonable to conclude that the transition point on the trace coincided with the onset of streamline centrifuging conditions. This was therefore regarded as the zero time in all subsequent calculations.

The irregular sedimentation patterns ('streaming'), discussed by Rippon (361) and by Jones (201) for two-layer sedimentation systems, are less likely to occur with the homogeneous technique. Nevertheless, they have been observed (Jones, personal communication) and this observation was confirmed with the present instrument. However, they were shown to occur only occasionally at concentrations of diluted emulsions 100-fold higher than the dilution which produced the maximum response of the optical wedge. Repeated observation of more usable dilutions failed to produce any evidence of irregularity in the sedimentation pattern. This may well fit in with the suggestion by Burt (48), Burt & Kaye (49) and Kaye & Jackson (209) that a critical concentration exists, below which this form of hindered or irregular settling is unlikely to occur.



3.4.3 Linearity of the servo-assisted optical wedge

This wedge was known to be a circular disc with a maximum optical density of 0.1, graduating to complete clarity (Coulter Electronics Ltd., personal communication). Although the usable portion of the wedge was marked in degrees of rotation (0° to 270°) it was not clear if the wedge increased in density in a regular fashion. Accordingly this was checked by making quantitative dilutions of a standard preparation, itself an accurate dilution of the emulsion CTAB/B/O in aqueous cotrimide. A volume of 450 ml of each dilution was poured into the clean tank rotating at 1500 r.p.m. and the optical density-time relationship followed for a few minutes after commencement of filling. The optical density, expressed as the graduation at the edge of the optical wedge at the transition point noted above, is shown as a function of concentration in Fig. 3.10. The linearity of the wedge would appear to be satisfactory and movement of the wedge expressed in degrees is a direct function of concentration. The linearity between concentration and recorded optical density is also partial confirmation that measurement of zero time from the transition point between rapid and slow changes on the chart has some real meaning.

3.4.4 Standard technique with the centrifugal photosedimentometer

(a) Dispersants

No systematic examination of dispersants or concentrations was undertaken as for the Coulter Counter since this appeared to be unnecessary. However, dispersions were prepared in aqueous solutions of the same emulsifier and at the same concentration as the preparation under examination.

The dispersion technique was similar to that described for the Counter.

(b) Method

Since the optical wedge was thrown out of balance by dispersions with an excessive optical density it was necessary to dilute each dispersion until it had an optimum optical density. This was achieved by matching a dilution with a standard using a Hilger Biochem Absorptionmeter. The instrument was adjusted to a reading of 60% transmission with a standard suspension containing 0.1 mg kaolin (Speswhite, V & H grade) per ml in 1.0% sodium polynetaphosphate (Calgon S) solution. Dilutions of the materials under examination were adjusted to give 82 to 90% transmission on the Absorptionmeter.

The centrifuge servo mechanism required at least 10 minutes' running from the cold before responding. Accordingly, the tank was cleaned and filled with distilled water. With the tank running at 1300 r.p.m. the pen recorder was adjusted so that, with the sensitivity control at 1/32nd sensitivity, movement of the wedge from 50° and 250° was a full scale deflection. Base lines at the different sensitivities were established and the recorder calibrated by manual movement of the balancing optical wedge. The tank was then stopped, emptied and re-run with the servo mechanism 'active' for at least 10 minutes. In the meantime 450 ml of the dilution was prepared and poured into the empty tank. Simultaneously the chart was started at its maximum speed and the 1/32nd sensitivity setting. As discussed earlier, timing of the run was commenced at the end of the initial upsurge phase (Point B, Fig 3.9) and continued until the base line was regained; sensitivity settings and chart speeds were changed as required.

Table 3.2 A typical set of results, obtained during the centrifugal photosedimentation size analysis of CTAB/3/60

From Stokes' Law

$$\text{Particle diameter} = D = \left[\frac{3.778 \times 10^{11} \times \eta}{N^2 t (\rho_1 - \rho_2)} \cdot \log_{10} \frac{R_2}{R_1} \right]^{\frac{1}{2}} \text{ micron}$$

Where $\eta = 0.8545 \times 10^{-2}$ poises, $N = 1500$ rpm, $R_1 = 12.35$ cm,

$R_2 = 10.80$ cm, $\rho_1 = 0.8843$, $\rho_2 = 0.9970$, t in seconds.

$$\therefore D^2 = \frac{784.94}{t}$$

A calibration curve of wedge value vs chart reading was obtained by moving the wedge H_1 (Fig 3.8).

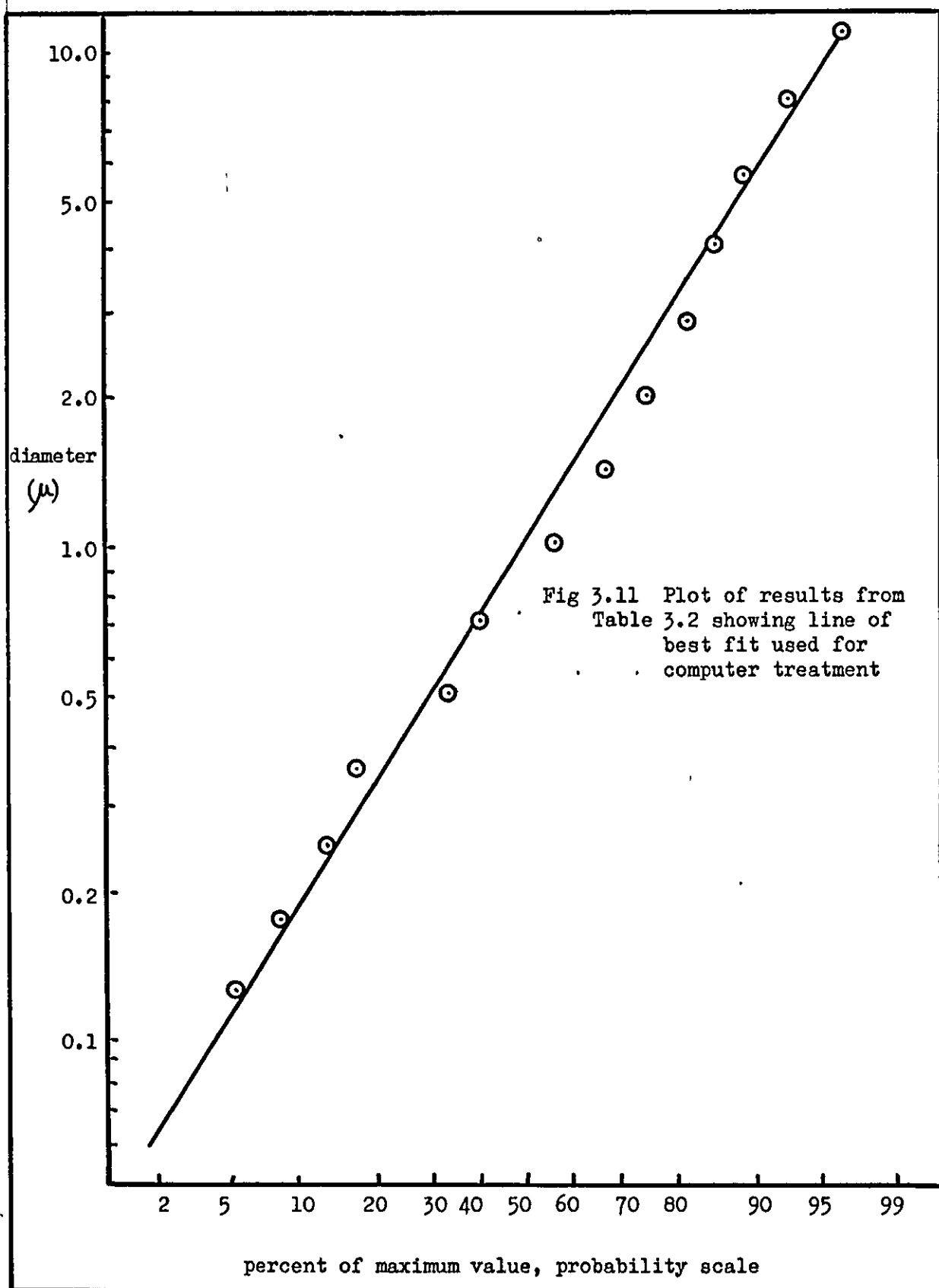
Maximum chart reading (point 3, Fig 3.9) at 1/32nd sensitivity = $43.5 \equiv 149^\circ$ on wedge.

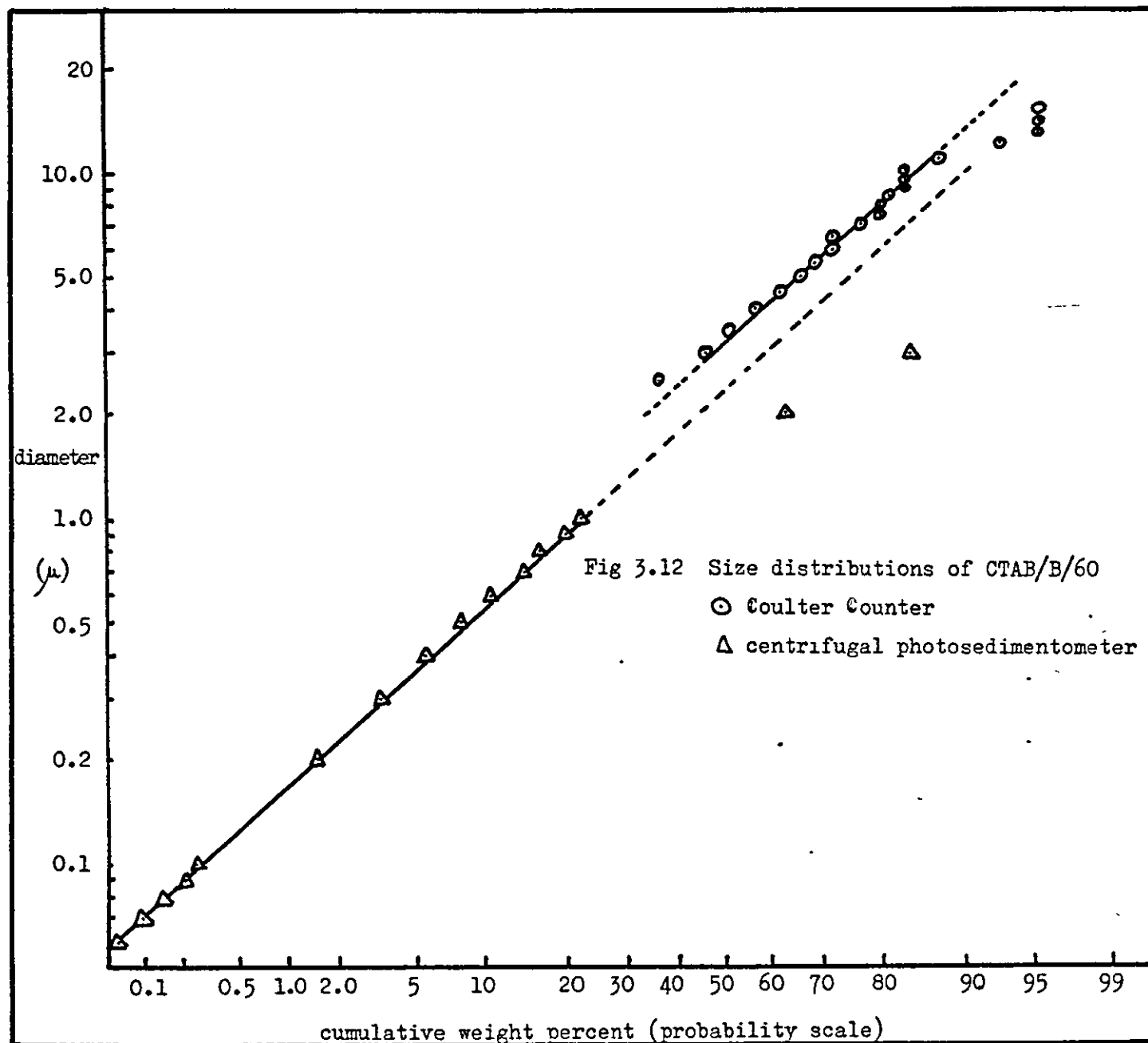
Maximum (zero) at 1/8th sensitivity = $45 \equiv 73^\circ$ on wedge.

Hence total movement = $149^\circ - 73^\circ = 76^\circ$

Readings from chart were converted to movement of the optical wedge as follows:

Equiv. particle diameter μ	Time hr/min/secs	Recorder Sensitivity	Chart Reading	Wedge value	Wedge movement	Wedge Movement of wedge as % of total
11.32	6.1	1/32	42	146	73	96.2
8.00	12.3	1/32	41	143.5	70.5	93.0
5.66	24.5	1/32	40	141	68	89.5
4.00	49.1	1/32	39	138.5	65.5	86.2
2.83	1 33	1/32	38	136	63	82.9
2.00	3 16	1/32	36	130.5	57.5	75.6
1.41	6 33	1/32	34	125	52	68.5
1.00	13 5	1/32	31	117	44	57.9
0.707	26 10	1/32	26	104	31	40.8
0.500	52 20	1/32	24	99	26	34.2
0.354	1 44 40	1/32	19	86	13	17.1
0.250	3 29 20	1/32	17	83	10	13.15
0.177	6 53 40	1/8	59	80	7	9.2
1.125	13 57 20	1/8	51	77	4	5.27
0.0834	27 54 40	1/8	45	73	0	0



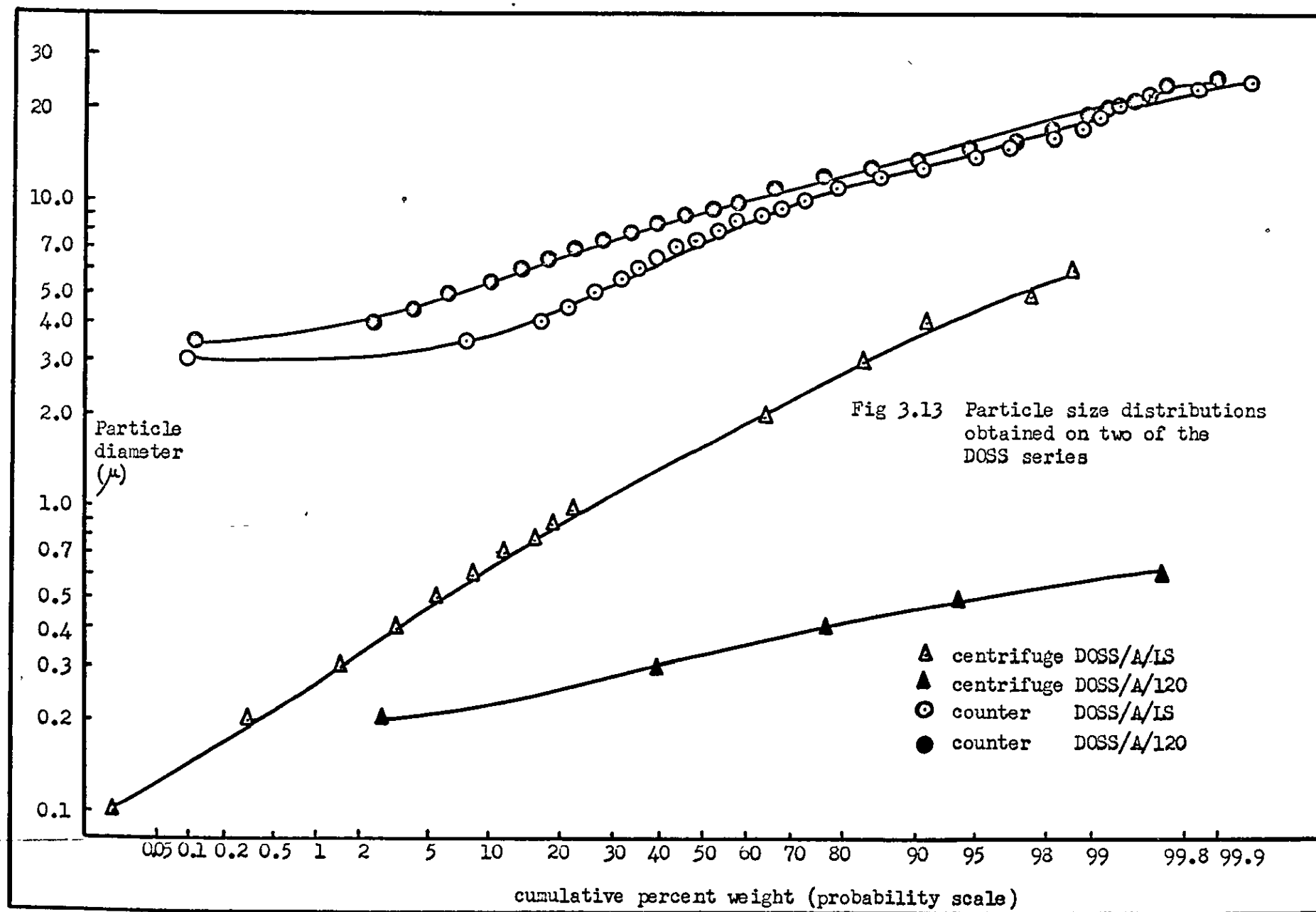


When the run was completed the optical densities were read off at time intervals corresponding to $\sqrt{2}$ increments of particle Stokes' diameter. These were plotted on log. probability paper and a smoothed curve used to present results for computer treatment according to Kerack's method (204). A typical set of results is given in Table 3.2 and Figs 3.11 and 3.12.

3.5 Discussion and conclusions

No one particle sizing technique in isolation is adequate to cover the wide range of particle sizes which can occur in emulsion systems. It was suggested (151) that a combination of the Coulter Counter and the centrifugal photosedimentometer had advantages. The former instrument covers the same range of sizes as the light microscope but the counting rate is such that the sampling errors associated with microscopy are largely overcome. The photosedimentometer was applicable to emulsion systems and was capable of detecting most of the sub-micron particles present in the model.

As would be anticipated, it was a general experience that the two methods gave parallel distributions. Following the detailed comparison of replicated samples of the same material shown in Appendix Two it appeared reasonable to normalise the two results in order to define as closely as possible the mid-portion of the log-probability distribution lying between 20 and 80% probability (96). This procedure yielded consistent results in all but the DOSS series. In this system as the period of ultrasonic irradiation was increased the Coulter results did not change significantly whereas the centrifuge results indicated a progressive reduction in particle size



and distribution. The size distribution of the two extreme members of this series are shown in Fig 3.13. Light microscopy confirmed that the centrifuge results were valid, no particles $> 1 \mu$ being visible in DOSS/A/120. With hindsight, it would appear that the dispersion system in electrolyte described for this series was not sufficient to prevent aggregation. As shown in Fig 3.6, the dilutions all yield the same mean size which in fact is larger than the initial values and it seems likely that this is a manifestation of aggregation behaviour.

3.6 Summary

1. A detailed comparative size analysis of a model system confirmed that sub-micron particles were present. 3.2
2. No one method of size analysis appeared to be adequate to cover the wide range of particle size that can exist in an emulsion system. 3.2
3. Extrapolation techniques yield serious underestimates of sub-micron particles. 3.2 (151)
4. A combination of Coulter Counter and centrifugal photosedimentometer offer the best means at present available for sizing emulsion systems. 3.2
5. The necessary presence of electrolyte caused flocculation and aggregation effects to influence results obtained from the Coulter Counter. 3.3.2
6. These could be overcome by the addition of emulsifier but conditions were shown to be critical. 3.3.2
7. The centrifugal photosedimentometer could only be employed using a homogeneous suspension technique. 3.4.2

Table 3.3 The particle size distributions of all the dispersions examined in this investigation, from normalised log-probability plots of the cumulative weight distributions obtained by Coulter Counter and centrifugal photodiffraction. (Formulations Table 4.1 p92)

Code	Dispersion		Mean size (μ)	Standard deviation	Specific surface area (m^2/g_{phase})
CTAL	A	LS	0.50	2.03	0.2390
		60	2.40	2.33	0.5979
CTAB	B	LS	3.40	2.35	0.4519
		0	5.00	1.94	0.2416
		5	1.90	2.37	0.7478
		10	1.90	2.53	0.7849
		15	1.80	2.55	0.8625
		20	3.00	2.40	0.4584
		25	1.90	2.90	0.8976
		30	4.00	2.54	0.3833
		45	2.50	2.16	0.5212
		60	2.20	3.37	1.0237
		120	1.15	3.22	1.5424
CTAB	C	LS	3.30	2.45	0.7597
		LS	3.30	2.27	0.4169
		LS	3.20	2.27	0.6279
		LS	3.20	2.44	0.4643
		LS	2.90	2.14	0.4582
		LS	3.80	2.37	0.3681
		LS	4.00	2.31	0.3857
		LB	2.10	2.19	0.6472
		LS	3.00	2.20	0.4582
		LS	3.90	2.13	0.3585
		LS	4.40	2.10	0.3000
		LS	3.00	2.20	0.4582
		LS	3.50	2.14	0.3755
		LS	2.00	1.90	0.5919
CTAB	L/L	LS	2.90	2.07	0.4395
		LS	4.80	2.39	0.2998
		LS	2.70	2.27	0.4901
		LS	3.30	2.12	0.3809
CPC	A	LS	3.60	2.56	0.3533
CPC	B	0	3.40	1.925	0.2250
		15	3.30	2.73	0.5123
		20	3.00	2.40	0.4817
		25	2.20	2.82	0.7634
		30	2.00	3.00	0.9327
		45	1.75	2.51	0.8562
		60	1.70	2.83	0.9420
		120	1.35	2.55	0.9695
CPC	C	LS	2.10	2.00	0.3554
		LS	2.00	1.90	0.5845
BNZ	A	LS	2.60	2.23	0.4913

(cont over)

Table 3.3. (cont.)

Code	Dispersion	Mean size (μ)	Standard deviation	Specific surface area (m^2/g disperse phase)
C-11	A LS	2.50	2.64	0.6248
	0	1.75	2.115	0.7298
	15	3.00	3.333	0.6692
	30	1.90	2.32	0.7473
	60	1.75	3.07	1.0018
	120	2.10	2.38	0.6760
D-33	A LS	1.50	2.00	0.8155
	0	2.20	2.28	0.5940
	15	3.00	3.27	0.6643
	30	0.80	2.69	2.0482
	60	0.50	1.60	2.1845
	120	0.31	1.29	3.3738

CHAPTER FOUR

THE EMULSION SYSTEMS UNDER INVESTIGATION, THEIR PREPARATION AND PROPERTIES.

- 4.1 Introduction
- 4.2 Materials employed
- 4.3. Formulations
- 4.4 The density of the disperse phase
- 4.5 The density and viscosity of the continuous phases
- 4.6 Methods of emulsification
- 4.7 The appearance of the emulsions
- 4.8 The relationship between concentration and particle shape
- 4.9 The theoretical and experimental emulsion densities
- 4.10 Discussion
- 4.11 Summary

4.1 Introduction

Most of the semisolid emulsions used as vehicles in the pharmaceutical and cosmetic industries are of waxy materials in aqueous solutions of surface active agents. Any study of relevance to the industrial application and preparation of these systems should of necessity be confined to materials of commercial origin since these are used in practice. As noted (2.2.1) some highly purified materials may give different experimental results from the commercial variety.

A survey of books of recipes and formulae available over recent years showed that high quality paraffin oils constitute the commonest oil phases employed in pharmaceutical emulsions. This is mainly because they are inexpensive, inert, stable and readily available. A variety of waxy materials are used but one of the most frequently used is a mixture of solid aliphatic alcohols known in commerce as cetostearyl alcohol. A mixture

of paraffin oil and cetostearyl alcohol was therefore a simple and appropriate model system upon which to work.

The choice of surface active agent as emulsifier is however extremely wide. It became clear that similar emulsion systems could be prepared with the same disperse phase but using a wide variety of different types of surface active agent. Representative materials were therefore selected from each of the three main groups (391, 392).

4.2 Specifications of materials employed

All materials were obtained from the warehouses of Boots Pure Drug Co. Ltd., Nottingham.

LIQUID PARAFFIN B.P. (Batch D11) (Burmah Oil Co.)

Kinematic viscosity (37.8°) 80.6 centistokes, weight per ml (20°) 0.890.

Complied with Pharmaceopoeial limits for carbonisable substances, solid paraffins and sulphur compounds.

LIGHT LIQUID PARAFFIN B.P.C. (Batch 37469M) (Purofinol Ltd.)

Kinematic viscosity (37.8°) 11 centistokes, weight per ml (20°) 0.855.

Complied with limit tests for carbonisable substances and sulphur compounds.

CETOSTEARYL ALCOHOL B.P. (Batch 301013M) (Prices (Bromborough) Ltd.)

Acetyl value 181, Iodine value 0.2, Saponification value 0.8, Solidifying point 49.8°C .

A typical analysis by gas-liquid chromatography (D. A. Elvidge, personal communication): approximately 49% cetyl alcohol, 45% stearyl alcohol, 3% myristyl alcohol, 2% lauryl alcohol and 1% of five, unidentified, minor components.

CETRIMIDE B.P. (Batch 54940Y) (I.C.I. Ltd.)

Loss on drying (105°) 0.9%, Assay (dried material) 100.5%.

Complied with limits on sulphated ash and clarity of solution. When examined by gas-liquid chromatography using the method of Laycock & Mulley (239) the sample was found to contain the following homologues: C₍₁₂₎ 21.5, C₍₁₄₎ 69.0, C₍₁₆₎ 9.0, C₍₁₈₎ 0.5 % w/w (P. Henry, personal communication).

CETILPYRIDINIUM CHLORIDE B.P. (Batch 46103 S) (F. I. Berk Ltd).

Assay 99.1%, Chloride content 9.9%, Melting point 82.6°, Loss of weight in vacuum 0.41%, Sulphated ash 0.05%, pH of 1% solution = 5.6.

BENZALKONIUM CHLORIDE B.P.C.

A sample of Onyx 50% Solution U.S.P. grade received from Organon Laboratories Ltd.

SODIUM LAURYL SULPHATE B.P. (Batch 64123 G) (Marchon Products Ltd.)

Assay 90.1%, Total alcohols 59.9%, Sodium chloride 0.73%, Sodium sulphate 3.17%, Unsulphonated alcohols 0.9%. Complied with limit on free alkali.

DIOCTYL SODIUM SULPHOSUCCINATE (Batch 64196 G) (100% material, shredded, Hardman and Holden Ltd., as Manoxol OT (100%)).

Assay 94.9%

CETONACROGOL 1000 B.P.C. (Batch 63312 G) (Glovers Ltd., as Texofor AIP)

Hydroxyl value 47.5, Acid value 0.1, Melting point 40.3°, Refractive index (60°) 1.452, saponification value 0.5, Water 0.5.

THIOMERSAL B.P. (Batch 57558 w 64961) (Hopkin and Williams Ltd).

Glycerol was of Pharmacopoeial grade and water was freshly prepared distilled water.

4.3 Formulations

Each formulation was prepared in 200 g quantities and stored in clear glass wide mouth jars with metal screw caps and waxed card liners. All preparations were stored in a room where there was no direct inlet of light or heat and the ambient temperature was generally in the region 20 to 25°. Formulations are tabulated in Table 4.1, together with the codes by which they are identified. The first group of letters identify the emulsifier, the second the specific formulation and the final figures or letters the method of preparation. Since the preparations were allowed to age for three to six months before investigation thiomersal was added as a preservative to the preparations which did not contain quaternary ammonium compounds. This was selected since it is soluble in cold water, is not volatile and does not react with the stainless steel vessel used in the preparation of some of the emulsions.

4.4. The density of the disperse phase

Since a knowledge of the density of the disperse phase of each emulsion was required for the centrifugal photosedimentometer size analyses this was measured at 20° using a pyknometer technique. The pyknometer was partially filled with the molten mixture of liquid paraffin and cetylstearyl alcohol, taking care to avoid bubbles. After allowing the mixture to set the bottle was weighed and then filled with water, reweighing

Table 4.1 The formulations and coding of all the preparations investigated.

Formulae are by weight and are adjusted to 100 parts by weight with water.

EMULSIFIER and other constituents	Concen- tration	Liquid paraffin	Cetostearyl alcohol	CODE LETTERS	
Cetrimide	0.1	10	10	CTAB/A	(1)
	0.5	10	10	CTAB/B	
	1.0	10	10	CTAB/C	
	5.0	10	10	CTAB/D	
	10.0	10	10	CTAB/E	
	1.0	5	5	CTAB/F	(2)
	1.0	15	15	CTAB/G	
	1.0	20	20	CTAB/H	
	1.0	25	25	CTAB/I	
	1.0	5	15	CTAB/J	
	1.0	5	25	CTAB/K	
	1.0	15	5	CTAB/L	
	1.0	25	5	CTAB/M	
	0.5	50	5	CTAB/N	
	1.0	50	5	CTAB/O	
	10.0	50	5	CTAB/P	
	1.0	5*	15	CTAB/J/L	
	1.0	25*	5	CTAB/M/L	
	1.0	15*	5	CTAB/L/L	
	1.0	10*	10	CTAB/C/L	
Cetylpyridinium chloride	0.1	10	10	CPC/A	(3)
	0.5	10	10	CPC/B	
	1.0	10	10	CPC/C	
	10.0	10	10	CPC/D	
Benzalkonium chloride	1.0	10	10	BENZ/A	(5)
Diethyl sodium sulphosuccinate	2.0	10	10	DOSS/A	
Sodium lauryl sulphate	0.5				
Glycerol	5.0				
Thiomersal	0.02				
Cetomacrogol 1000	2.0	10	10	CEMI/A	(4)
Thiomersal	0.02				

Notes : * Light liquid paraffin

(1) Cetrimide Cream B. Vet. C. 1953

(2) Cetrimide Cream B.P.C. 1963

(3) based on formulation in White, (506)

(4) based on Hydrocortisone Cream B.P.C. 1963

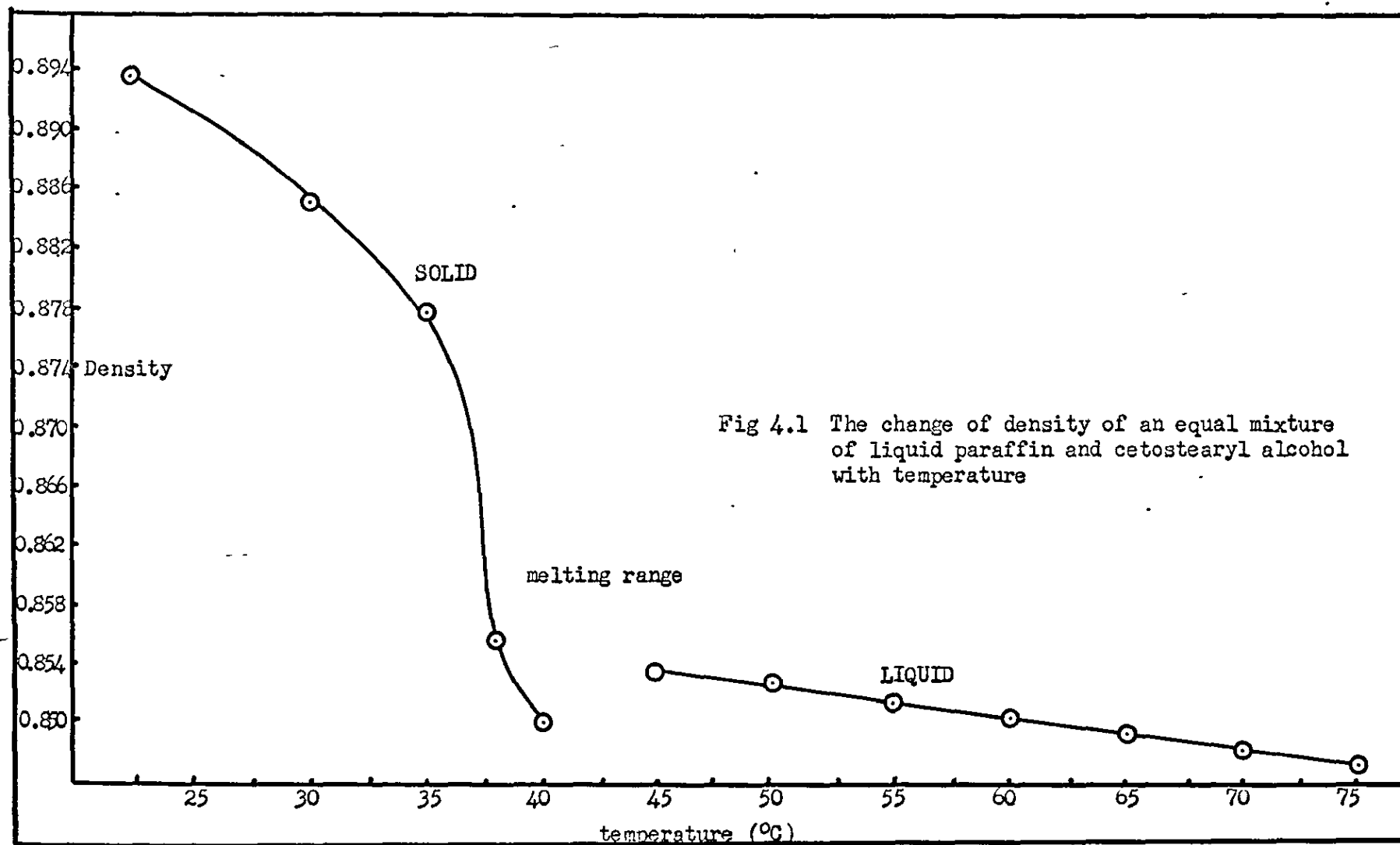
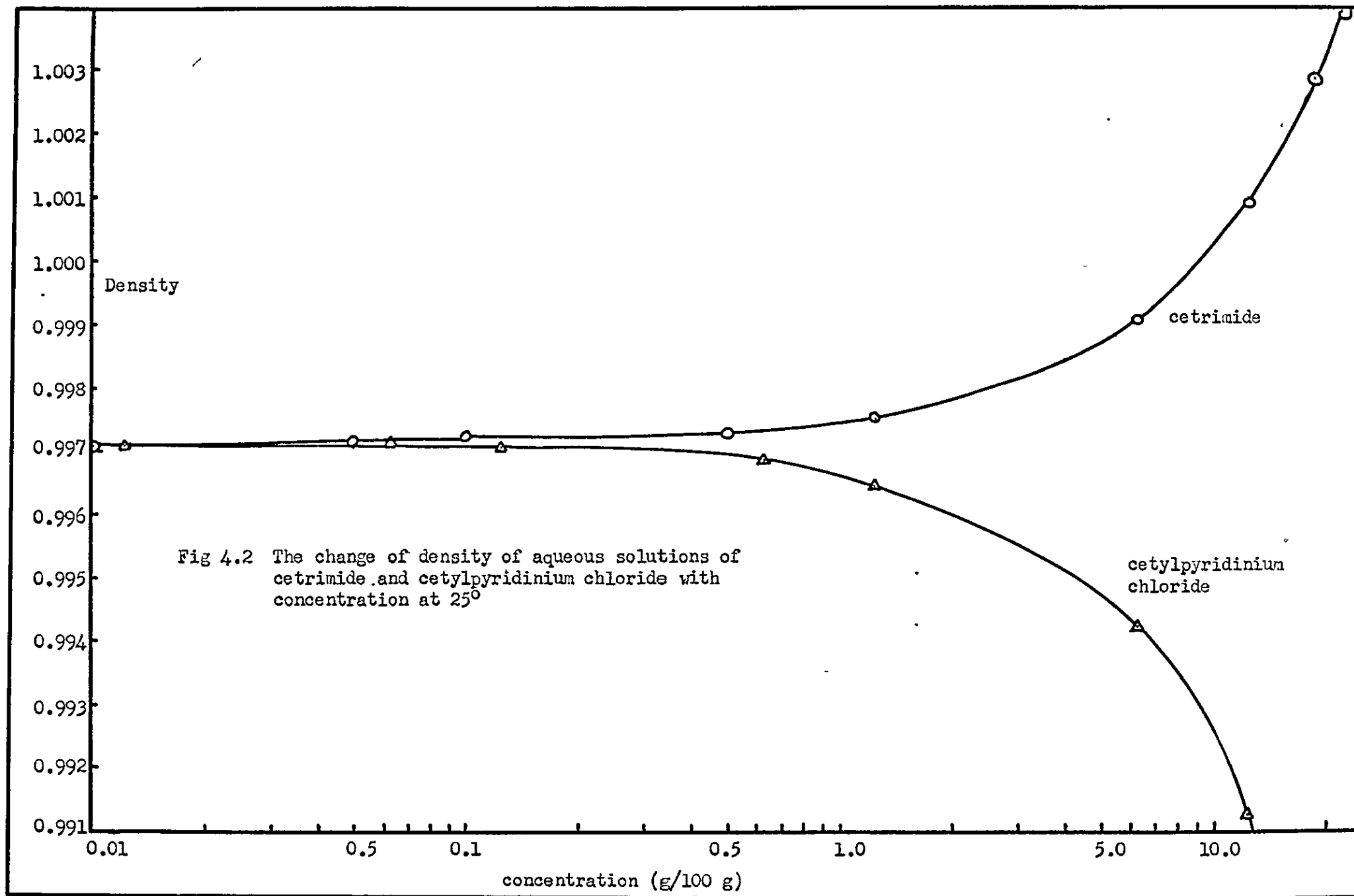


Fig 4.1 The change of density of an equal mixture of liquid paraffin and cetostearyl alcohol with temperature



after equilibration at 30°. Results are shown in Table 4.2.

Table 4.2 The densities of the emulsion disperse phases at 30°

Disperse phase for emulsions	Density
A, B, C, D, E, F, G, H, I	0.8848
J	0.8633
L	0.8730
K	0.8498
M	0.8750
N, O, P	0.8772
C/L	0.8533
J/L	0.8503
H/L	0.8623
L/L	0.8576

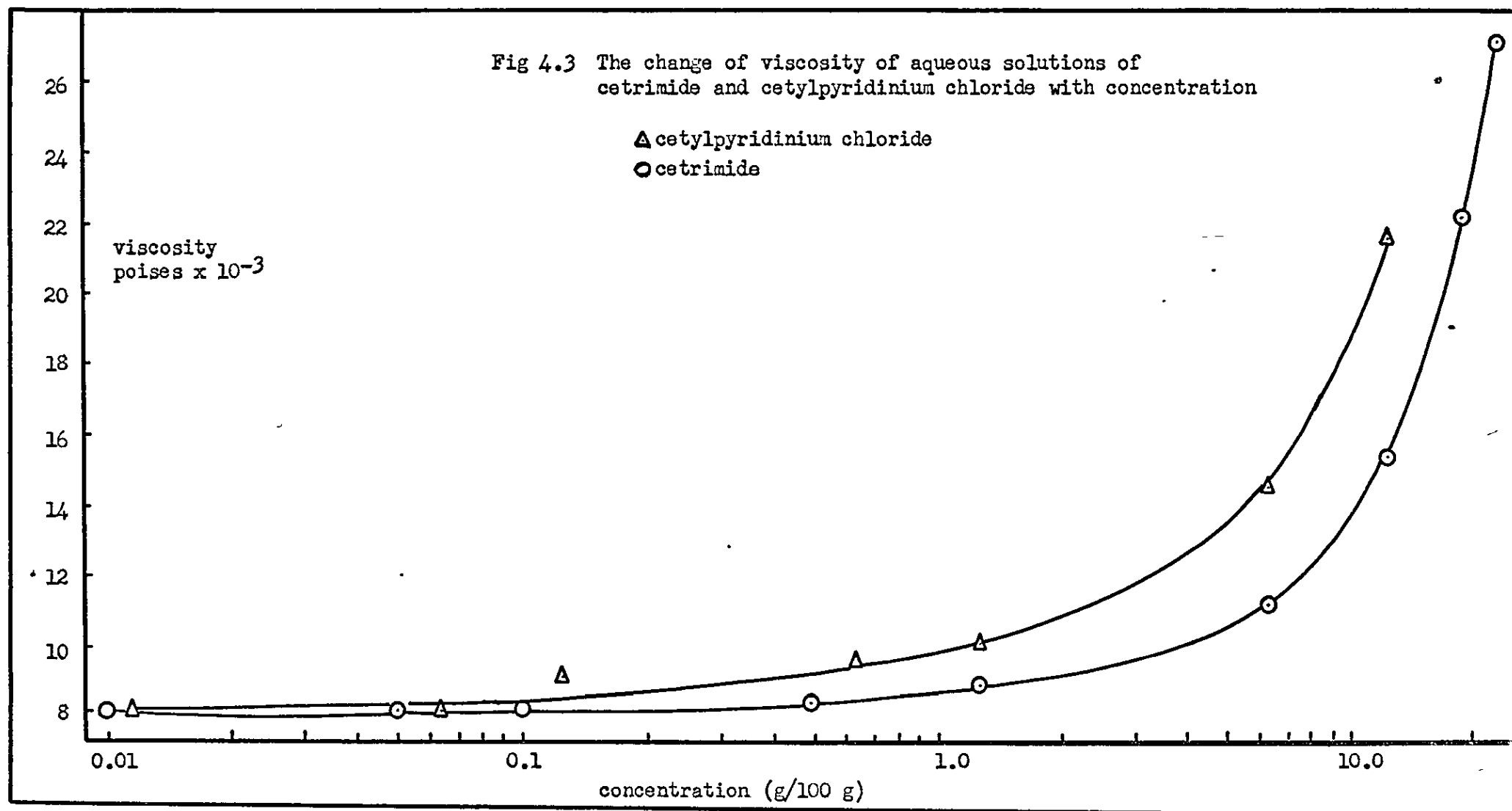
It later became apparent that the change in density with temperature was significant. Accordingly, this was measured in detail for the equal mixture of the two components over the range 75° to 22.5° and the results are presented in Fig 4.1. The discontinuity between solid and liquid phases is shown as occurring between 40° and 45°. This seemed the most likely melting point range of this mixture but an independent measurement gave values of between 30° and 35° (150). The results obtained with these materials are dependent upon the rate of heating and are by no means sharply defined.

4.5 The density and viscosity of the aqueous phases

(a) Densities

The densities of all the aqueous phases used in the preparation of the dispersions were measured at 25° ($\pm 0.1^\circ$) using a pycnometer. The results for the cetrinide and cetylpyridinium chloride were plotted (Fig 4.2) and values for individual preparations obtained by interpolation. Aqueous solutions of other surface active agents were prepared

Fig 4.3 The change of viscosity of aqueous solutions of cetrимide and cetylpyridinium chloride with concentration



equivalent to the concentration present in the formulation, ignoring adsorption effects (Table 4.3).

(b) Viscosities

Viscosities of all the above solutions were measured using a suspended level viscometer (BS/IP/SL N^o 1A). The method of British Standard B.S. 188:1957 was followed. Measurements were made at $25^{\circ} \pm 0.1^{\circ}$. The viscosity of freshly distilled water was taken as 8.949×10^{-3} poises (International Critical Tables). Results are shown in Fig 4.3 and Table 4.3.

Table 4.3. The density and viscosity of some of the aqueous phases at 25.0^o

Surface active agent	Concentration % w/w	Density	Viscosity poises $\times 10^{-3}$
Benzalkonium chloride	1.25	0.9966	9.64
Cetomacrogol 1000	2.5	0.9996	10.72
Dioctylsodium sulphosuccinate +	2.5	1.0171	12.45
Sodium lauryl sulphate	0.625		

4.6 Methods of emulsification

A preliminary investigation was sufficient to demonstrate that the selected surface active agents were powerful emulsifiers requiring specialised techniques to produce changes in the particle size distribution of a system.

In all cases a simple gentle stirring by hand with a spatula was sufficient to produce an emulsion after addition of the melted oil and cetostearyl alcohol to a warm aqueous solution of the surface active agent. Slow stirring was continued until the emulsion had solidified and preparations made in this fashion are designated 'LL' (low shear). Since the scale of investigation

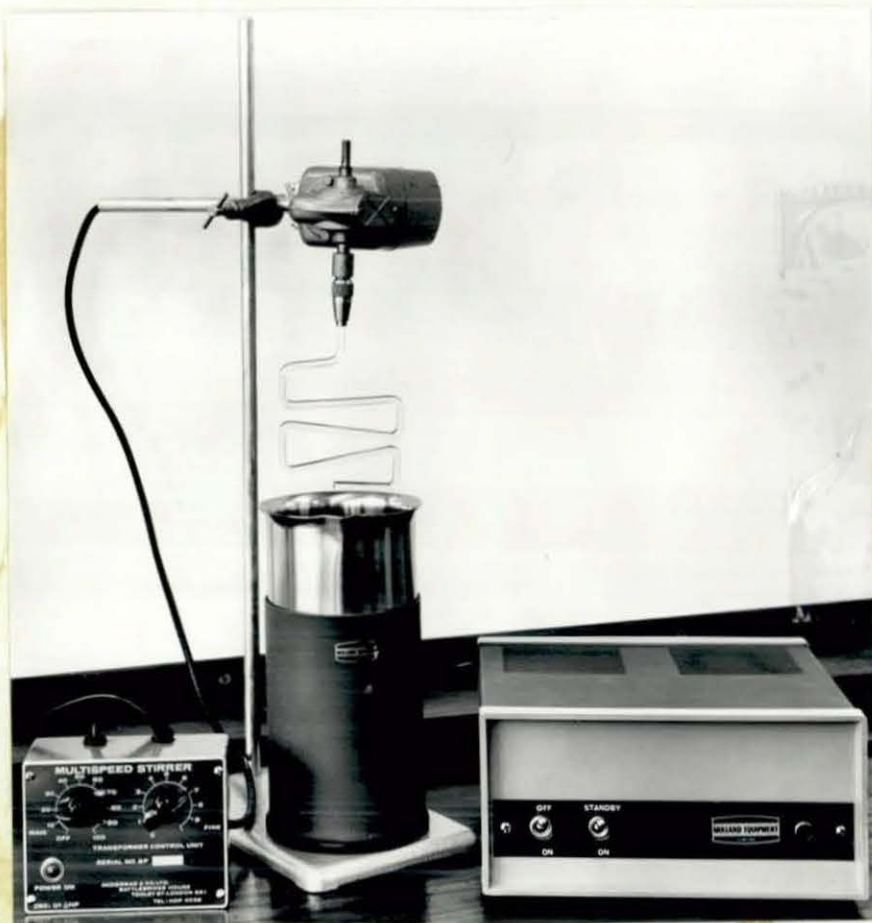


Fig 4.4 (a) The ultrasonic cleaning bath used for the preparation of emulsions.

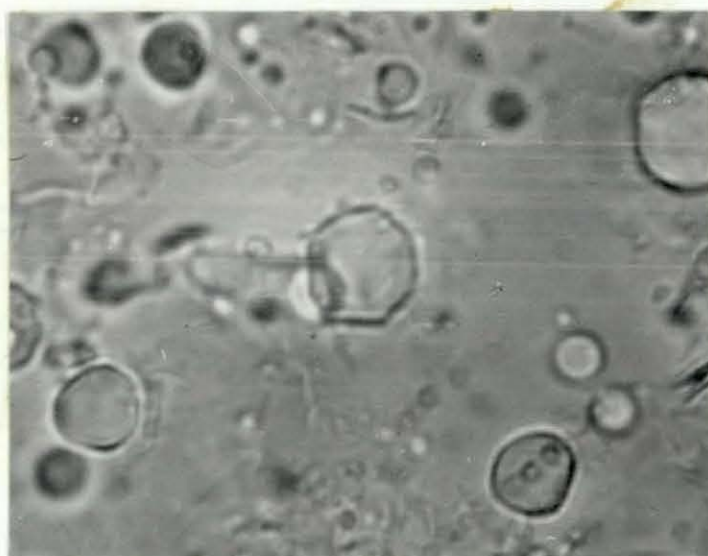


Fig 4.4 (b) Photomicrograph of CTAB/B₁₂₀ mounted in glycerol, x 625 (approx.)

was limited to the laboratory bench, conventional homogenisers were not considered. A means of broadening the spread of the particle size distribution was sought in order to allow adequate evaluation of the influence of particle size on the properties of a system in which all other parameters were closely controlled. Electrostatic emulsification procedures were examined but conclusions drawn by Swift & Friedlander (455) could only be confirmed and this approach was not continued.

From the literature it appeared that ultrasonic irradiation had some potential since particles are made to shear as well as to coalesce (2.1.5). After initial experimentation, the device shown in Fig 4.4.a was found to have a degree of success in this direction. Basically it consists of an ultrasonic cleaning bath fitted with a constant speed gate stirrer. The ultrasonic bath consists of a 35 w Mullard ultrasonic amplifier (Type L537) driving a 1 litre ultrasonic cleaner (Type L615) at 22 kc/s. Unlike the apparatus used by Singiser & Beal (455) the transducer cemented to the base of the stainless steel beaker was of the magnetostrictive type. When the beaker was half filled with liquid the area of maximum cavitation could be seen to be limited to the centre portion. As noted by Singiser & Beal free oil was prone to separate at the top of the bath and for this reason a glass stirrer gate, shown elevated in Fig 4.4.a, was used to remix the two phases, and pass all the material through the zone of cavitation. It was found to be sufficient to stir at a fixed speed of 127.5 r.p.m. Prolonged periods of irradiation proved possible because the bath temperature did not fall below 45° until the transducer was switched off. A standardised procedure was therefore

developed for all preparations made in this fashion, as follows:

The aqueous phase containing the surface active agent and other ingredients was heated to 65° - 70° and placed in the stainless steel beaker. The weighed oil phase was warmed to 60° and added to the aqueous phase when this had cooled to the same temperature. Immediately the transducer was switched on and stirring commenced. Irradiation was continued for a known time, after which the transducer was switched off. Stirring was continued at the same speed until the preparation had cooled to about 30° and was beginning to set to a semisolid consistency.

Preparations made in this fashion were coded according to the number of minutes of irradiation, e.g. -/0 indicated that the preparation was made in the ultrasonic bath which was not switched on, -/15 indicates irradiation for 15 minutes, etc.

4.7 The appearance of the emulsions

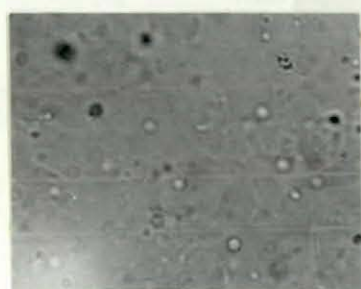
Hitherto it has been an implicit assumption that the disperse phase particles of an emulsion are spherical droplets. However, microscopic examination of some of the preparations described in the last section revealed the occasional presence of irregularly-shaped particles, many with straight sides. A typical field showing the occasional non-spherical particle can be seen in Fig. 4.4.b. The possibility that these particles were an artifact lessened when particles on electron-micrographs were found to have the same appearance, Fig 3.2. Axon (14) suggested that particles in an aged system containing cetyl alcohol, liquid paraffin and sodium lauryl sulphate tended to have a crystalline appearance if the ratio of alcohol to oil was greater than 8 : 5. An examination of this type of preparation showed that the particles had an acicular appearance,

quite different from the polyhedra visible in Figs. 4.4.b and 3.2. Preparations containing different ratios of oil and alcohol in a 0.5% cetrimide emulsion were made and stored for six months. The approximate numbers of irregular particles at the beginning and end of this period were similar and Axon's explanation is not applicable.

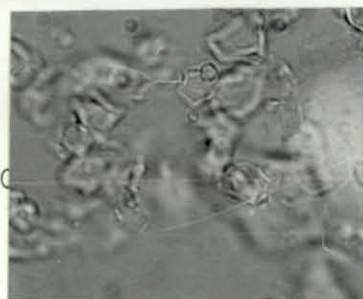
Accordingly, after consideration of alternative theories (Section 2.2.4) the hypothesis was advanced that the phenomenon was due to localised close packing (150).

4.8 The relationship between concentration and particle shape

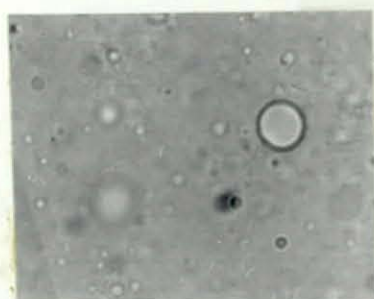
The system in which polyhedra were first noted to any degree was that of CTAB/3/120 in which the disperse phase ratio (o mass) was 0.2, or at 25°C, 0.225 by volume. Thus, although Menegold (256) had previously pointed out that the theoretical limiting value for the close packing of spheres of equal diameter was ϕ volume = 0.74, it was clear that the system as a whole could not be close packed. Nevertheless, inhomogeneities could exist where localised close packing occurred, especially as the system had a wide range of particle sizes. Such areas are clearly visible in Fig. 3.2 where inadequate dispersion of the sample has left flat-sided particles adjacent to each other. If this were a valid picture of the whole increasing the disperse phase ratio of a standardised system should produce an increase in the number of polyhedra in the system. As noted in Chapter Two, it is unlikely that a standardised method of emulsification exists. A procedure was adopted in which as many parameters as possible were controlled in order to make a range of emulsions of an equal mixture by weight of ceto-stearyl alcohol and liquid paraffin in a 0.5% w/v solution of



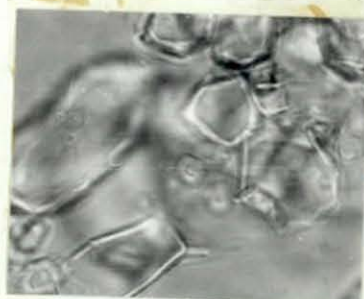
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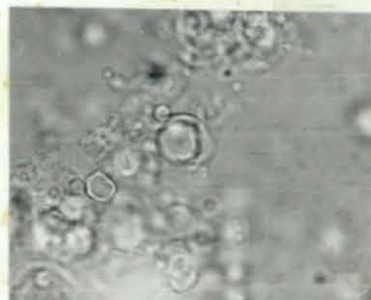
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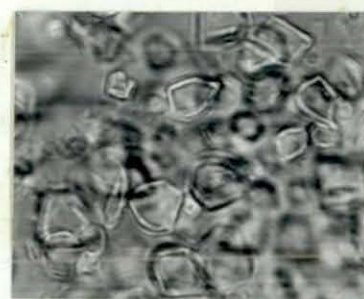
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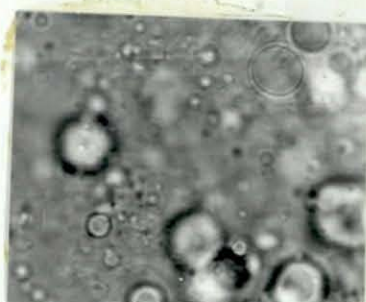
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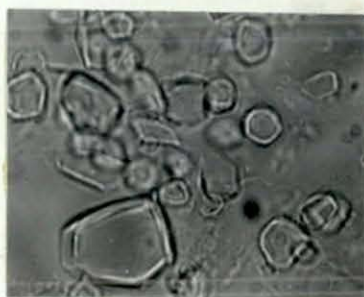
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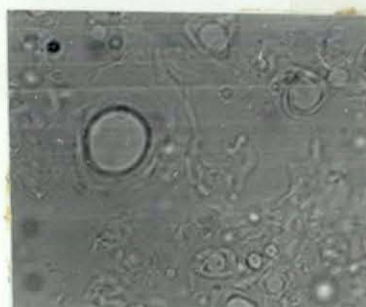
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0.15



0.55



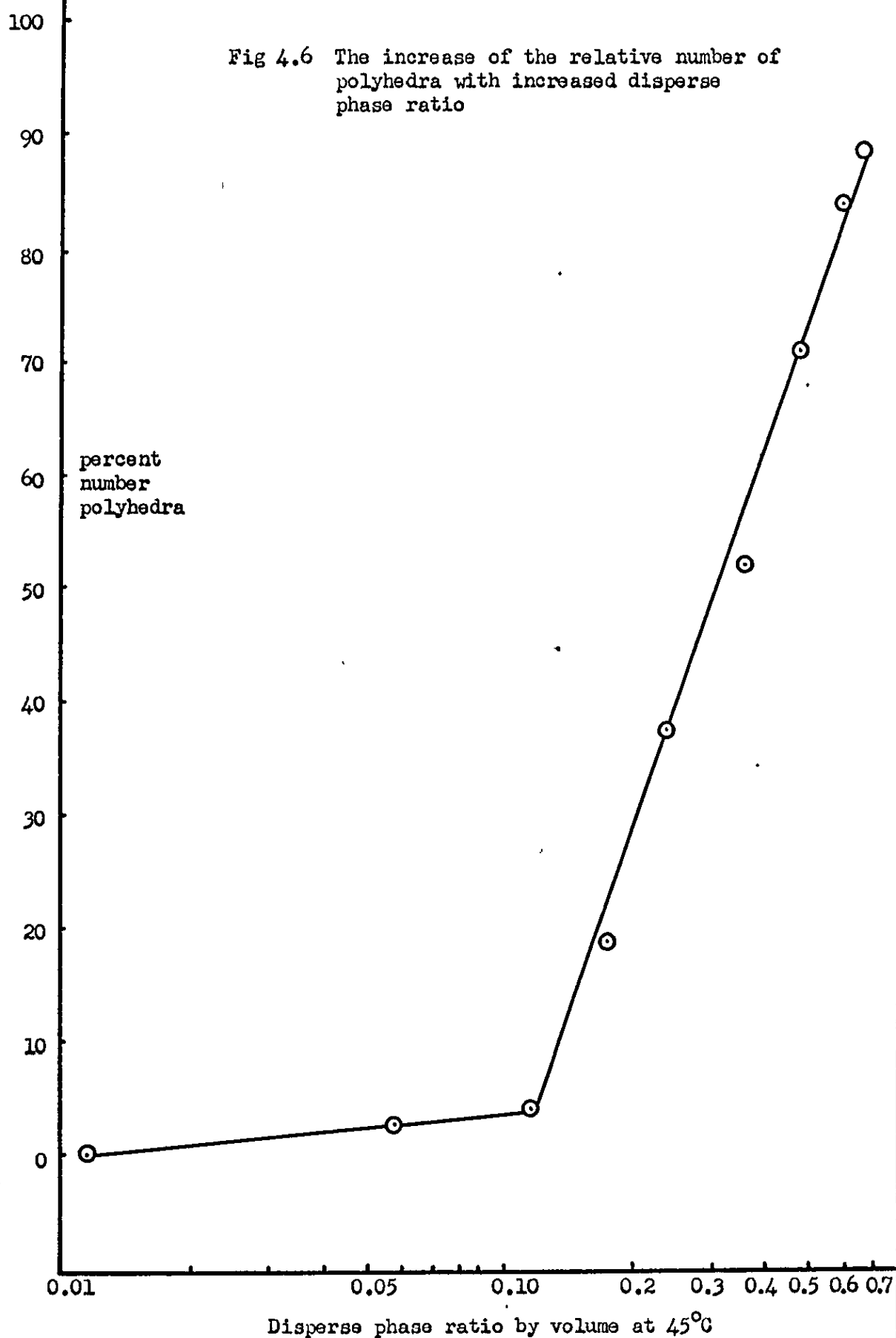
0.20

Scale: 1 division = 5 μ



Fig 4.5 The progressive change in the particle size and particle shape with increasing disperse phase ratio (Figures = ϕ mass)

Fig 4.6 The increase of the relative number of polyhedra with increased disperse phase ratio



cetrimide. Both phases were heated and mixed at 75°. A Silverson laboratory homogeniser was used to stir the emulsion at maximum speed until it had cooled to 30° when the homogeniser was switched off and the cooling allowed to proceed undisturbed. This procedure was employed to prepare 100 g samples of a number of preparations of different disperse phase ratio varying from 0.01 to 0.55 by weight. It was of interest to note that preparations containing a disperse phase ratio $\phi = 0.55$ tended to be unstable as manifested by syneresis of a clear paraffin layer, i.e., these emulsions had undergone inversion as described by Manegold (loc. cit.).

The particle shape was evaluated from photomicrographs, classifying spherical (and rounded) particles and polyhedral particles separately. Samples were dispersed in glycerol and photomicrographs taken in green light at a magnification of x 400 using a Leitz Ortholux microscope fitted with a Watson eyepiece camera. The actual magnification was determined by photographing a 20 μ grid on a Thoma haemocytometer slide under the same conditions. Four photomicrographs of each sample were taken, enabling at least 1000 particles to be classified.

A selected area of a photomicrograph from each sample is shown in Fig 4.5. The most obvious feature of this Figure is the progressive increase in both particle size and relative number of polyhedral particles with increased disperse phase ratio. The relative number of polyhedra is plotted directly as a function of disperse phase ratio in Fig 4.6. and particle size distributions are shown in Table 4.4.

Table 4.4 Properties of the emulsions prepared with increasing disperse phase ratio

g mass	o volume (Fig. 4.1)			% nos. polyhedra	Particle size distribution		
	25°	45°	75°		D ₅₀	D ₀₅	D ₉₅
					(μ)	(μ)	
0.01	0.0112	0.0117	0.0118	0	2.75	3.20	21
0.05	0.056	0.059	0.059	1.93	3.40	2.03	13
0.10	0.112	0.117	0.118	4.01	5.30	1.89	16
0.15	0.168	0.176	0.177	19.74	5.0	1.90	15
0.20	0.225	0.235	0.236	37.11	4.65	1.87	17
0.30	0.337	0.352	0.354	51.54	4.85	2.06	19.3
0.40	0.449	0.469	0.473	70.30	8.30	1.92	21.5
0.50	0.561	0.586	0.590	84.20	8.5	2.00	22
0.55	0.617	0.645	0.650	88.60	8.0	2.21	24

4.9 The theoretical and experimental emulsion densities

It is generally agreed that the interfacial layer between the dispersed phase and the continuous phase has different properties from either of the two constituent phases (Chapter Two). Martynov (270) noted that thermodynamically this resulted in a change in the volume of the system, meaning that the density of the interfacial layer is distinct from the densities of the two phases. He showed how this difference could be used to calculate the approximate thickness of the layer. The theoretical density of an emulsion was calculated and compared with the experimental value.

The theoretical density was calculated as follows:-

$$\text{theoretical density} = \rho_t = \frac{100}{\frac{\phi}{\rho_o} + \frac{(100 - \phi)}{\rho_w}} \quad (1)$$

From Table 4.1 ϕ is the total mass of dispersed phase in 100 g of the formulation, ρ_o is the density of the disperse phase (Table 4.2) and ρ_w is the density of the continuous phase from Fig 4.2 or Table 4.3.

The experimental densities were measured by adding a weighed amount (8 to 9 g) in a dry tared, graduated centrifuge tube of conical section. This was centrifuged for one hour at 4000 r.p.m. to remove occluded air before equilibrating in a water bath at 25.0° ($\pm 0.1^{\circ}$) and measuring the volume. The apparent density of each preparation was measured four times. Results are shown in Table 4.5.

4.10 Discussion

The properties of the solid-liquid emulsion systems under investigation are of considerable interest. For example, the fact that it proved impossible to prepare a system containing much more than 55% by weight of a mixture of liquid paraffin and cetostearyl alcohol suggested that this system was close to the close packing limit. However, even allowing for expansion on heating this does not approach the theoretical limit of 74% by volume, assuming that the disperse phase particles were spheres of equal dimensions.

The presence of polyhedral particles has been demonstrated in a number of the systems under investigation. The data presented in Fig 4.6 provides adequate confirmation of the original suggestion (150) that this is due to localised close packing within the systems, probably at the point of changing from liquid droplets to solid particles. The increase in the relative number of polyhedra above a disperse phase ratio of $\phi = 0.1$ and the linearity of the relationship is striking, providing adequate confirmation that the phenomenon is not due to crystallisation (14). The change in viscosity from Newtonian to non-Newtonian behaviour also occurs for systems of disperse phase ratio $\phi > 0.1$ (Fig 5.1). This confirms the suggestion that particle-particle

interactions occur at concentrations well below the theoretical limit of $\psi = 0.74$.

The differences noted between the theoretical and actual densities of the emulsions indicates that Marynov's suggestion that the interfacial layer has a different density from the two constituent phases may have some substance. Some additional conclusions and speculations are discussed in Chapter Six.

4.11 Summary

1. The formulations of emulsions examined in this investigation are given. Table 4.1
2. The physical properties of the constituent phases are determined. 4.4.5
3. Methods of emulsification are described. 4.6
4. Some of the emulsion systems contain non-spherical particles. 4.7
5. The relative number of non-spherical particles increases in one system as the disperse phase ratio is increased. 4.8
6. The apparent density of all the emulsion systems is smaller than the theoretical density. 4.9 Table 4.5

Table 4.5 The theoretical and apparent densities of the formulations shown in Table 4.1

CODE	LETTERS	Theoretical	Apparent density
CTAB	A/LS	0.9725	0.9527
	A/60	0.9725	0.9553
CTAB	B/LS	0.9742	0.9521
	0	0.9742	0.9471
	5	0.9742	0.9450
	10	0.9742	0.9406
	15	0.9742	0.9521
	20	0.9742	0.9461
	25	0.9742	0.9416
	30	0.9742	0.9430
	45	0.9742	0.9473
	60	0.9742	0.9473
	120	0.9742	0.9416
CTAB	C/LS	0.9743	0.9460
	D/LS	0.9755	0.9475
	E/LS	0.9760	0.9503
	F/LS	0.9858	0.9500
	G/LS	0.9632	0.9408
	H/LS	0.9523	0.9295
	I/LS	0.9410	0.9185
	J/LS	0.9691	0.9514
	K/LS	0.9519	0.9447
	L/LS	0.9728	0.9359
	M/LS	0.9599	0.9295
	N/LS	0.9505	0.8924
	O/LS	0.9306	0.9019
	P/LS	0.9350	0.8911
CTAB	LL/LS	0.9679	0.9532
	HL/LS	0.9548	0.9254
	JL/LS	0.9656	0.9530
	CL/LS	0.9668	0.9460
CPC	A/LS	0.9740	0.9484
CPC	B/0	0.9738	0.9504
	15	0.9738	0.9459
	20	0.9738	0.9416
	25	0.9738	0.9414
	30	0.9738	0.9439
	45	0.9738	0.9416
	60	0.9738	0.9379
	120	0.9738	0.9275
CPC	C/LS	0.9735	0.9453
	D/LS	0.9696	0.9536
BENZ	A/LS	0.9759	0.9414
CEM	A/LS	0.9759	0.9576
	0	0.9759	0.9444
	15	0.9759	0.9401
	30	0.9759	0.9488
	60	0.9759	0.9444
	120	0.9759	0.9347

contd/over

Table 4.5 continued

CODE	LETTERS	Theoretical	Apparent density
DOSS	A/LS	0.9813	0.9563
	0	0.9813	0.9467
	15	0.9813	0.9453
	30	0.9813	0.9556
	60	0.9813	0.9478
	120	0.9813	0.9433

CHAPTER FIVE

THE MEASUREMENT OF THE EMULSION FLOW CHARACTERISTICS

- 5.1 Introduction
- 5.2 Description of the viscometer
- 5.3 Method for flow characteristic measurements
- 5.4 Typical results
- 5.5 Application of the Williamson equation
- 5.6 Discussion and conclusions
- 5.7 Summary

5.1 Introduction

Emulsions of the type under investigation exhibit complex flow patterns. Unsophisticated methods of flow measurement are not suitable for this investigation since they are unable to give meaningful results for the parameters associated with non-Newtonian flow such as yield value, hysteresis and viscosity at infinite shear rates. The choice of a suitable instrument was discussed in Chapter Two and cone-plate viscometers were preferred on a number of grounds. The Ferranti-Shirley viscometer was selected since end effects are reduced to a minimum, shear heat is rapidly dissipated and temperature control can be maintained within close limits. The main advantage of this instrument is that cone speeds are continuously variable without the necessity for stepwise changes associated with the use of a gear box. The instrument is fitted with a programming device which enables the cone to be accelerated to a maximum rotational speed over a period of time and then reduced to a standstill over the same period. This has the advantage that conditions of measurement can be standardized, enabling the

instrument to plot out a flow curve, or rheogram, characteristic of the sample under examination and comparable to those of other samples measured under the same conditions.

There is an intuitive feeling amongst workers in this field that rotational viscometers can act as homogenisers when applied to emulsion systems, i.e., they are capable of breaking down particles by the application of shear forces (141). Little evidence for this supposition has been presented. However Kostenbauder & Martin (221) and Henderson et al (170) suggested that pharmaceutical emulsions and ointments would be subjected to a shear rate of up to approximately 200 secs.^{-1} on ejection from a collapsible tube, 120 secs.^{-1} when spread onto the skin or 150 secs.^{-1} when manipulated with a spatula. Conditions of measurement were therefore limited to a maximum rate of shear of 188 secs.^{-1} .

5.2 Description of the viscometer

The Ferranti-Shirley cone plate viscometer (Ferranti Ltd., Hoston, Manchester 10) was described in detail by McKennell (300). This particular instrument was fitted with the automatic cone-plate setting unit to maintain the gap between the apex of the cone and the plate at a constant level. The signal from the torque dynamometer and the automatic speed control was monitored by an X-Y recorder (Scientific Instruments Ltd., Cheshire, Autoplotter Unit, Model XY - IP), having a 0-10 mv movement along each axis and a minimum frequency response time of 1 sec. Water at 25.0°C was circulated from a large Townson and Mercer circulating water bath. The temperature of the sample was measured by thermocouples set in the plate and connected to a Solartron Digital voltmeter, Model LI 1420. The temperature was

measured to $\pm 0.01^\circ$, and varied by no more than $\pm 0.1^\circ$ during any one run.

The instrument was used with a large cone, radius 3.50 cm and cone angle $19'13''$ ($= 0.00557392$ radians). A sweep time of 600 seconds was selected to reduce inertial effects to a minimum, using a speed range of 0 to 10 r.p.m.

The maximum shear rate is therefore given by angular velocity/cone angle (radians)

$$= \frac{10}{0.00557392} \times \frac{2\pi}{60} \text{ secs.}^{-1}$$

$$= 188 \text{ secs.}^{-1}$$

The torque spring constant (supplied with the instrument) is 2.45 g c /div.

$$\text{Shear stress} = \frac{3G}{2R^2} = T \text{ dynes/cm}^2$$

where G = reading on the x 500 scale setting

Shear stress = $T = 26.8 \times$ reading on x 500 scale.

The instrument therefore measured a maximum applied shear rate of 188 secs.^{-1} and a stress of $13,400 \text{ dynes/cm}^2$.

5.3 Method of flow characteristic measurement

After a great deal of experimentation it was demonstrated that all samples were subject to shear-thinning which was generally slowly reversible. Accordingly, the method of measurement was inevitably a compromise since the sample must always be disturbed when moving it from the original container to the gap between the cone and the plate.

Samples of each formulation were centrifuged to remove occluded air and flow behaviour measured at about the same time as the particle size distributions. Samples were equilibrated overnight in the same room as the instrument. The cone and

plate were cleaned with acetone and the instrument allowed to warm up to the temperature of measurement. A 1 to 2 g 'block' of the semisolid was carefully cut from the bulk container with a 1" spatula and placed on the plate with the minimum amount of disturbance. The cone rotating at 20 r.p.m. was lowered onto the sample and, immediately the gap setting was reached, the rotational speed reduced to zero and the motor taken out of gear. Excess sample was removed from around the cone and exactly 10 minutes allowed for the sample to warm up to 25.0° (only a few minutes were required) and to 'recover'. The instrument was then set in motion to record the stress-strain relationship as the sample was sheared from zero to 10 r.p.m. and back to zero over a total time of 20 minutes.

Replicate measurements over a period of weeks on the same material treated in the above fashion produced superimposable rheograms provided the material was initially more than a week old. For this reason samples were generally at least three months old before examination. Repeated shearing of the same sample was sufficient to demonstrate the slow rate of recovery (Fig. 5.3). Shearing the same sample at the maximum speed of the instrument (100 r.p.m.) for 20 minutes produced no measurable increase in temperature and it is presumed that shear-heating did not occur in the materials under investigation.

5.4 Typical results

As anticipated, the flow curve demonstrated complex non-Newtonian flow behaviour. Most of the preparations demonstrated thixotropic hysteresis so the types similar to those seen in Fig. 2.1.b, c and d were the most frequent. An interesting series of curves from preparations with increased

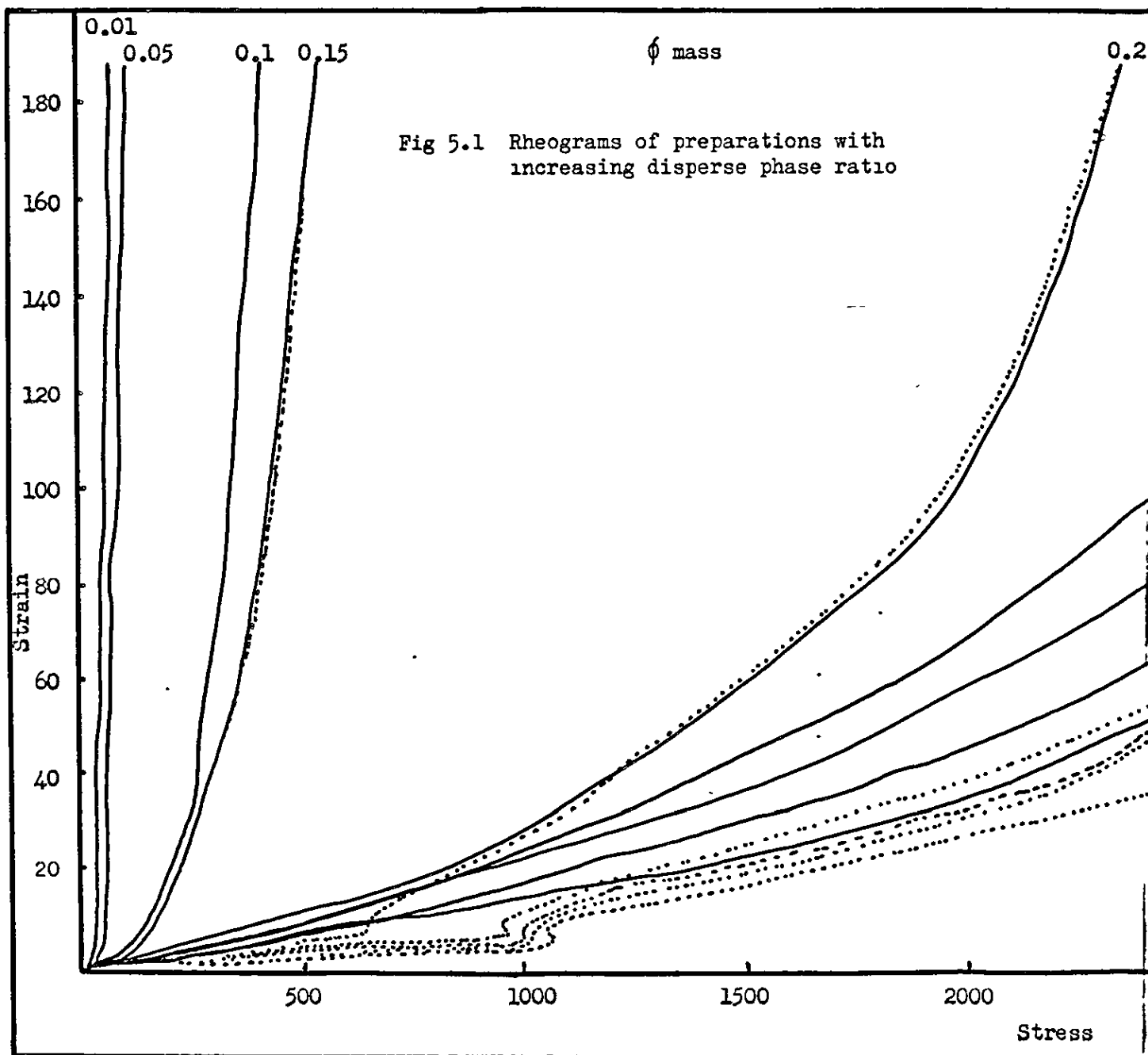
concentration of disperse phase is shown in Fig 5.1. Taking the DOSS series the effect of progressively increased periods of ultrasonics is shown in Fig 5.2. Some selected curves are shown in Fig 5.3. to illustrate the following features. Fig A (CTAB/B/120) shows a pronounced yield point and considerable thixotropic breakdown between the up and down curves. Fig B is the curve obtained when Sample A was allowed to rest for five minutes and the measurement repeated. The ultimate viscosities are slightly different, probably owing to instrument variation. Fig C shows substantially the same features as A but on a much reduced scale indicating that the preparation has failed to recover in the rest period. Fig G (CTAB/B/20) is a typically pseudoplastic flow curve.

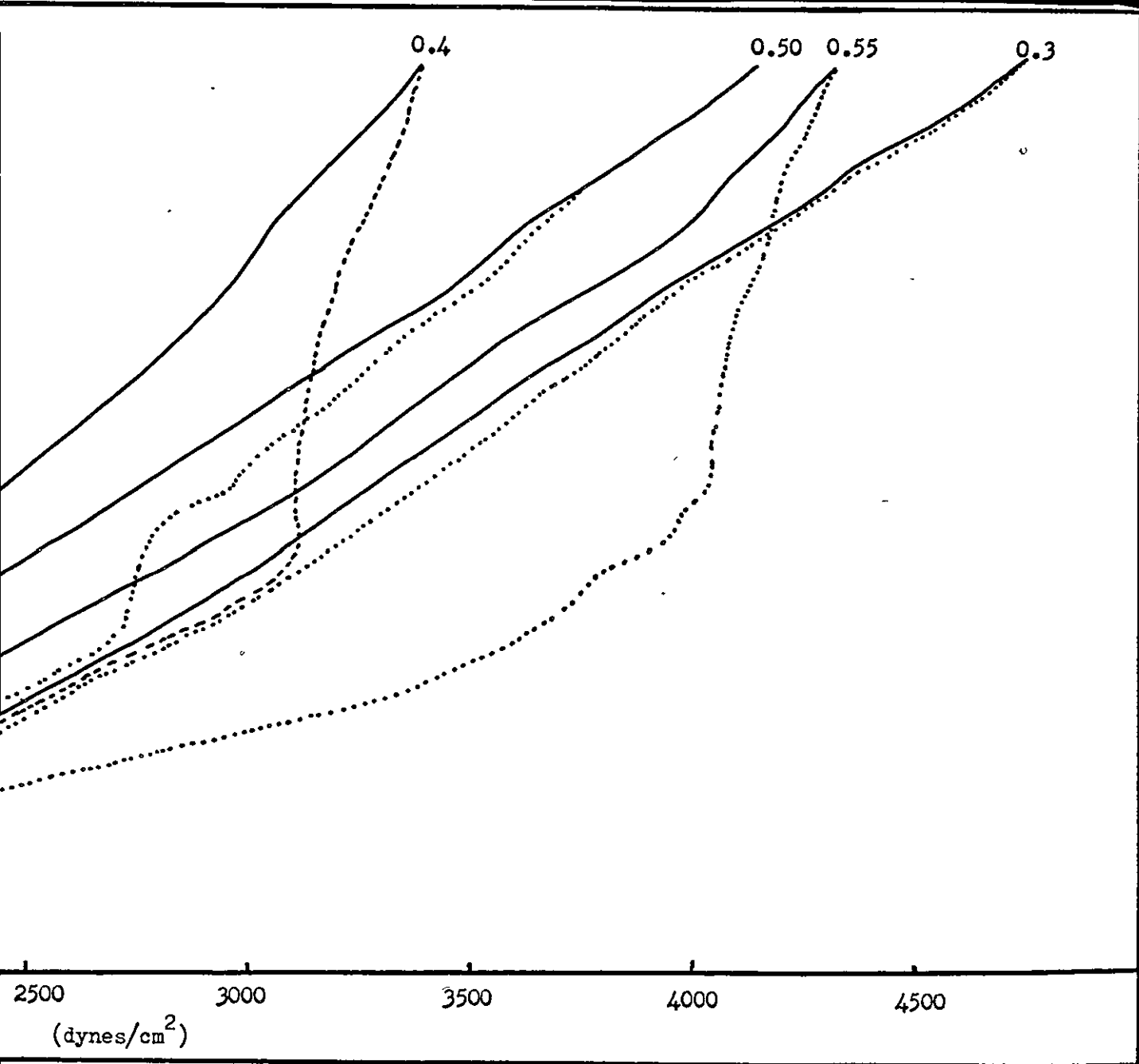
The characteristics of all the emulsions examined are shown in Table 5.1 and additional results are shown in Appendix Four (pocket).

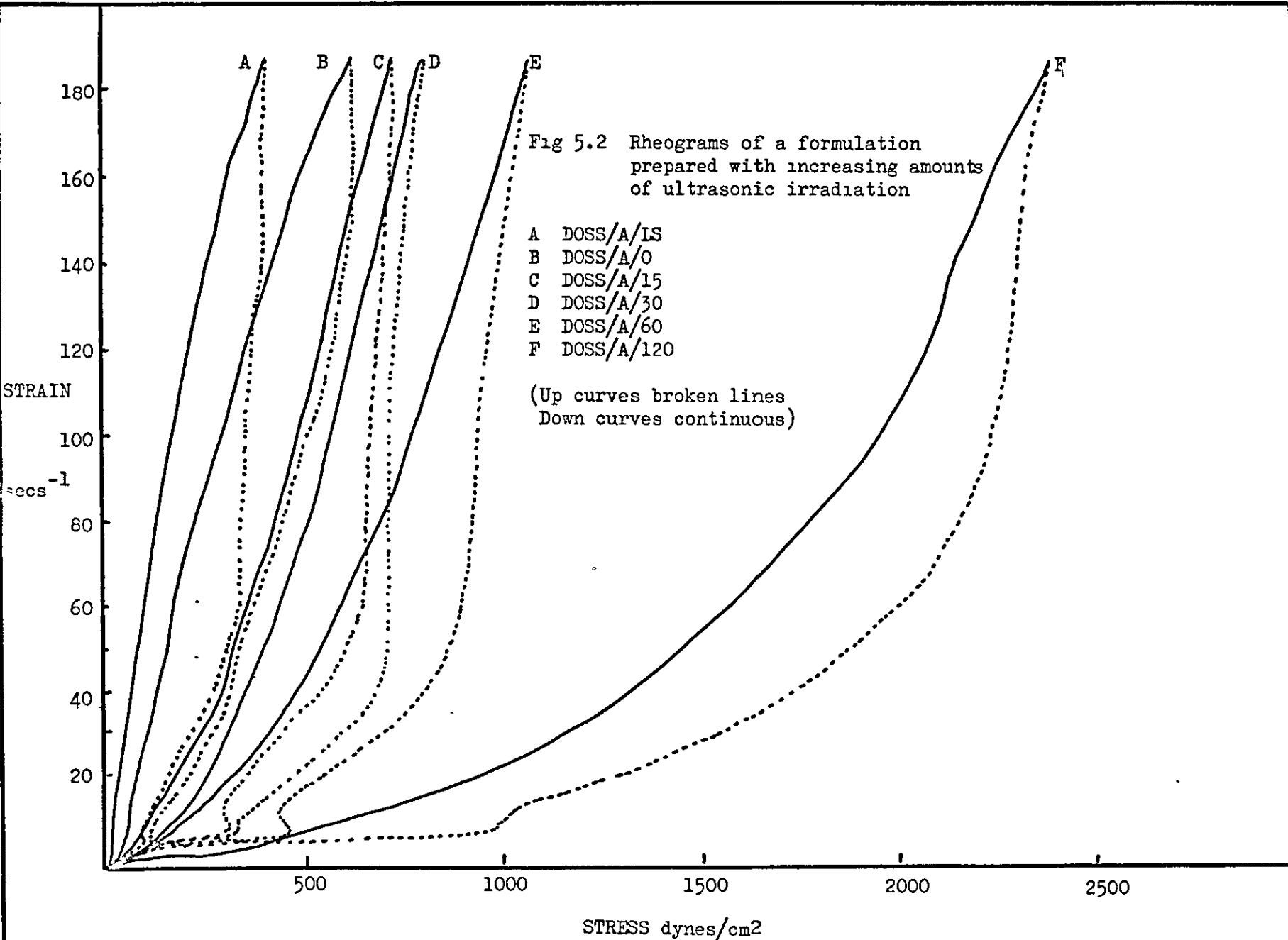
5.5 Application of the Williamson equation

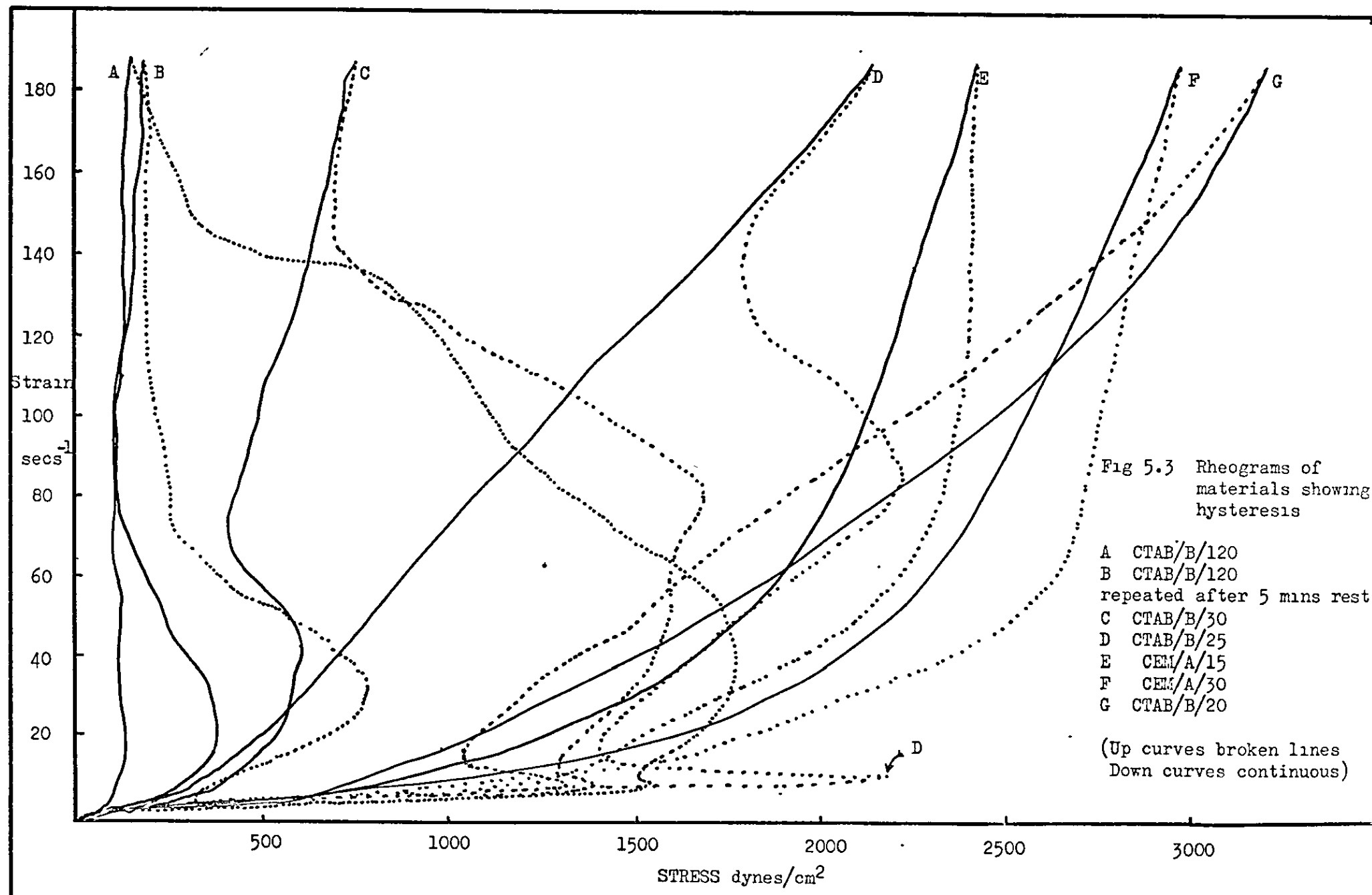
Two equations are claimed to provide a fit of pseudoplastic flow curves (2.3.3); Williamson's (910) and the structure equation of Shangraw et al (399).

Tests of the two curves were therefore carried out on data obtained in this investigation. Plots of $1/F$ vs $1/S$ or vs $e^{-0.661S}$ should be linear. The Williamson plots of representative flow curves are shown in Fig 5.4 and, as noted by Shangraw (398), experimental values show a trend away from linearity in the upper and lower regions of shear. However, structural equation plots (Fig 5.5) are non-linear over the whole range of shear.









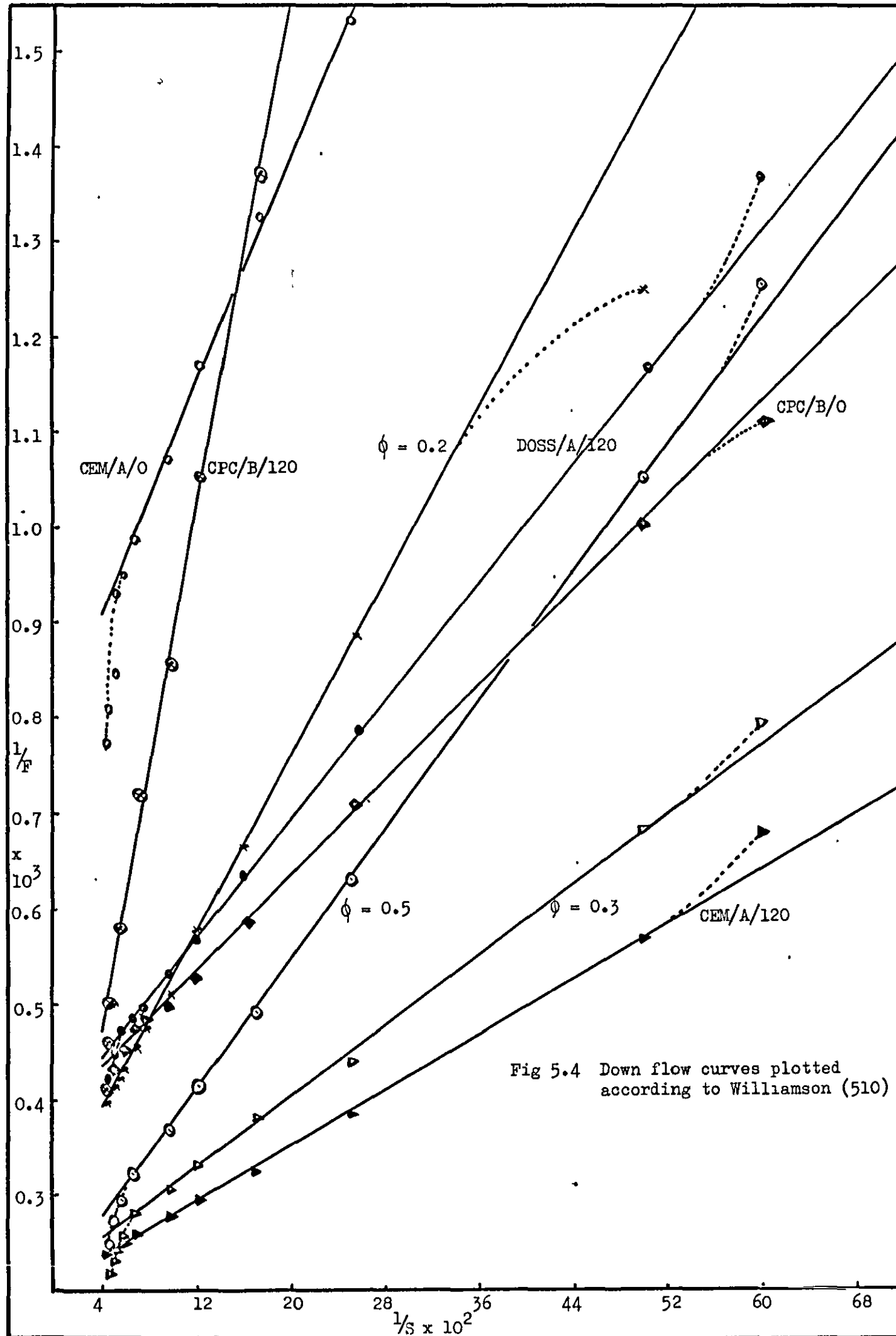


Fig 5.4 Down flow curves plotted according to Williamson (510)

Fig 5.5 Down flow curves plotted according to Shangraw et al (399)

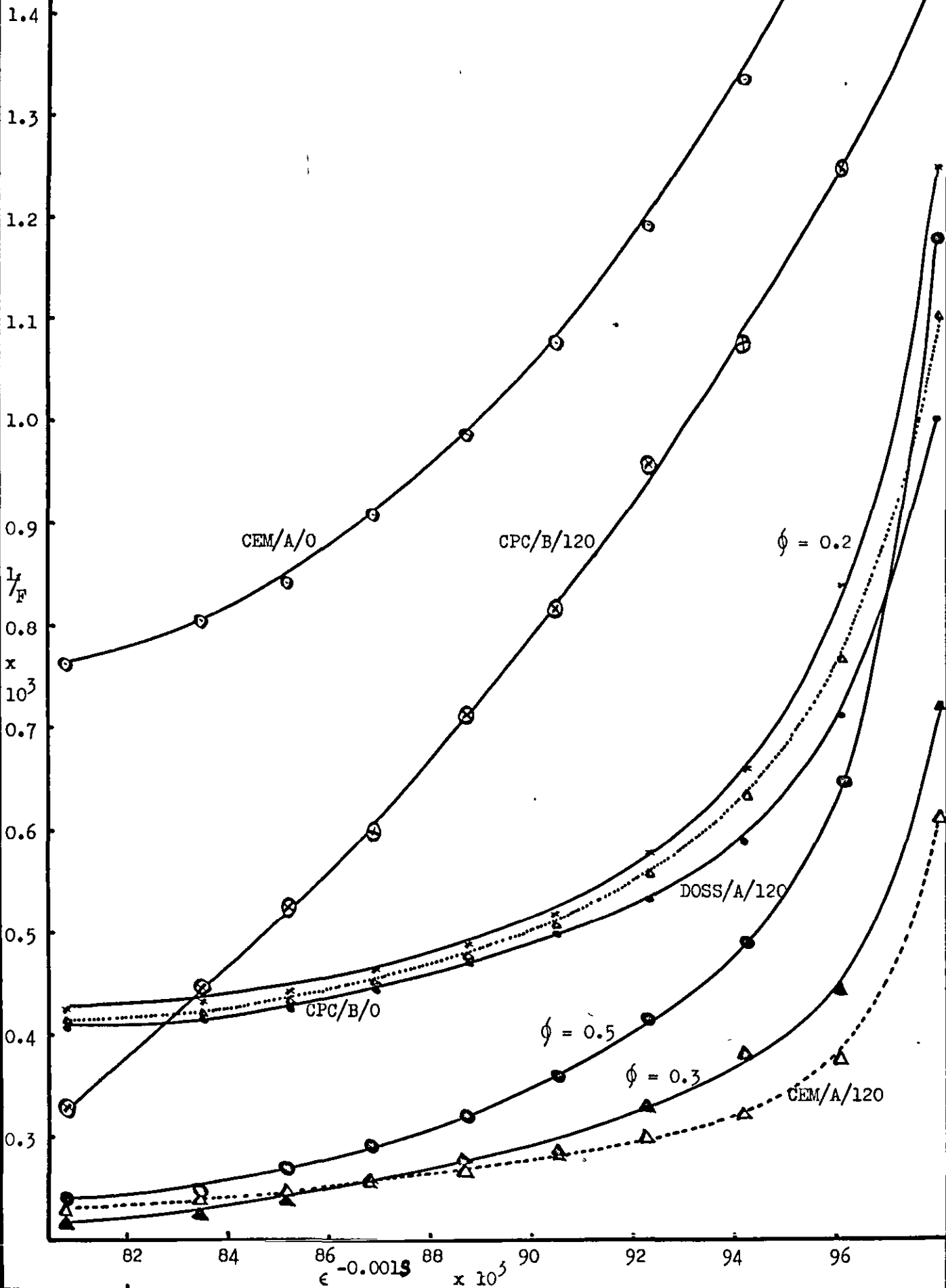


Table 5.1 Data from the flow curves plotted by the
Ferranti-Shirley viscometer

CODE	DISPERSION	Stress AT 100 secs. ⁻¹ STRAIN ² dynes/cm ²	Apparent viscosity at yield point (poises)	Thixotropic index (area of hysteresis)
CTAB	A/LS	620	20.0	6.79
	A/60	950	37.0	37.25
	B/LS	1650	50.0	9.55
	B/ 0	3000	113.5	12.20
	B/ 5	2800	38.4	21.43
	B/10	3300	115.0	14.95
	B/15	2710	40.5	15.07
	B/20	3220	140.0	17.88
	B/25	2160	220.0	66.79
	B/30	430	153.0	75.11
	B/45	5900	60.0	27.92
	B/60	160	165.0	93.30
	B/120	160	171.0	98.05
CTAB	C/LS	5100	160.0	20.96
	D/LS	1000	76.6	16.22
	E/LS	1000	92.5	14.37
	F/LS	520	12.5	3.88
	G/LS	1500	190.0	199.50
	H/LS	3600	325.0	275.80
	I/LS	3760	342.0	530.20
	J/LS	930	160.0	141.10
	K/LS	3200	252.3	196.20
	L/LS	600	55.3	5.78
	M/LS	340	40.0	4.25
	N/LS	1240	100.0	3.45
	O/LS	1020	62.5	37.55
	P/LS	1740	40.0	31.30
CTAB	L/L/LS	630	45.5	3.46
	M/L/LS	660	22.5	3.60
	J/L/LS	1700	157.2	187.40
	C/L/LS	2000	66.7	14.22
CPC	A/LS	620	46.0	9.50
CPC	B/10	2340	147.2	9.84
	B/15	3000	112.8	15.02
	B/20	3800	145.5	14.08
	B/25	3400	153.0	18.30
	B/30	1220	200.0	55.84
	B/45	3560	180.0	23.13
	B/60	320	192.0	99.60
	B/120	2260	206.6	70.02
CPC	C/LS	5960	122.7	34.02
	D/LS	4100	35.1	163.50
BENZ	A/LS	950	56.0	34.82

cont'd/ over

Table 5.1 continued

CODE	DISPERSION	STRESS AT 138 secs. ⁻¹ STRAIL dynes/cm ²	Apparent viscosity at yield point (poises)	Thixotropic index (area of hysteresis)
CLM	A/L3	1440	56.3	10.87
	A/ 0	1530	35.7	5.66
	A/15	2450	111.3	25.57
	A/30	3000	100.5	19.73
	A/60	3040	110.0	13.18
	A/120	4300	120.0	43.14
DOSS	A/L3	410	8.0	13.66
	A/ 0	630	24.0	17.46
	A/15	740	30.6	13.35
	A/30	800	38.6	17.40
	A/60	1100	58.5	20.40
	A/120	2400	100.0	26.57
φ series (L.8)	0.01	70	0	0
	0.05	105	0	0
	0.10	410	0	0
	0.15	540	0	1.92
	0.20	2360	0	9.56
	0.30	4710	107.3	15.70
	0.40	3370	108.3	56.50
	0.50	4120	112.2	32.25
	0.55	4310	113.3	69.60

Accordingly, for the purpose of this present investigation it was assumed that the Williamson equation has greater applicability to the experimental data.

Using standard techniques the Williamson equation was converted to linear form and a computer programme written to derive the constants by the method of least squares. This technique, due to Shaugraw (398), was improved by using Taylor's expansion (513) to continue calculating until successive values varied by no more than 1%, or until ten attempts to fit the curve had been made. Measurements of F and S were taken from each down curve and used to compute the values shown in Table 5.2. The machine rejected results as invalid where:-

- (i) γ_{∞} was negative,
- (ii) f , the intercept on the stress axis, was negative
- (iii) s , the curvative, was negative, indicating dilatant flow
- or (iv) the variance increased as the calculation progressed.

5.6 Discussion and conclusions

The Ferranti-Shirley viscometer was capable of measuring some features of the flow behaviour.

An experimental value for the yield point was obtained although it has been suggested (481) that the inertia of the cone has a considerable influence on the result. Nevertheless, the yield point appears to be consistent within an emulsion system (Table 5.1) suggesting that it may have a real as opposed to apparent value. Since the instrument was run at its slowest programmed increase of speed the inertial effects are likely to be at a minimum but there is no means at present

Table 5.2 Constants in the Williamson equation for pseudo-plastic flow derived by computer curve fitting

Dispersion Code - (T ₂) _{4.1}	γ_0	f	s	variance	v llo + invalid -
CTAB A LS	2.573	184.2	9.010	729.1	+
60	2.342	377.6	6.362	1.054x10 ⁴	+
CTAB B LS	-6.051	7131	395.0	1.426x10 ⁶	-
0	5.629	2671	60.37	2.242x10 ⁴	+
5	5.519	2185	34.62	4.517x10 ⁴	+
10	9.500	1256	26.50	3.020x10 ⁴	+
15	8.803	1296	31.60	2.619x10 ⁴	+
20	0.210	2056	24.80	3.050x10 ⁵	+
25	9.777	510.7	0.3114	1978.	+
30	-0.0764	384.5	1.478	3.673x10 ⁵	-
45	15.78	1203	1.62	1.407x10 ⁴	+
60	-0.5312	185.0	-1.921	1.712x10 ⁴	-
120	-0.0265	255.3	-2.673	4.084x10 ⁴	-
CTAB C LS	12.13	927.7	10.53	1.014x10 ⁴	+
D LS	1.940	639.1	11.63	956.1	+
E LS	1.459	765.6	10.89	2069	+
F LS	0.8007	380.5	11.07	868.8	+
G LS	2.647	-7.255x10 ⁷	-1.91x10 ¹⁰	3.081x10 ⁶	-
H LS	12.55	26.99	-0.01457	3.505x10 ⁷	-
I LS	43.24	-3.120x10 ¹³	3.767x10 ¹⁴	9.052x10 ⁵	-
J LS	2.484	237.5	-0.9602	1.017x10 ⁵	-
K LS	15.40	452.6	0.7327	2.571x10 ⁵	-
L LS	0.9690	455.6	22.45	1321	+
M LS	1.261	592.3	50.62	1031	+
N LS	2.105	911.7	15.90	790.2	+
O LS	4.845	48.28	-5.478	6627	-
P LS	4.254	1042	8.249	7657	+
CTAB L/L LS	1.026	533.9	14.71	2504	+
n/L LS	1.129	511.8	25.34	7611	+
J/L LS	4.157	529.2	2.029	2.924x10 ⁵	-
C/L LS	5.615	1623	45.86	2.115x10 ⁴	+
CPC A LS	2.801	309.7	7.506	1532	+
CPC B 0	2.697	2115	25.75	6595	+
15	-0.9763	4591	79.30	4.437x10 ⁴	-
20	8.033	5292	69.40	4.082x10 ⁴	+
25	-0.1062	1.427x10 ⁴	507.8	1.265x10 ⁵	-
30	1.857	1246	81.31	963.2	+
45	15.01	1300	21.93	8.296x10 ⁴	+
60	0.03220	296.5	2.765	4134	+
120	10.45	240.0	-4.149	7.955	-
CPC C LS	-1.768	7736	155.4	2.125x10 ⁴	-
D LS	6.550	3018	9.266	2.394x10 ⁴	+
BLN2 A LS	5.759	187.2	1.020	9540	+
CLN A LS	5.947	706.4	7.534	1947	+
0	5.350	590.0	7.815	618.9	+
15	1.105	2450	21.12	2240	+
30	2.011	2380	20.88	4524	+
60	-5.253	4146	31.41	1.716x10 ⁵	-
120	24.02	470.4	-0.1412	6.745x10 ⁶	-

continued over

Table 5.2 continued

Dispersion	Code	γ_{∞}	f	S	variance	valid + invalid
DOSS	A L3	33.90	2.579×10^{13}	-5.063×10^{17}	1.527×10^8	-
	0	3.223	-6.620	-24.44	5404	-
	15	2.272	353.5	34.31	593.6	+
	30	2.304	411.7	20.03	893.2	+
	60	2.317	632.8	29.42	495.9	+
	120	2.207	2037	29.45	4516	+
series	0.01	0.2540	2412	1.289	13.03	+
(4.3)	0.05	0.3377	33.60	0.05249	54.50	+
	0.10	0.8705	260.6	9.714	305.3	+
	0.15	0.9560	394.5	18.93	463.5	+
	0.20	-1.014	3351	73.34	6903	-
	0.30	12.20	277.5	32.23	5.960×10^4	+
	0.40	7.178	2372	49.62	6.042	+
	0.50	12.08	2323	48.56	7452	+
	0.55	9.130	3332	51.77	6378	+

available for estimating the magnitude of these effects. The extrapolated values obtained by curve-fitting to the down curve have real meaning, but as already noted some of the experimental curves did not show typical pseudoplastic flow properties. Similarly, the viscosities at infinite shear rates calculated by curve fitting as opposed to direct measurement are likely to have more real meaning where the data is amenable to this treatment.

The instrument in the form employed was only capable of drawing a two-dimensional plot of stress vs strain. As noted in Chapter Two (2.3.2) thixotropy is a time dependent phenomenon requiring time as an additional axis. An initial investigation suggested that one way of investigating thixotropy was to consider it as a mass-action phenomenon, measuring a half-life. This requires an instrument fitted with a time-axis recorder which was not available. However, initial results using a stop watch were sufficiently encouraging to suggest that this might prove a fruitful line for a future investigation. The use of the area of the hysteresis loop as suggested by Pryce-Jones as an index of thixotropy (352, 353) is of less value but the values obtained are presented in Table 5.1 for purposes of comparison.

5.7 Summary

1. A Ferranti-Shirley cone-plate viscometer was used 5.2
to measure the flow curves, continuously recording
the stresses produced by applied shear strains of
up to 183 secs.⁻¹

2. The instrument produced reproducible flow curves, 5.3
from which are recorded yield point, maximum stress Table
and area of hysteresis. 5.1
3. Pseudo-plastic flow curve fitting by the methods 5.5
of Millerson and Shangraw showed that the data was
more closely fitted by the former.
4. Constants derived from all the flow curves are 5.2
presented.

CHAPTER SIX

DISCUSSION AND CONCLUSIONS

- 6.1 The accuracy and reproducibility of the particle size analysis methods
- 6.2 The effects produced by ultrasonic irradiation on the particle size and particle size distribution.
- 6.3 The influence of formulation factors on the particle size of the disperse phase
- 6.4 The influence of formulation factors on emulsion viscosity
- 6.5 The presence of an interfacial film.
- 6.6 A theory of pseudoplastic flow
- 6.7 The influence of particle size upon the flow behaviour of emulsions
- 6.8 Summary

6.1 The accuracy and reproducibility of the particle analysis methods

The problems of determining accuracy and reproducibility of particle size analysis methods have been discussed by Becher (25) and in British Standard BS 3406. An estimate of the error due to instrument variation can be obtained by repeatedly analysing the same sample, as shown in Appendix Two. These results are summarised in Table 6.1.

Table 6.1 The standard error for the Coulter Counter and centrifuge methods. Mean value as a percentage of the mean weight of material within given size intervals (A 2.2.1)

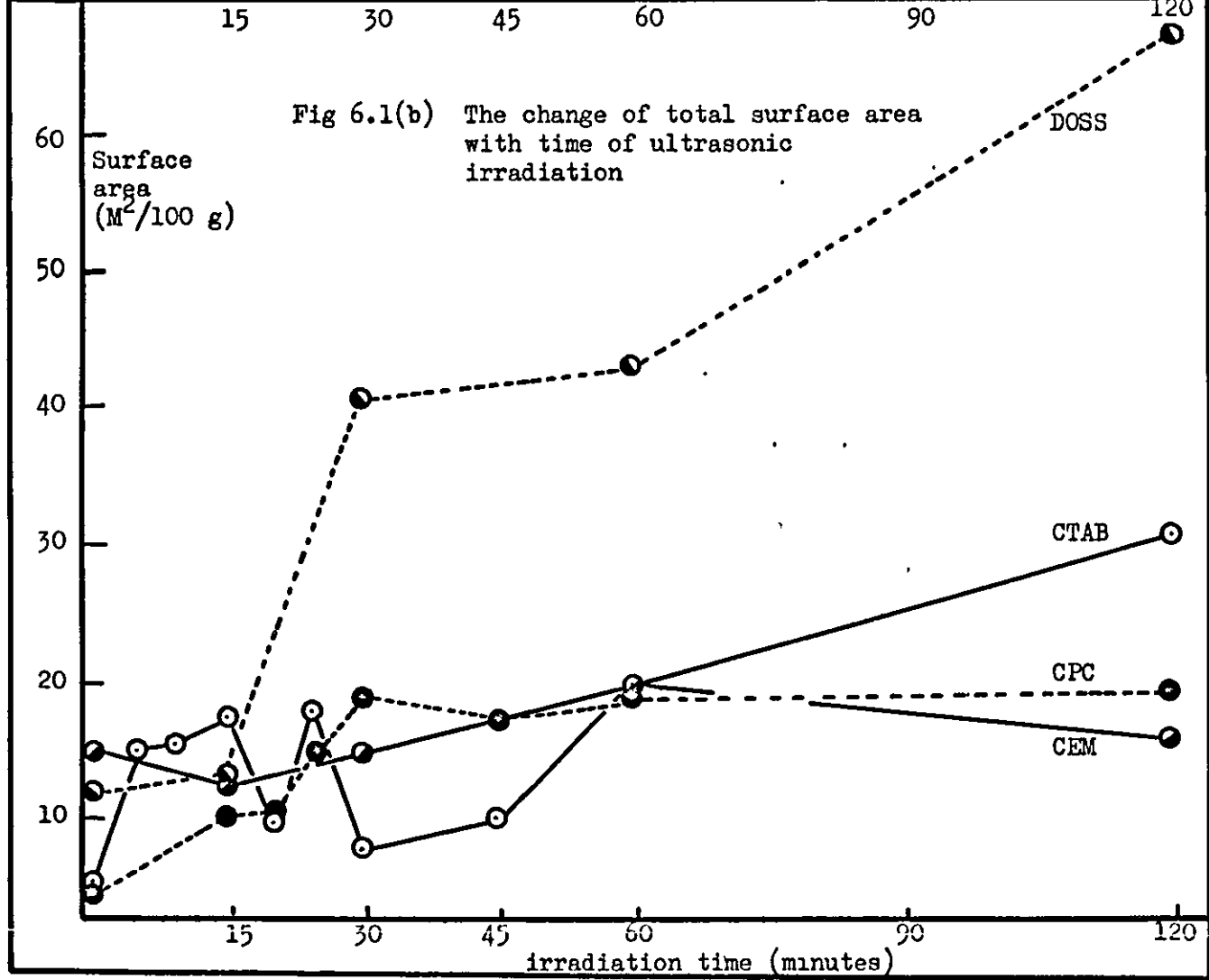
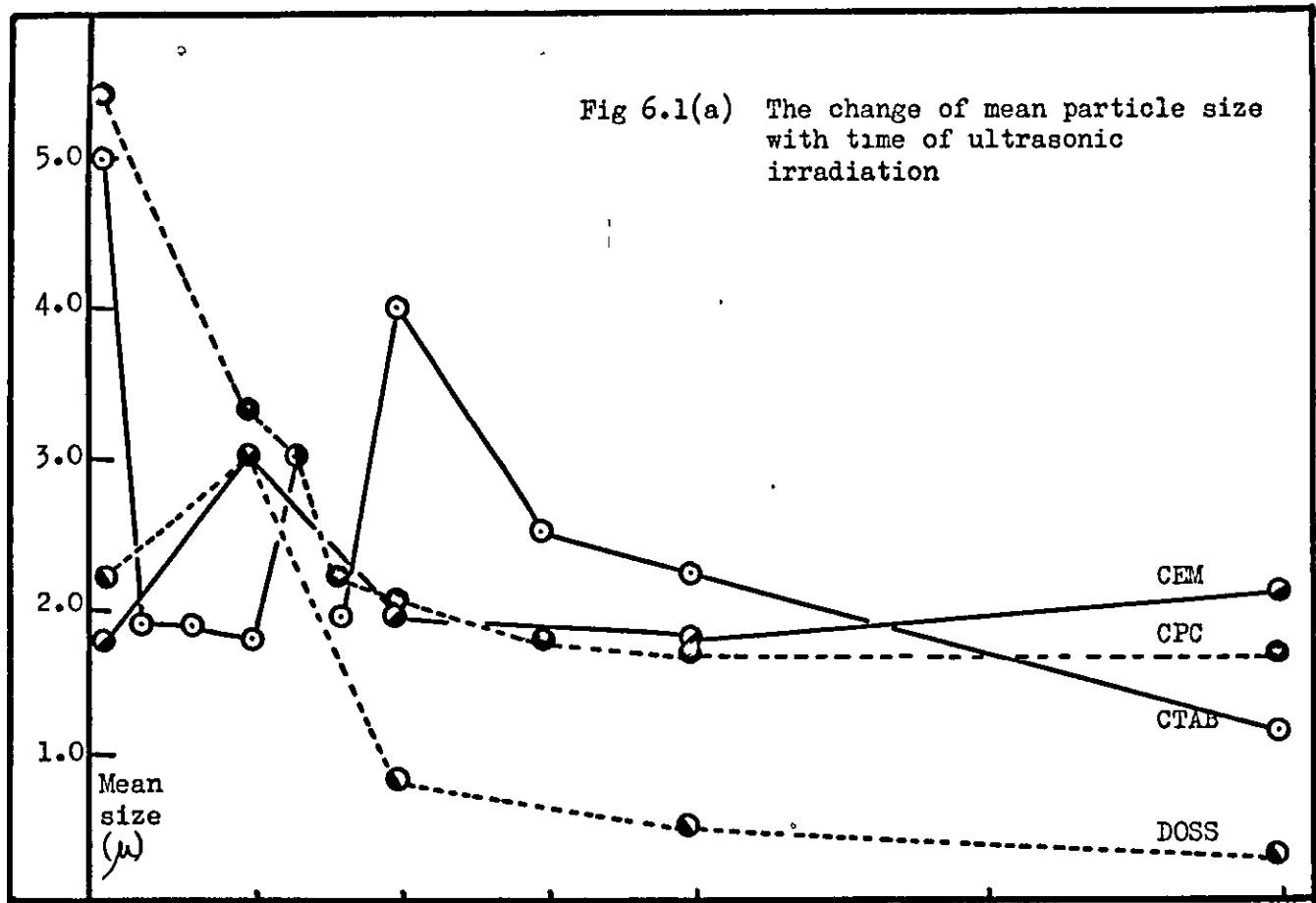
	Coulter Counter	Centrifugal photo-sedimentometer
repeated sampling	14.09	3.94
repeated analysis of the same sample	2.19	3.56

Since errors are additive these values suggest that the reproducibility of the Coulter Counter is well within the 5% claimed by the manufacturers. Results from the centrifugal photosedimentometer are only slightly less reproducible and sampling error is considerably reduced. One reason for this may lie in the differences in principle of the two methods. The sample size for the centrifuge is much larger than that for the Coulter, albeit that the latter instrument counts a vastly larger number of particles than those counted during a typical microscope size analysis.

An estimate of the absolute accuracy or meaning of the particle size distribution obtained by any one method can only be obtained by comparing results with those from other methods. As shown in Appendix Two, a statistical examination of the results obtained from the Coulter Counter and the centrifugal photosedimentometer over most of the range common to both suggests that here at least the results can be compared. The variance ratio indicates that the samples are derived from the same population and the normalising procedure used to extend the range of each method appears to be justified.

It is doubtful if errors, especially those due to sampling, can be eliminated or reduced to levels significantly lower than those shown in Table 6.1

A log-probability distribution has been presumed throughout, although it is admittedly an imprecise method of describing a particle size distribution. However, until the particle size distribution of an emulsion system can be described more accurately the assumption would appear to be a reasonable one. The biggest part of the problem is to reduce



sampling error. The centrifugal photosedimentometer is less subject to this error than the Counter over the range of 3 - 10 μ . More work is required to establish the absolute accuracy of the instrument over the whole of the size range, especially for sizes below a micron (7.2)

6.2 The effects produced by ultrasonic irradiation on the particle size and particle size distribution

Laboratory scale homogenisers failed to produce any significant effect on the particle size or distribution of size of a model system. The simple device shown in Fig 4.4(a) produced some alteration in the emulsion properties and it was therefore used to emulsify an equal mixture of liquid paraffin and cetostearyl alcohol in various emulsifiers. The particle size and the total surface area (reflecting the particle size distribution) are shown in Figs 6.1(a) and (b) as a function of the ultrasonic irradiation time for each of these systems.

All the emulsion systems were unstable when maintained at 45° without stirring, indicating that coalescence of the disperse droplets was occurring. As noted in Chapter Two ultrasonic irradiation may accelerate both breakage and coalescence processes but not necessarily at an equal rate. The effects produced in these systems are variable and appear to be a function of the emulsifier since all other factors are equal. For example, the mean particle size of the cetylpyridinium chloride (CPC) system falls with the irradiation time but the total surface area shows only a slight increase over the same time. This suggests that as the larger particles are broken the smaller ones coalesce so that the net surface area increases only slowly. On the other hand particles in the

anionic (DOSS) series are reduced in size and the surface area increases rapidly, suggesting that the coalescence rate of the smaller particles is at least much slower than the breakage rate. Particle size and surface area of the cetomacrogol (CEM) preparation remain almost unaffected by the ultrasonic irradiation. The particle size of the cetrinide (CTAB) system fluctuates initially but after the first thirty minutes of irradiation the particles tend to become smaller and the total surface area shows a comparatively rapid rate of increase.

This observation might form the basis of a method of ranking emulsifiers in order of efficiency since an efficient emulsifier would be expected to produce a maximum disperse phase surface more rapidly than a less efficient one. From Fig 6.1(b) for example the emulsifiers would be ranked:

0.1% CEM > 0.5% CPC > 0.5% CTAB >> 2.0% DOSS + 0.5% SLS

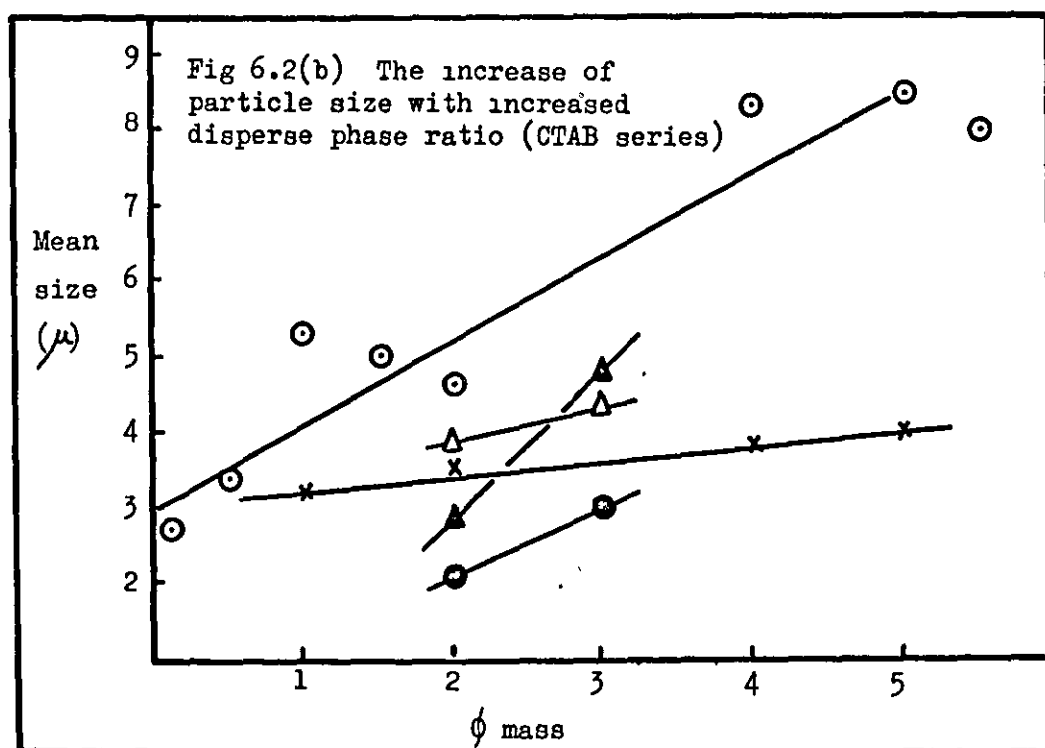
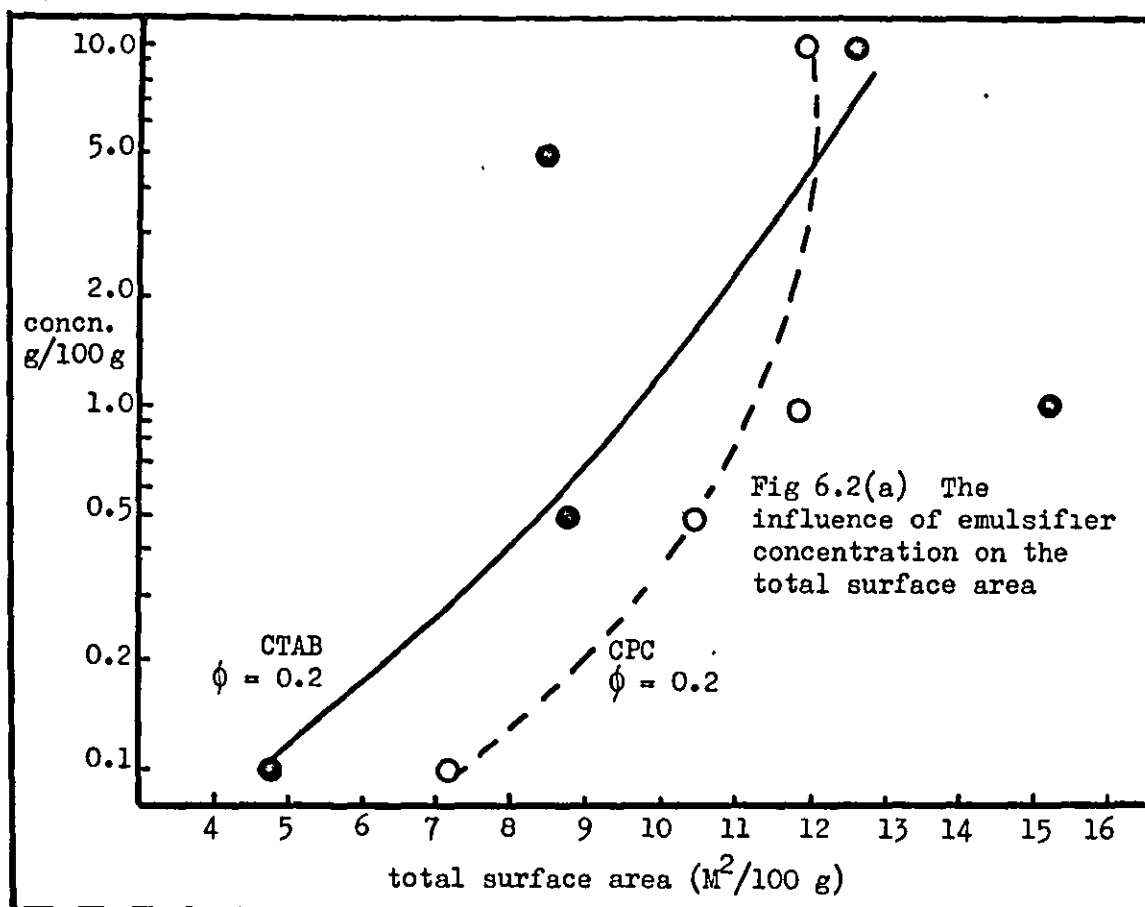
6.3 The influence of formulation factors on the particle size of the disperse phase

It was evident that the factors influencing emulsion flow behaviour are both numerous and complex. Sherman (412) reviewed the flow properties of emulsions and listed some of the factors that contributed to the viscosity, Table 2.1.

Since the systems in the present investigation have a solid disperse phase at room temperature the viscosity of the disperse phase droplets can be discounted but it was of interest to determine if other factors could influence the particle size.

Sherman (406) examined the influence of emulsifier concentration on emulsion viscosity and proposed an equation in the form

$$\ln \eta_{rel} = A C \phi + B \quad \quad \quad -(1)$$



where η_{rel} is the relative viscosity, C equals emulsifier concentration, ϕ the disperse phase ratio and A and B are constants. The relationship did not appear to be valid for the present data and an alternative explanation may be obtained by supposing that an increase in emulsifier concentration can produce an effect upon the particle size. Although no standardised method of emulsification has been employed this would seem from the data shown in Fig 6.2(a) to be a valid generalisation, the total surface area showing a tendency to increase as the emulsifier concentration is increased. The chemical nature of the emulsifier may account for the marked differences noted between them, shown by comparing the mean sizes (Table 6.2).

Table 6.2 The particle size of preparations containing different emulsifiers.

Emulsifier	code Table 4.1	mean size (μ)	total surface area($m^2/100g$)
CTAB	B/O	5.00	4.83
CPC	B/O	5.40	4.50
BENZ	A/LS	2.60	9.82
CEH	A/O	1.75	14.60
DOSS	A/O	2.20	11.88

The effect of increasing the disperse phase ratio appears to be one of increasing the mean particle size, shown in Fig 6.2(b). This may well be because at elevated temperature (above the melting point), particle interactions and coalescence are likely to be greater as the system becomes more concentrated.

An examination of the results presented in Table 3.3 suggests that there is no effect of disperse phase constitution

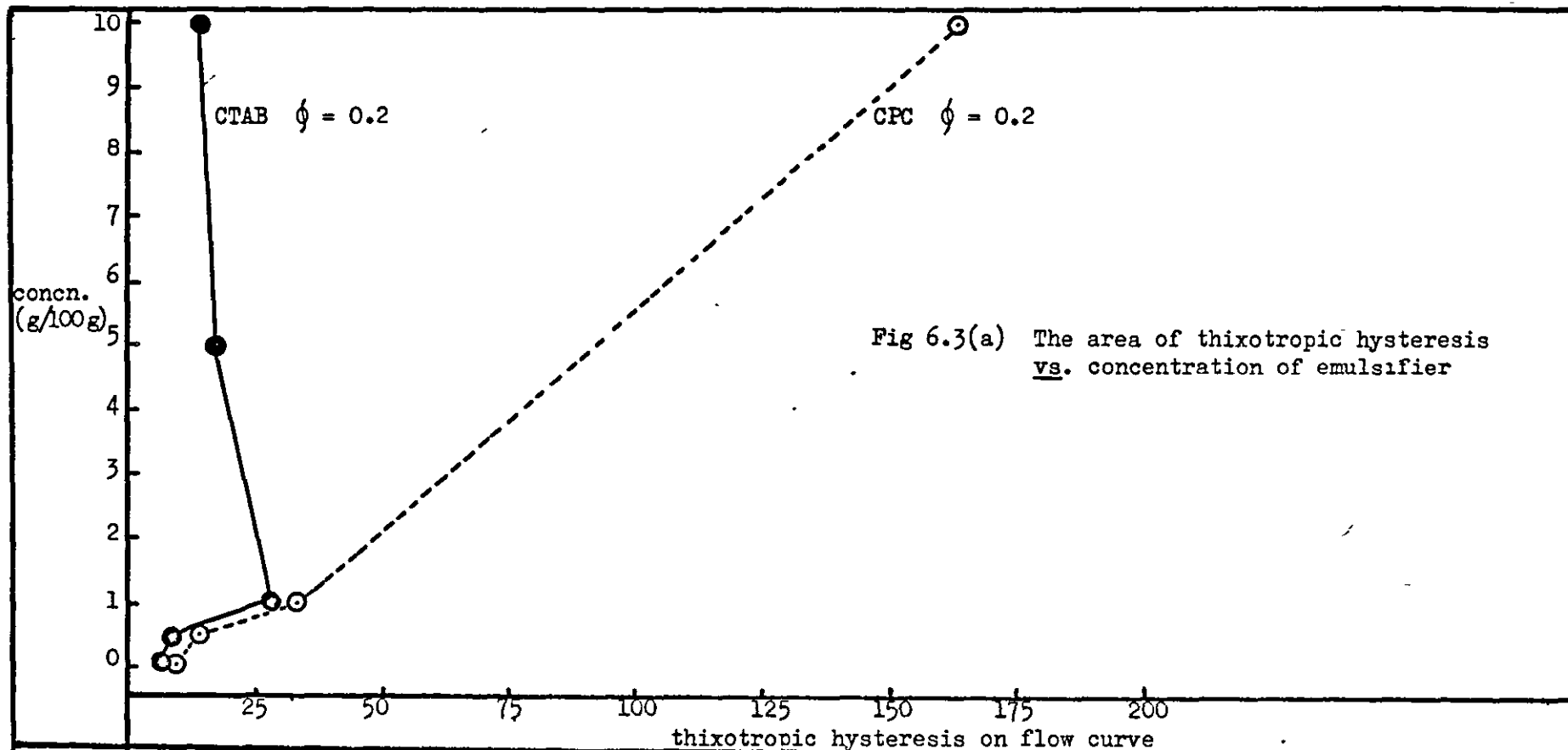


Fig 6.3(a) The area of thixotropic hysteresis vs. concentration of emulsifier

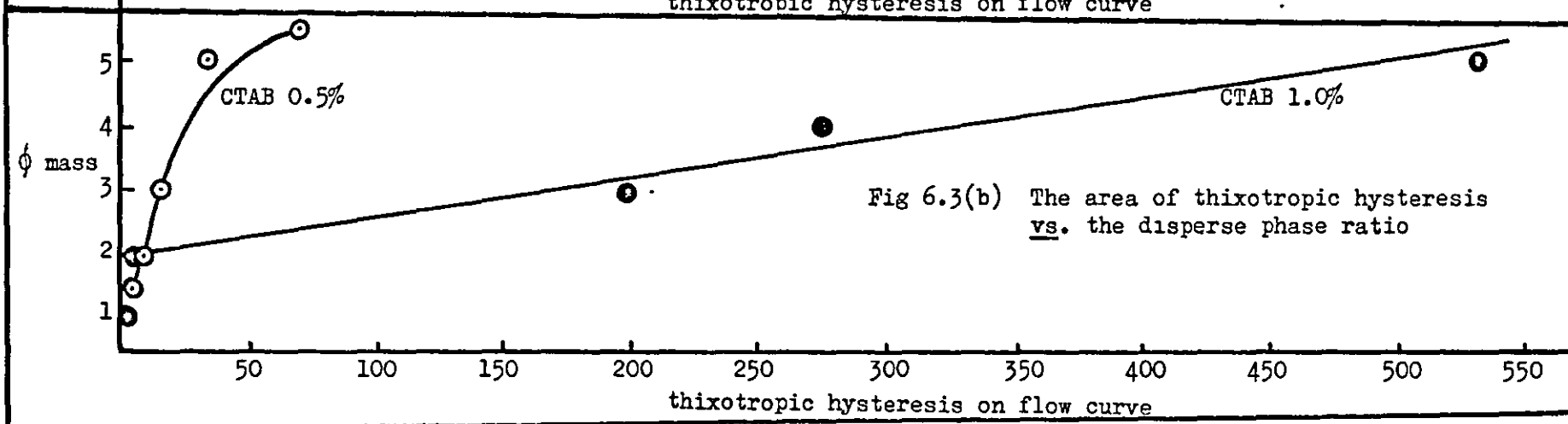


Fig 6.3(b) The area of thixotropic hysteresis vs. the disperse phase ratio

on the particle size. These systems are substantially the same, differing only in the proportions or viscosity of paraffin oil, and if Shermans' criterion of chemical constitution is correct, an influence would not be anticipated.

6.4 The influence of formulation factors on emulsion viscosity

The flow behaviour of the systems examined in the present investigation was almost entirely non-Newtonian. Application of the Williamson equation enabled the systems to be divided into two categories: those in which the down-flow curve was typically pseudoplastic and those in which the system exhibited even more complex behaviour. In general all systems had typical exaggerated yield points and a degree of hysteresis between the up- and down-flow curves. Sherman (405, 409, 411, 414) examined the influence of formulation upon viscosity and deduced that the equations relating particle size to viscosity were not valid for heterodisperse systems or very concentrated systems ($\phi \sim 0.7$). However, in many cases the Williamson equation was not even valid for systems in which the disperse phase ratio was as low as 0.2, and other factors appear to be operating. The measurement of thixotropy in terms of hysteresis alone is unsatisfactory since the phenomenon is time-dependent (54, 431). However, the area of hysteresis (Table 5.1) is at least an indication of the strength of the forces holding the floccules together and it was of interest to correlate this with formulation factors. The variable effect due to the nature of the emulsifier is shown in Table 6.3.

The effect due to increasing the concentration of the emulsifier is by no means simple, as indicated in Fig 6.3(a) but a general increase in the hysteresis can be seen for at

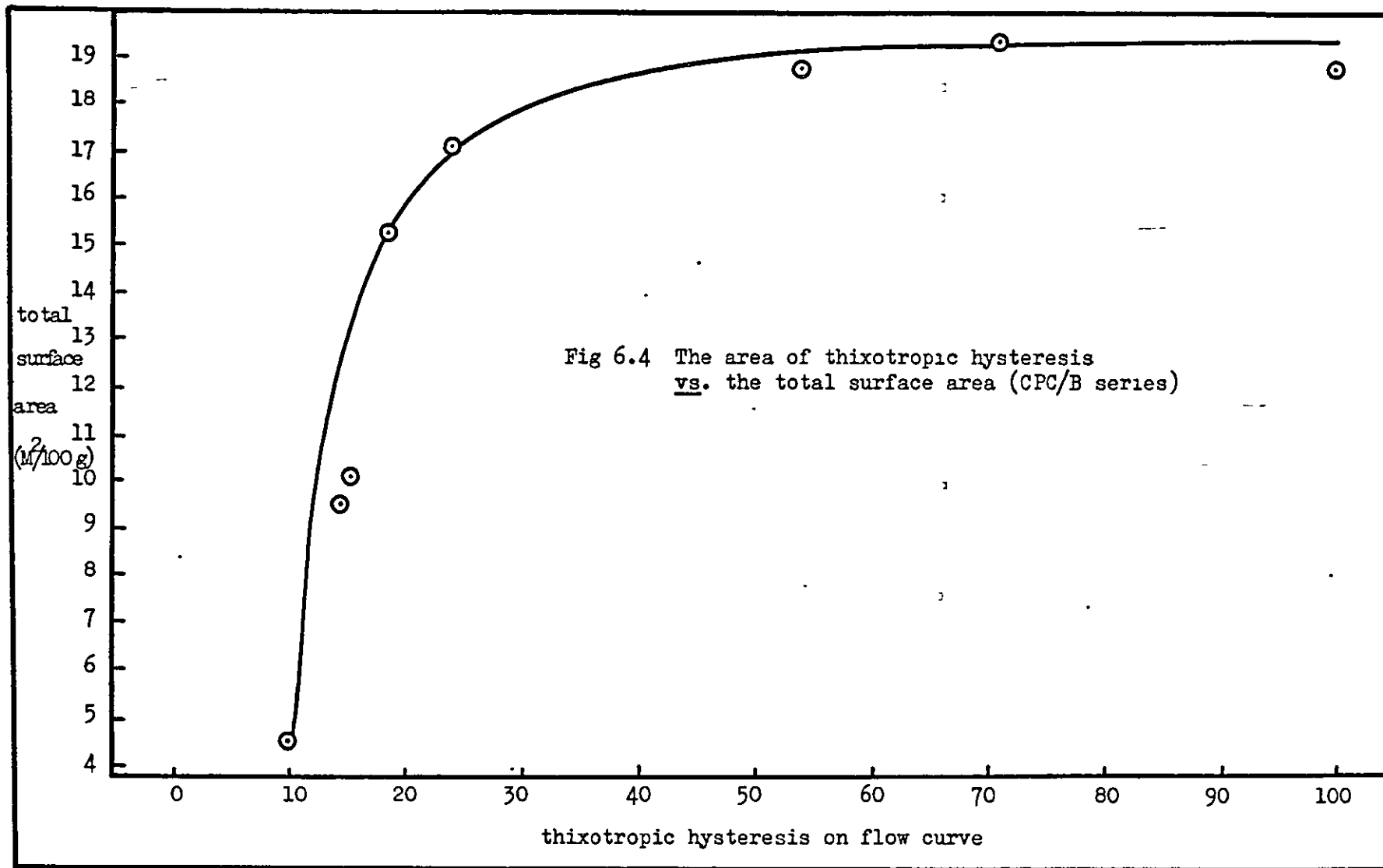


Table 6.3 The area of hysteresis of different emulsions

Emulsifier	Code (Table 4.1)	Area of hysteresis
CTAB	B/O	12.20
CPC	B/O	9.34
BENZ	A/LS	34.82
GEM	A/O	5.66
DOSS	A/O	17.46

least the lower concentrations.

The predictable increase of thixotropy with increased concentration or disperse phase ratio is shown in Fig 6.3(b), indicating, also, the increase of thixotropy with increase of concentration of emulsifier.

It would be anticipated that decreasing the particle size would also affect the flocculation and, hence, the thixotropy. A number of other factors must be superimposed upon this relationship but the effect is illustrated for the CPC series, Fig 6.4.

Examination of the results in Tables 5.1 and 5.2 showed that the computer did not always reject results from systems with a large thixotropic hysteresis. Thus whilst it is possible that all the floccules were broken down into primary particles at the maximum shear rate it is also possible that the down curve was a measure of the flow properties of a suspension of stable aggregates. This may account for some anomalies but there is no method at present for distinguishing the two states.

6.5 The presence of an interfacial film

As noted in Chapter Two, there is a considerable body of evidence to support the existence of an energy barrier of finite thickness at the interface of each emulsion droplet,

each particle behaving as if its true volume was greater than it should be from direct measurements made upon it. In the present investigation additional support for the existence of this interfacial film has been obtained by consideration of the particle shape and the emulsion density.

The presence of polyhedral particles in the type of emulsions under investigation has been demonstrated and the data shown in Fig 4.6 gives adequate confirmation of the original suggestion (150) that this is due to localised close packing, not crystallisation. The rheograms of these systems (Fig 5.1) show that particle-particle interactions occur well below the theoretical maximum for close packing of spheres ($\phi = 0.74$). The rapid increase of numbers of polyhedra with disperse phase ratios in excess of 0.1 indicates the same effect. Some conclusions may be drawn from the available data. As discussed by Lissant (247) globules under close packing conditions distort to dodecahedra:

(a) If a polyhedral particle be regarded as a sphere under constraint so that it becomes a dodecahedron, the particle volume is the same but the particle behaves as if it has a larger surface, equivalent to that of the circumscribing sphere. From geometrical considerations (18) a 3.42μ diameter dodecahedron, the size of the mean particle in the system $\phi = 0.55$, has a circumscribing sphere of 3.53μ , i.e. there is a layer 800 \AA thick around it.

(b) Extending the same argument, the particle size analyses of the series of CTAB emulsions prepared with increasing disperse phase ratio (Table 4.4) were recalculated to take into account the known number of polyhedra within each sample.

The actual surface area, assuming the polyhedra to be regular dodecahedra and the surface area of spheres of equivalent volume were calculated to yield, first, a mean surface area, and then, the radii: the difference in radii being a measure of the thickness of the layer of 'sphere of influence'. These calculations are summarised in Table 6.4. Whilst they are admittedly approximate and there are insufficient values at the upper end of the range the value for this difference rises to a limit of between 700 and 900 Å when extrapolated to the limiting disperse phase ratio.

(c) Experimentally it was noted that emulsions containing disperse ratios $\phi_{\text{mass}} > 0.55$ tended to 'crack', or exhibit synecrosis, indicating that this might approximate to the limiting disperse phase ratio, $\phi_{\text{volume}} \approx 0.74$. Expansion of the disperse phase on heating did not account for this alone suggesting that the particles might be behaving as if they were larger than appeared from direct measurement.

Thus, volume (V) occupied by N particles of diameter d

$$= N \frac{\pi}{6} d^3$$

If each particle is surrounded by a layer of thickness λ the actual volume occupied

$$= N \frac{\pi}{6} (d + 2\lambda)^3$$

The maximum volume (0.74) and the actual volume may be equated such that

$$d^3 = V \times \frac{6}{N\pi}, \quad (d + 2\lambda)^3 = 0.74 \times \frac{6}{N\pi}$$

$$(d + 2\lambda)^3 / d^3 = \frac{0.74}{V}$$

$$\therefore \lambda = \frac{d}{2} \left[\left(\frac{0.74}{V} \right)^{\frac{1}{3}} - 1 \right] \quad - (2)$$

Equation (2) is analogous to Sherman's equation for the mean

Table 6.4 Dimensions of the particles in the series of emulsions prepared with increasing disperse phase ratio, taking into account the known number of polyhedra present (Fig. 4.6)

ϕ Mass	Number of particles in 100 g of emulsion $\times 10^{16}$	Total surface area		Area per particle		Radius per particle		Difference
		Theoretical	Actual	Theoretical	Actual	Theoretical	Actual	
		$\text{cm}^2 \times 10^9$	$\text{cm}^2 \times 10^9$	μ^2	μ^2	μ	μ	μ
0.05	3.253	1.220	1.221	3.75	3.75	0.546	0.546	-
0.10	4.639	2.135	2.136	4.60	4.60	0.605	0.605	-
0.15	4.492	2.776	2.790	6.18	6.21	0.700	0.703	0.003
0.20	3.883	3.145	3.166	8.10	8.15	0.804	0.806	0.002
0.30	3.382	4.041	4.112	11.95	12.16	0.975	0.982	0.007
0.40	2.276	4.575	4.690	20.10	20.16	1.266	1.281	0.015
0.50	1.646	4.979	5.125	30.25	31.14	1.555	1.575	0.020
0.55	1.338	4.909	5.151	36.70	38.51	1.710	1.754	0.044

distance of separation (a_{11}) discussed in 2.5.3., page 63.

Taking the data shown in Table 6.4 and allowing for expansion of the disperse phase at 45° the likely lowest temperature before solidification commences (Fig 4.1), the 3.42μ diameter particles of the system $\phi = 0.55$ have a layer 720 \AA around them.

(d) As discussed in Section 4.9 (p. 99) there is a marked difference between the theoretical and experimental emulsion densities, tabulated in Table 4.5. Martynov (270) discussed this anomaly in detail and showed that, where the radius of curvature of the surface of separation, or the thickness of the film of one of the phases greatly exceeds the sphere of influence of the molecular forces (e.g. in the case of highly concentrated emulsions) the volume of the system (V) is given by:

$$V = V_0 + \lambda S \quad -(3)$$

where V_0 is the volume of the system in the complete absence of a surface of separation, i.e. in practical terms, when the phases have separated into two macrolayers, λ is the thickness and S is the surface area. Since the mass is unchanged, continuing with the terminology of equation (1), page 99, we can write

$$\rho_a = \text{apparent density} = \frac{100}{\frac{\phi}{\rho_o} + \frac{(100-\phi)}{\rho_w} + \frac{\lambda S}{100}} \quad -(4)$$

(eq. 1, p.99)

$$\rho_t = \text{theoretical density} = \frac{100}{\frac{\phi}{\rho_o} + \frac{(100-\phi)}{\rho_w}} \quad -(5)$$

$$\therefore \frac{1}{\rho_a} - \frac{1}{\rho_t} = \frac{\lambda S}{100} \quad -(6)$$

(contd. p. 128)

Table 6.5 Calculated values for mean distance of separation (a_m) and thickness of interfacial film (λ).

Code	Dispersion	a_m (μ)	λ (μ)
CTAB	A LS	3.155	0.1033
	60	1.165	0.0330
CTAB	B LS	1.650	0.0601
	0	2.428	0.1093
	5	0.920	0.0479
	10	0.920	0.0518
	15	0.872	0.0319
	20	1.455	0.0680
	25	0.920	0.0454
	30	1.943	0.1010
	45	1.214	0.0541
	60	1.069	0.0476
	120	0.557	0.0304
CTAB	C LS	1.699	0.0798
	D LS	1.600	0.0743
	E LS	1.069	0.0679
	F LS	2.780	0.0183
	G LS	0.841	0.0355
	H LS	0.680	0.0337
	I LS	0.368	0.0317
	J LS	0.987	0.0293
	K LS	0.840	0.0115
	L LS	1.870	0.1166
	M LS	1.285	0.0698
	N LS	0.174	0.0368
	O LS	0.203	0.0320
	P LS	0.158	0.0269
CTAB	L/L LS	1.362	0.0803
	M/L LS	1.365	0.0768
	J/L LS	1.248	0.0267
	C/L LS	1.522	0.0538
CPC	A LS	1.650	0.0753
CPC	B 0	2.620	0.1014
	15	1.600	0.0795
	20	1.455	0.0784
	25	1.135	0.0578
	30	0.970	0.0400
	45	0.847	0.0456
	60	0.824	0.0496
CPC	120	0.800	0.0221
	C LS	1.019	0.0480
CPC	D LS	0.970	0.0257
BENZ	A LS	1.260	0.0725

/contd. over

Table 6.5 continued

Code	Dispersion	$a_m (\mu)$	$\lambda (\mu)$
CEM	A LS	1.212	0.0364
	0	0.847	0.0445
	15	1.455	0.0870
	30	0.920	0.0413
	60	0.847	0.0445
	120	1.019	0.0705
DOSS	LS	0.726	0.0217
	0	1.135	0.0277
	15	1.455	0.0092
	30	0.388	0.0163
	60	0.242	0.0134
	120	0.015	0.0095

The surface area per 100 g emulsion = $\frac{6 \phi}{d \phi_0}$

$$\therefore \lambda = c. \frac{(\phi_t - \phi_a) \phi_0}{6. \phi_t \phi_a \phi} \times 10^{-2} \text{ microns} \quad -(7)$$

Equation(7) was used to calculate values of λ from the data of Table 4.5 and these are tabulated in Table 6.5. From this table it was immediately clear that the value of λ was unaffected by the concentration of the emulsifier, the disperse phase ratio or the particle size of the systems but there was a marked correlation between systems with the same surface active agent. A statistical comparison of this data is shown in Table 6.6.

Table 6.6 A comparison of the values of λ (Table 6.5)

Emulsifier system	Mean value of λ (Å)	Number	Fiducial limits (P = 0.95)
CTAB	543.7	31	98.45
CPC	566.7	11	145.02
CEM	540.3	6	160.56
DOSS	163.0	6	45.82

Test of significance (Students 't' test)

CTAB vs CPC not significantly different

CTAB vs CEM not significantly different

CTAB vs DOSS significantly different ($P < 0.001$)

It is only possible to take speculation a little further. Sherman (406,410) discussed the work of Derjaguin and his school on the viscosity of fluid films of the continuous medium, very thin films having much higher viscosities than the bulk liquid. Sherman supposed that changes in the emulsifier concentration affected the thickness of the layer and hence the viscosity; the supposition is not supported by the data in Table 6.5 although more work is required to establish this more clearly. Nevertheless, Sherman must be correct in his assertion (410) that previous work using the term η_o (viscosity of the continuous phase) in equations describing viscosity of emulsions may require revision. At shear rates large enough to cause deflocculation the globules in concentrated emulsions will be separated by very thin films of continuous medium and the true viscosity of the continuous medium will not be represented by the bulk viscosity η_o . It was also suggested that a contributory factor in increased viscosity of emulsions with increased homogenisation was due to the presence of a much thinner film between the globules. However, since the thickness of the film does not appear to be affected by the particle size this seems unlikely.

More recently Derjaguin (86) and others (520) have reported on thin films of water or adsorbed surface active agents. The relevance of the observation in Table 6.6 that the interfacial layer appears to be of approximately the same thickness for

a number of different emulsifiers is not at present certain, but the values obtained are close to those of some of the boundary layers measured by these workers.

6.6 A theory of pseudoplastic flow

As discussed in Chapter Two (pps. 65 and 66) there is general agreement that the particle size and distribution of particle size are important when considering the flow behaviour of suspensions of spherical particles. It is pointed out that workers in this field can be classified into those who consider the particle mechanics only and those who consider only the properties of the surfaces, a combination of the two points of view offering some attractions.

The structure of emulsions from the consideration of surface properties is discussed in Section 2.5.4. Recently Gillespie (525, 525) has shown how a consideration of the number of structural links in a disperse phase can be used to predict with some precision the flow behaviour of dilatant or thixotropic suspensions. This work, derived from the Goodeve theory of structure (12) - 131), requires a knowledge of the number of links in unit volume and it seems clear that this must be influenced by the surface area of the disperse phase. Accordingly, a tentative approach to this problem was made by making simplified assumptions about the properties of the links and treating the process visualised by Goodeve as a mass-transfer phenomenon. The derivation of the following equation is described in Appendix Three.

$$\eta_{\infty} = b.X \int \frac{f(x).dx}{(Xx + K_1)} \quad -(3)$$

As described, X and the integral are essentially the particle size distribution transformed and b is a measure of the binding energy of the links. Using the data of Tables 3.3 and 5.2 values of b were calculated for the materials for which the Williamson equation was apparently valid, Table 6.7. Inspection of this table shows that with some exceptions there is a broad measure of agreement. In view of the number of approximations made this must be considered reasonably satisfactory. It might prove possible to improve the approach by, for example, considering the properties of the links in the fashion suggested by Takano (456) or by Gillespie (loc.cit.). However, one obstacle which is likely to remain is that of knowing for certain the viscosity at infinite shear rates is due to primary particles within the system and not to stable aggregates, p.122. This may be used to reject arbitrarily inconsistent results but more work is required on this aspect. The wide variation noted in the C.P.C. series may be due to this effect since, as can be seen in Fig 6.4, there is apparently considerable interaction as the surface area of the systems increases. This is shown by the increased thixotropic hysteresis which appears to be a manifestation of a flocculation or aggregation phenomenon.

A suggestion for additional work along these lines concerns the formation of links within an emulsion system at rest. Many authors have considered the number of contact points between particles in a packed system (27,182, 311, 514-6, 526) but the problem has not yet been solved for a random size distribution. The approach outlined by Debbas & Rumpf (526) may have promise although these authors did not, in fact, succeed in obtaining

Table 6.7 Values of the link binding energy (b) obtained from equation (3)

System (Table 4.1)	Link energy dynes/cm $\times 10^4$
CTAB A LS	1.09×10^4
A 60	12.0
CTAB B 0	1.23×10^4
B 5	6.50
B 10	6.71
B 15	4.03
B 20	71.3
B 25	1.35
B 45	189
CTAB C LS	195
D LS	56.4
E LS	5.44
F LS	25.6
L LS	117
M LS	172
N LS	9.9
O LS	65.9
CTAB LL LS	72.8
ML LS	59.5
CL LS	259
CPC A LS	77.1
CPC B 0	1.06×10^4
B 20	69.8
B 30	0.22
B 45	6.23
B 60	5.67×10^{-3}
CPC D LS	1.01
CEH A LS	4.58
A 0	10.35
A 15	0.15
A 30	3.42
DOSS A 15	0.39
A 30	0.04
A 60	0.40
A 120	0.20
BENZ A LS	3.76
B 0.05	0.34
0.10	0.87
0.15	0.96
0.30	12.20
0.40	7.18
0.50	12.10
0.55	9.18

The mean of CTAB results $< 10^3$, except μ series = 73.8 ± 37
(P=0.95) Variation in CPC series is wide but mean $> 1 < 10^3$ = 63.4
Mean CEH = 4.63
Mean DOSS = 0.25

a solution. However, it is probable that there is a connection between the strength and number of links (contact points) and the yield value of an emulsion system. An empirical attempt to relate yield value and surface area was not successful using the present data and it is clear that a more detailed theoretical approach to the problem is required.

6.7 The influence of particle size upon the flow behaviour of emulsions

In order to summarise the contribution made by the present investigation it may be useful to consider the conclusions drawn by earlier workers, especially Sherman who has discussed the relationship between particle size and flow in a number of papers.

Sherman has rightly drawn attention to the influence that particle size have upon the flow behaviour of emulsion systems. He clearly considers the mean distance of separation, a_{11} , to be of importance and this is discussed in 2.5.3., page 63. For the purpose of comparison the values of a_{11} are tabulated in Table 6.5 and no correlation could be drawn in the manner he suggested. However, the value of a_m is essentially a derivative of the mean particle size and disperse phase ratio if the maximum packing disperse phase ratio is a constant. This latter assumption is not a good one although, as noted, there is some reason to support it in at least the systems investigated here. (Unlike Sherman's systems (409) there is ^{no} evidence of multiple emulsion formation on microscopic examination, e.g. Figs 3.1, 4.4(b) and 4.5). Hence although Sherman does not use the mean particle size directly he is using a derivative of it. Unfortunately, his use is not consistent since he relates γ_{11}

to η_r in two equation as follows:-

$$\ln \eta_r = C \left(\frac{1}{a_{11}} \right) + X \quad (403, 414) \quad -(9)$$

$$\ln \eta_r = C - X a_{11} \quad (410) \quad -(10)$$

The form of equation (9) may vary with the degree of inhomogeneity of the system since the constant C depended upon the mean size (414).

Equation (9) is consistent with his use of the mean diameter (d_{11}) :-

$$\eta_r = \frac{X}{d_{11}} + B \quad (409) \quad -(11)$$

$$\text{and } \eta_r = \frac{X}{d_{11}} + C \quad (407) \quad -(12)$$

Equation (10) was claimed (410) to have a highly significant statistical correlation with the data over all values of ϕ studied. In a more recent publication (414) data was compared from earlier authors using equation (9) and gave satisfactory correlations. This would appear to be an unwise general deduction since these authors used in the main dispersions of solid spheres of narrow size distribution. Sherman also relied upon the particle size distributions of emulsions and on viscosity measurements obtained by earlier workers. As previously noted much of the particle size data must be regarded as unreliable since it was obtained by microscope analysis. This comment also applies to Sherman's own data. Detailed analyses are given (407) where the minimum size is usually 0.95 μ , indicating that submicron particles are largely discounted although the maximum sizes quoted indicate that the size distributions are surprisingly

narrow. Sherman later proposed (415) that a reciprocal diameter be utilised in order to emphasize the numerical contribution made by the smaller particles.

Hence, although it must be concluded that Sherman's generalisations do not apply to the systems examined in the present investigation this may well be due to the inherent properties of these systems or to the lack of reliability of his data. It seems reasonable to conclude that his suggestion lacks utility since it is based upon a suspect empirical approach and does not take into account some of the other factors which, from this present work, also appear to affect the flow behaviour of emulsions. These factors are in addition to the condition of the disperse phase and include:-

- (i) aggregation and flocculation behaviour
- (ii) concentration and type of emulsifier
- (iii) disperse phase ratio.

As described in the earlier sections of this Chapter, there appear to be some inter-relationships between particle size and distribution of size and these three additional factors. For example, the larger the disperse phase ratio the greater is the interaction between particles and this also apparently results in an increase of mean particle size of the system, p.120. The concentration and type of emulsifier may well have a direct effect upon the condition of the disperse phase especially since some emulsifiers appear to be more efficient than others. Using the index of thixotropic hysteresis as a measure of the aggregation-flocculation behaviour the concentration and type of emulsifier have well-defined effects. In the proposed equation (8) the factor b , is essentially an indirect measure of the forces involved in the emulsion structure. The approach

is therefore a combination of the two schools of thought on the properties of emulsions. Whilst a great deal more work requires to be done in order to clarify and improve the approach it would at least appear promising. Better definition of the particle size distribution of an emulsion system is called for in this type of investigation since previous workers have tended either to discount the presence of particles below the limit of visibility of the microscope or, like Sherman, admitted their presence but been unable to measure them. Sherman suggested (414) that the small particles may exert considerable effects upon viscosity. From Fig 6.4 it will be seen that a slight increase in surface area can result in a very large increase of hysteresis or aggregation behaviour. This suggests that this type of behaviour may result where the particles are no longer large enough to resist Brownian motion, causing them to come together in aggregates or floccules. Since this is generally true for submicron particles it might, at least in part, account for the influence that such small particles can have upon flow behaviour. Mechanistic interpretations may also be invoked, such as the filling of voids between larger particles or forming 'bridges'.

Finally, it is concluded that the solid-liquid emulsions of the type investigated have complex non-Newtonian flow behaviour that is influenced by the following parameters:-

- (i) a derivative of the particle size distribution
- (ii) the concentration and type of the emulsifier
- (iii) the disperse phase ratio.

6.8 Summary

1. The accuracy and reproducibility of the particle size methods are satisfactory. 6.1
2. The effects produced by ultrasonic irradiation are variable and appear to be a function of the emulsifier. 6.2
3. The effect of emulsifier concentration on emulsion viscosity may be due to an effect upon the disperse phase particle size. 6.3
4. The particle size increases with the disperse phase ratio. 6.3
5. Thixotropic hysteresis is affected by the disperse phase ratio, the type and concentration of the emulsifier and the particle size of the disperse phase. 6.4
6. The density anomaly noted in Chapter Four is consistent with the presence of an interfacial film. 6.5
7. The thickness of the film appears to be similar in the presence of three of the emulsifiers employed. 6.5
8. From mass-transfer theory a simplified relation between the viscosity at infinite shear rates, the particle size and size distribution and a measure of the binding energy is derived. (Appendix Three) 6.6
9. The influence of particle size upon the flow behaviour of emulsions is discussed. 6.7

CHAPTER SEVEN

SUGGESTIONS FOR FUTURE INVESTIGATIONS

7.1 Electrostatic emulsification

A considerable experimental advantage would be obtained if emulsions of known particle size could be prepared, preferably with narrow size distributions. The only method with potential in this direction appears to be the electrostatic process discussed in 2.1.4. It has a number of disadvantages since, although drops of uniform size can be produced in an aerosol, it is difficult to disperse them in an aqueous phase to make an emulsion. Nevertheless, if this drawback could be overcome and the process became practicable on a large scale there might also be economic advantages, as claimed by Denier (86).

7.2 Further work on the centrifugal photosedimentometer

In its present form the instrument uses a white light source to detect particles sedimenting under centrifugal conditions. Although the extinction coefficient is claimed (205,206) to vary only between 1 and 2 as the particle diameter approaches the wave length of the incident radiation this assumption is by no means proven. The effect this has upon the apparent size distribution is even less certain. Thus, it would be anticipated that the number of submicron particles would be overestimated, but the magnitude of any correction which is required cannot at present be calculated with certainty. More work is therefore required. One method which suggests itself is to carry out a particle size analysis of a model system of independently measured particle size using

the centrifuge and preferably monochromatic light sources of different wave lengths as well as light of mixed wave lengths. The use of x-rays could be considered if the oil or disperse phase contained an opaque substance such as tetraethyl lead or osmium tetroxide, although it was noted that the latter is not soluble in the saturated type of oil used in the present investigation.

7.3 The effect of process scale upon the properties of emulsions

The present investigation was deliberately confined to the scale of operation on the laboratory bench where stirring is efficient and rates of cooling are rapid. However, it is only rarely possible to extrapolate results obtained under these conditions to the large scale processes used to manufacture these types of product. For example, mixing tends to be less efficient and it may take a ton batch of a pharmaceutical emulsion several hours to cool from the initial mixing temperature to ambient conditions. A knowledge of the effects such differences can produce on the particle size and distribution of size would probably enable bench scale operations to be scaled up more readily, with obvious economies in the development costs of a product.

7.4 The thixotropy and dilatancy of concentrated emulsion systems

The suggestion developed to Takano (456,457) that emulsion particles are connected by links which are broken or reformed at different rates suggested that it might be possible to consider the flow of concentrated (non-Newtonian) emulsions and suspensions in an analogous fashion to chemical reaction

rates. It should then be possible to determine the 'order of reaction' and consider 'flow' and 'structure' in terms of a 'half-life'. The remarks of Carver (54) and Van Wazer et al (431) concerning the time dependence of thixotropy hysteresis have already been noted. An initial investigation using insensitive methods of measurement indicated that the idea may have some substance but clearly a great deal more experimental work is required. The idea may prove to be too superficial on closer investigation but would seem to justify further examination at this stage.

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APPENDIX ONE

Publications arising from this investigation

1. Freshwater, D. C., Groves, M. J., & Scarlett, B., "The particle size of pharmaceutical emulsions", Proc. 25th Int. Congr. Pharm. Sci., Prague (1965), in press
2. Freshwater, D. C., Scarlett, B., & Groves, M. J., "The particle size of pharmaceutical emulsions", Am. Perfumer. & Cosm., 81, 43-45 (1966)
3. Groves, M. J., & Scarlett, B., "Polyhedral emulsion particles", Nature (Lond.), 207, 288-9 (1965)
4. Groves, M. J., "Some aggregation effects observed with an emulsion dispersed in saline containing cetrimide", J. Pharm. Pharmac., 18, 305-311 (1966)
5. Groves, M. J., Scarlett, B., & Freshwater, D. C., "The particle size of emulsions", Proc. Particle Size Analysis Conf., Loughborough (1966), 281-286
6. Groves, M. J., & Freshwater, D. C., "Polyhedral emulsion particles", J. Pharm. Pharmac., 19, 193-194 (1967)

APPENDIX TWO

A statistical comparison of repeated analyses on one sample using different methods

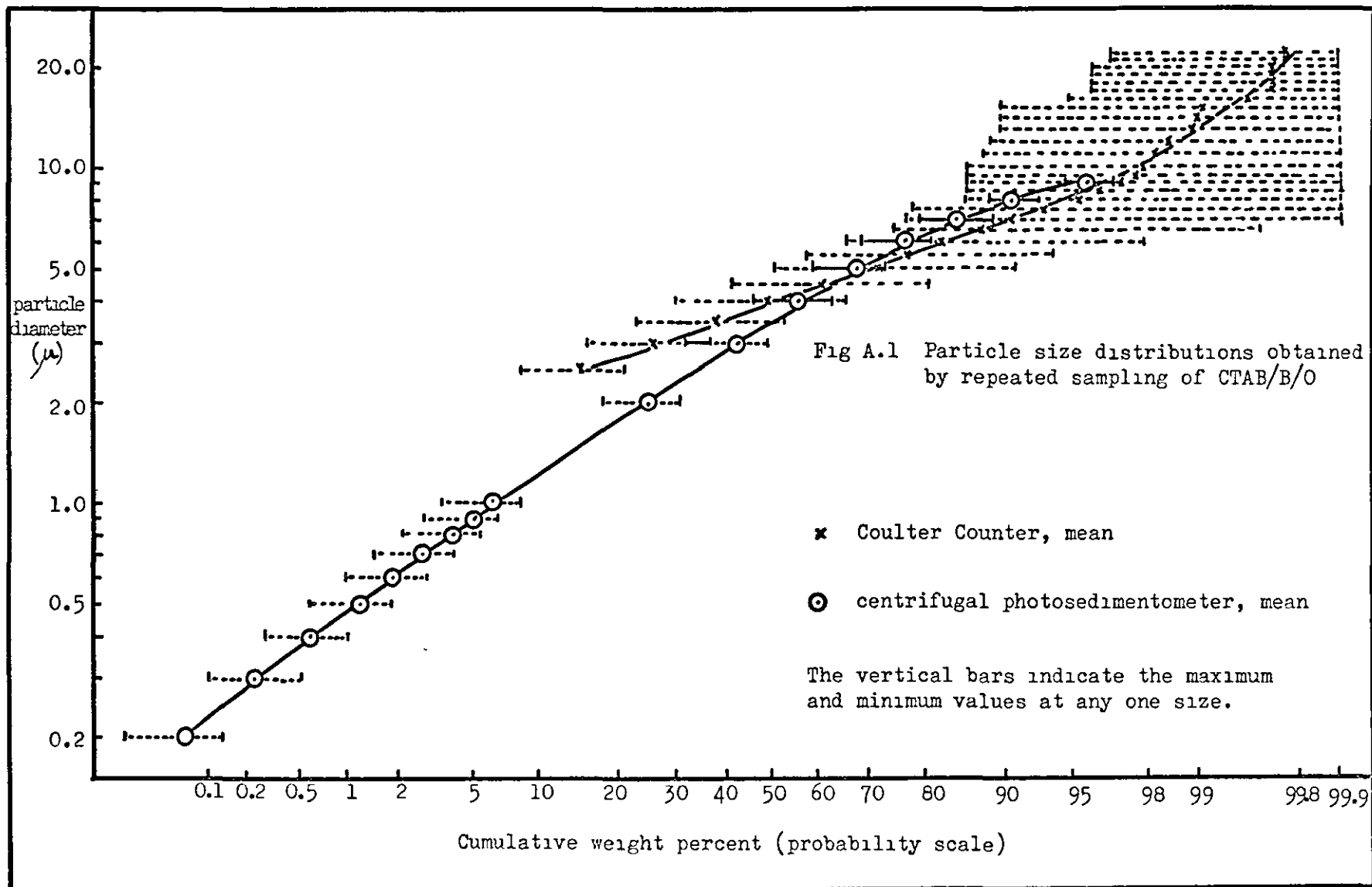
One emulsion system, CTAs/B/O, was selected at random and repeatedly sized using the standard techniques for the Coulter Counter and the centrifugal photosedimentometer.

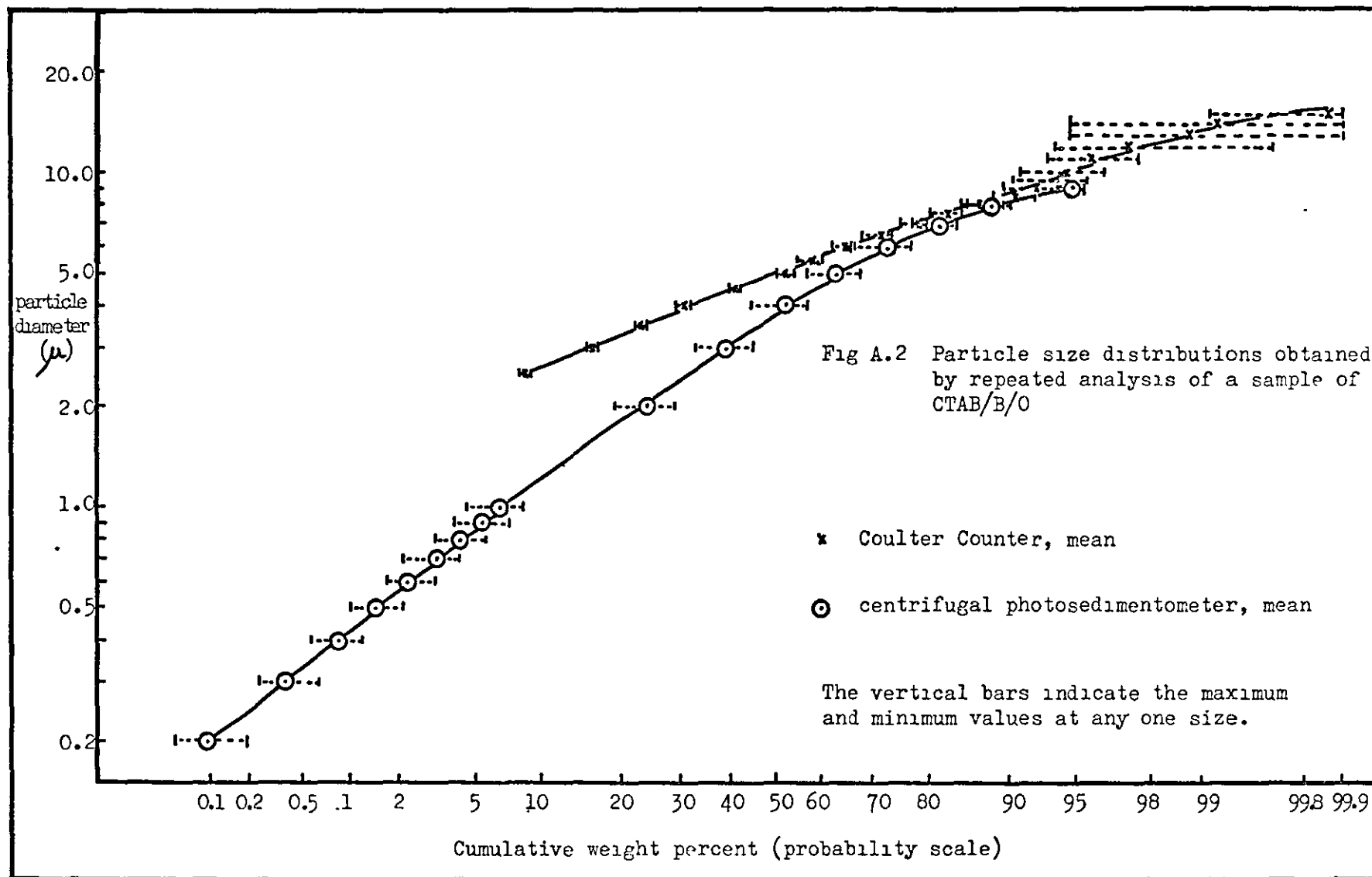
A.2 1.1

Coulter Counter

Results are shown in Fig A.1 and Fig A.2, plotted as a mean with the scatter of experimental data.

Upper limit of size range (μ)	Repeated sampling		Repeated analysis of same sample	
	Mean % weight cumulative (10 runs)	Standard error of mean	Mean % weight cumulative (12 runs)	Standard error of mean
22.0	99.74	0.26		
21.0	99.74	0.26		
20.0	99.67	0.33		
19.0	99.67	0.33		
18.0	99.67	0.33		
17.0	99.67	0.33		
16.0	99.57	0.43		
15.0	99.07	0.86	99.87	0.07
14.0	99.01	0.86	99.20	0.50
13.0	98.94	0.85	98.83	0.48
12.0	98.52	0.97	97.34	0.48
11.0	98.21	1.02	95.82	0.35
10.0	97.86	1.15	94.47	0.37
9.5	97.64	1.18	94.02	0.40
9.0	97.09	1.23	92.48	0.38
8.5	96.44	1.35	90.59	0.43
8.0	95.74	1.49	87.03	0.45
7.5	93.14	2.23	83.10	0.39
7.0	90.65	2.57	78.51	0.39
6.5	87.62	3.13	72.06	0.44
6.0	82.88	3.72	65.44	0.35
5.5	77.30	4.16	58.15	0.44
5.0	72.49	4.44	52.11	0.41
4.5	61.59	4.30	41.45	0.22
4.0	48.97	4.00	31.14	0.26
3.5	38.31	3.40	23.48	0.18
3.0	26.68	2.46	15.82	0.13
2.5	14.88	1.44	8.62	0.06





A.2 1.2

Centrifugal photosedimentometer method

Results are also shown in Fig A.1 and A.2, plotted as a mean, with the scatter of the experimental data.

Upper limit of size range (μ)	Repeated sampling		Repeated analysis of same sample	
	Mean % weight cumulative (10 runs)	Standard error of mean	Mean % weight cumulative (12 runs)	Standard error of mean
10.0	95.87	0.27	94.84	0.09
9.0	90.64	0.53	88.37	0.41
8.0	84.89	0.85	81.68	0.65
7.0	77.35	1.17	73.02	0.97
6.0	68.24	1.43	63.37	1.02
5.0	56.15	1.62	52.27	1.14
4.0	42.56	1.57	39.18	1.05
3.0	25.79	1.13	24.45	0.87
2.0	6.41	0.50	6.56	0.33
1.0	5.07	0.42	5.39	0.29
0.9	3.89	0.36	4.18	0.24
0.8	2.80	0.27	3.09	0.17
0.7	1.91	0.20	2.20	0.13
0.6	1.19	0.14	1.45	0.09
0.5	0.59	0.09	0.84	0.06
0.4	0.24	0.04	0.38	0.12
0.3	0.05	0.01	0.10	0.04

A.2 2.1

A comparison of the results from the two methods

The two methods gave results which overlapped between approximately 1 and 10 μ , divergence being marked at the limits. Accordingly, the results summarised above were recalculated to yield the weight per micron interval.

Repeated sampling, Coulter Counter

Upper limit (μ)	Mean weight % within interval	Variance	Standard error	Standard error as % of mean
10.0	1.83	1.57	0.56	30.58
9.0	3.43	3.27	0.74	21.58
8.0	5.68	9.69	0.99	17.35
7.0	7.66	7.95	1.22	15.95
6.0	10.39	8.37	0.84	8.04
5.0	23.51	5.62	0.68	2.95
4.0	22.38	26.47	1.54	6.88
3.0	26.68	74.72	2.50	9.35

mean 14.09

Repeated sampling, centrifugal photosedimentometer

Upper limit (μ)	Mean weight (%) within interval	Variance	Standard error	Standard error as % of mean	Variance ratio	Test of signifi- cance
10.0	5.39	0.70	0.24	4.48	2.24	NS
9.0	5.75	2.14	0.42	7.36	1.53	NS
8.0	7.54	1.80	0.39	5.14	5.35	NS
7.0	9.02	1.62	0.37	4.06	4.91	NS
6.0	12.19	0.54	0.21	1.74	15.50	S
5.0	13.69	0.80	0.26	1.89	7.25	S
4.0	16.77	1.39	0.34	2.03	19.75	S
3.0	19.68	10.87	0.95	4.84	6.88	S

mean = 3.94

NS indicates that the means of the result from the two methods are derived from the same population ($P = 0.01$) and the data is comparable over the range 6.0-10.0 μ . S indicates that the variance ratio is in excess of the tabulated value and the data is not therefore derived from the same population.

Repeated analysis of the same sample, Coulter Counter

Upper limit (μ)	Mean weight % within interval	Variance	Standard error	Standard error as % of mean
10.0	1.90	0.93	0.28	1.46
9.0	5.39	1.19	0.32	5.59
8.0	8.83	0.72	0.24	2.76
7.0	13.07	0.69	0.24	1.84
6.0	13.33	1.56	0.36	2.71
5.0	20.98	0.60	0.22	1.08
4.0	15.41	0.48	0.20	1.30
3.0	15.82	0.20	0.13	0.82

mean = 2.19

Repeated analysis of the same sample, centrifugal photosedimentometer

Upper limit (μ)	Mean weight (%) within interval	Variance	Standard error	Standard error as % of mean	Variance ratio	Test of significance
10.0	6.49	1.92	0.40	6.16	2.07	NS
9.0	6.60	1.48	0.35	5.31	1.24	NS
8.0	8.69	1.87	0.40	4.54	2.60	NS
7.0	9.58	0.97	0.29	2.97	1.41	NS
6.0	11.18	0.67	0.24	2.11	2.35	NS
5.0	13.09	0.85	0.27	2.03	1.42	NS
4.0	14.13	1.18	0.31	2.13	2.46	NS
3.0	17.89	4.07	0.58	3.25	20.35	S

mean 3.56

NS indicates that the means are derived from the same population ($P = 0.05$) and the data is comparable over the range 3.0-10.0 μ .

4.2 2.2

Correlation of results from the two methods

Since sampling error was superimposed on the results of analysis of repeated samples the results from the repeated analyses of the same sample were compared for correlation over the range 3.0-10.0 μ . The ratio of the means was used to normalise the data, superimposing the Coulter results upon those from the centrifuge.

Upper limit (μ)	mean weight (%) within interval		
	centrifuge	Coulter	normalised Coulter
10.0	6.49	1.90	1.69
9.0	6.60	5.39	4.81
8.0	8.69	8.83	7.88
7.0	9.58	13.07	11.66
6.0	11.18	13.33	11.88
5.0	13.09	20.98	18.73
4.0	14.73	15.41	13.74

mean 10.05 11.27 ratio centrifuge/Coulter = 0.8917

Let centrifuge results = X, normalised Coulter results = Y

$$\bar{X} = 70.36, \bar{X}^2 = 766.286, \frac{(\bar{X})^2}{n} = 707.2185$$

$$\bar{Y} = 70.39, \bar{Y}^2 = 904.777, \frac{(\bar{Y})^2}{n} = 707.8217$$

$$\bar{XY} = 696.1292, \frac{(\bar{X})(\bar{Y})}{n} = 707.5201$$

$$s_x^2 = 9.8446 \quad s_x = 3.0414$$

$$s_y^2 = 32.8259 \quad s_y = 5.72$$

$$c = -1.8984 \quad r = -0.0109, \text{ for 5 d.f. } <P = 0.1$$

Hence there is good correlation between results from the two methods and direct comparison is justified.

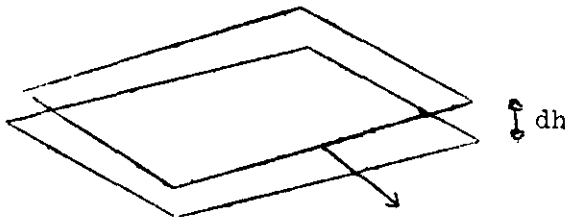
APPENDIX THREE: THE DERIVATION OF A RELATIONSHIP BETWEEN PARTICLE SIZE AND VISCOSITY.

A relationship may be arrived at by assuming that, at infinite shear rates, the flow of a packed bed of emulsion particles can be treated as being analogous to a mass transfer process.

We may assume the following:

- (1) That the non-Newtonian component of viscosity is due to the breaking of particle contacts.
- (2) That only one point contact need be broken in order to move one particle.
- (3) That a particle can move a distance $x + x_{\text{reach}}$ without breaking a contact, x being the particle diameter.
- (4) That all particles have the same mean velocity which is independent of size.
- (5) That the breaking strength of the contact point is also independent of the particle size.

Consider two unit areas separated by a small distance dh such that $dh \ll x_{\text{min}}$



Let the top area move relative to the lower one.

The volume, V , of particles which flow relative to the lower plane

$$V = (1 - \mathcal{E}) \cdot dh \quad \quad \quad -(1)$$

$$(\mathcal{E}) = \text{voidage} = (1 - \phi_{\text{volume}})$$

Suppose the size distribution by number of the particles is $f(x)$. This is normalised such that

$$\int_0^{\infty} f(x) \cdot \pi x^3 \cdot dx = (1 - \xi) \quad -(2)$$

$\int_0^{\infty} f(x) \cdot dx$ is now the number of particles per unit volume of the bed.

The number of particles in the upper layer which must move unit distance = n

$$= V \frac{\int_0^{\infty} f(x) \cdot dx}{\int_0^{\infty} f(x) \cdot \pi x^3 \cdot dx} \quad -(3)$$

where the number of particles of size x is $n(x)$

$$n(x) = \frac{f(x) \cdot n}{\int_0^{\infty} f(x) \cdot dx} \quad -(4)$$

From Assumption (3), the number of contact points broken for size x = $A(x)$

$$= n(x) \cdot \frac{1}{x + \frac{\int_0^{\infty} f(x) \cdot x \cdot dx}{\int_0^{\infty} f(x) \cdot dx}} \quad -(5)$$

The total number of broken contact points

$$= \int_0^{\infty} A(x) \cdot dx = A \quad -(6)$$

Combining equations (5) and (6)

$$A = \int_0^{\infty} \frac{n(x) \cdot dx}{\left(x + \frac{X_1}{X}\right)}$$

where $X = \int_0^{\infty} f(x) \cdot dx$
 $X_1 = \text{first moment} = \int_0^{\infty} f(x) \cdot x \cdot dx \quad \text{etc.}$

Substituting in equation (6)

$$A = \int_0^{\infty} \frac{n \cdot f(x) \cdot dx}{X \left(x + \frac{X_1}{X}\right)} = \int_0^{\infty} \frac{n \cdot f(x) \cdot dx}{(Xx + X_1)}$$

Substituting in equation (3)

$$A = \frac{6X}{\pi X_3} \int \frac{V \cdot f(x) \cdot dx}{(Xx + X_1)}$$

Substituting in equation (1)

$$A = (1 - \xi) \cdot dh \cdot \frac{6X}{\pi X_3} \int \frac{f(x) \cdot dx}{(Xx + X_1)}$$

Suppose each point contact has a binding energy b .

The energy supplied = Ab

This is supplied by the force dF moving unit distance

$$\therefore dF = Ab$$

$$\therefore \frac{dF}{dh} = (1 - \xi) \cdot b \cdot \frac{6X}{\pi X_3} \int \frac{f(x) \cdot dx}{(Xx + X_1)}$$

The shear force necessary to produce unit velocity gradient

$$F = \int_0^1 \frac{dF}{dh} \cdot dh$$

$$\therefore \eta_{\infty} = (1 - \xi) \cdot b \cdot \frac{6X}{\pi X_3} \int \frac{f(x) \cdot dx}{(Xx + X_1)}$$

From equation (2) we can write

$$\eta_{\infty} = b \cdot X \cdot \int \frac{f(x) \cdot dx}{(Xx + X_1)} \quad -(7)$$

The size distributions (Table 3.3) are presented on a weight basis.

The conversion to a number distribution and calculation of moments

from a logarithmico-probability relationship are described by Herdan

(172, p. 83).

x_g = geometric mean of number distribution, x'_g = mean weight

$$\mu_1 = \frac{\sum x_i n_i}{N} = \exp (\ln x_g + 0.5 \ln^2 \sigma_g) = X_1$$

$$\mu_2 = \sum \frac{x_i^2 n_i}{N} = \exp (2 \ln x_g + 2 \ln^2 \sigma_g) = X_2$$

$$\mu_3 = \sum \frac{x_i^3 n_i}{N} = \exp (3 \ln x_g + 4.5 \ln^2 \sigma_g) = X_3$$

x_g is converted to x'_g from the arithmetic mean of weight distribution x_w

$$\ln x_w = \frac{\sum x_i^4 n_i}{\sum x_i^3 n_i} = (\ln x'_g + 0.5 \ln^2 \sigma_g)$$

$$\therefore \ln x_g = (\ln x'_g - 3 \ln^2 \sigma_g)$$

$$\therefore X_1 = \exp (\ln x'_g - 2.5 \ln^2 \sigma_g)$$

$$X_2 = \exp (2 \ln x'_g - 4 \ln^2 \sigma_g)$$

$$X_3 = \exp (3 \ln x'_g - 4.5 \ln^2 \sigma_g)$$

The normalisation factor in equation (2) is given by

$$\frac{6}{\pi} \frac{(1 - \varepsilon)}{X_3} = \frac{6 \phi}{\pi X_3}$$

A computer programme was written to calculate the integral of equation (7), integrating over the limits of $\ln x_g \pm 2.576 \ln \sigma_g$ ($P = 0.99$) using Simpson's Rule.

APPENDIX FOUR: FLOW CURVES

Upcurves broken lines; Downcurves continuous

A.3	A	CTAB/A/LS	(Table 4.1)
	B	CTAB/A/60	
	C	CEM/A/O	
	D	CEM/A/LS	
	E	CPC/B/O	
	F	CPC/B/15	
A.4	A	CTAB/B/60	
	B	CTAB/D/LS	
	C	CTAB/B/LS	
	D	CTAB/B/O	
	E	CTAB/B/15	
	F	CTAB/B/5	
A.5	G	CTAB/B/10	
	A	CTAB/L/LS	
	B	CTAB/L/L/LS	
	C	CTAB/H/L/LS	
	D	CTAB/J/LS	
	E	CPC/A/LS	
	F	CTAB/M/LS	
	G	CTAB/O/LS	
	H	CTAB/N/LS	
	I	CTAB/P/LS	
A.6	J	CTAB/C/L/LS	
	A	CTAB/J/L/LS	
A.7	B	CPC/C/LS	
		CTAB/I/LS	
A.8	A	CEM/A/60	
	B	CPC/B/25	
	C	CPC/B/20	
	D	CEM/A/120	
A.9	A	CTAB/E/LS	
	B	CTAB/G/LS	
	C	BENZ/A/LS	
	D	CTAB/C/LS	
	E	CTAB/H/LS	
	F	CTAB/K/LS	
	G	CTAB/B/45	
	H	CPC/D/LS	
A.10	A	CPC/B/60	
	B	3FC/B/30	
	C	CPC/B/120	
	D	CPC/B/45	

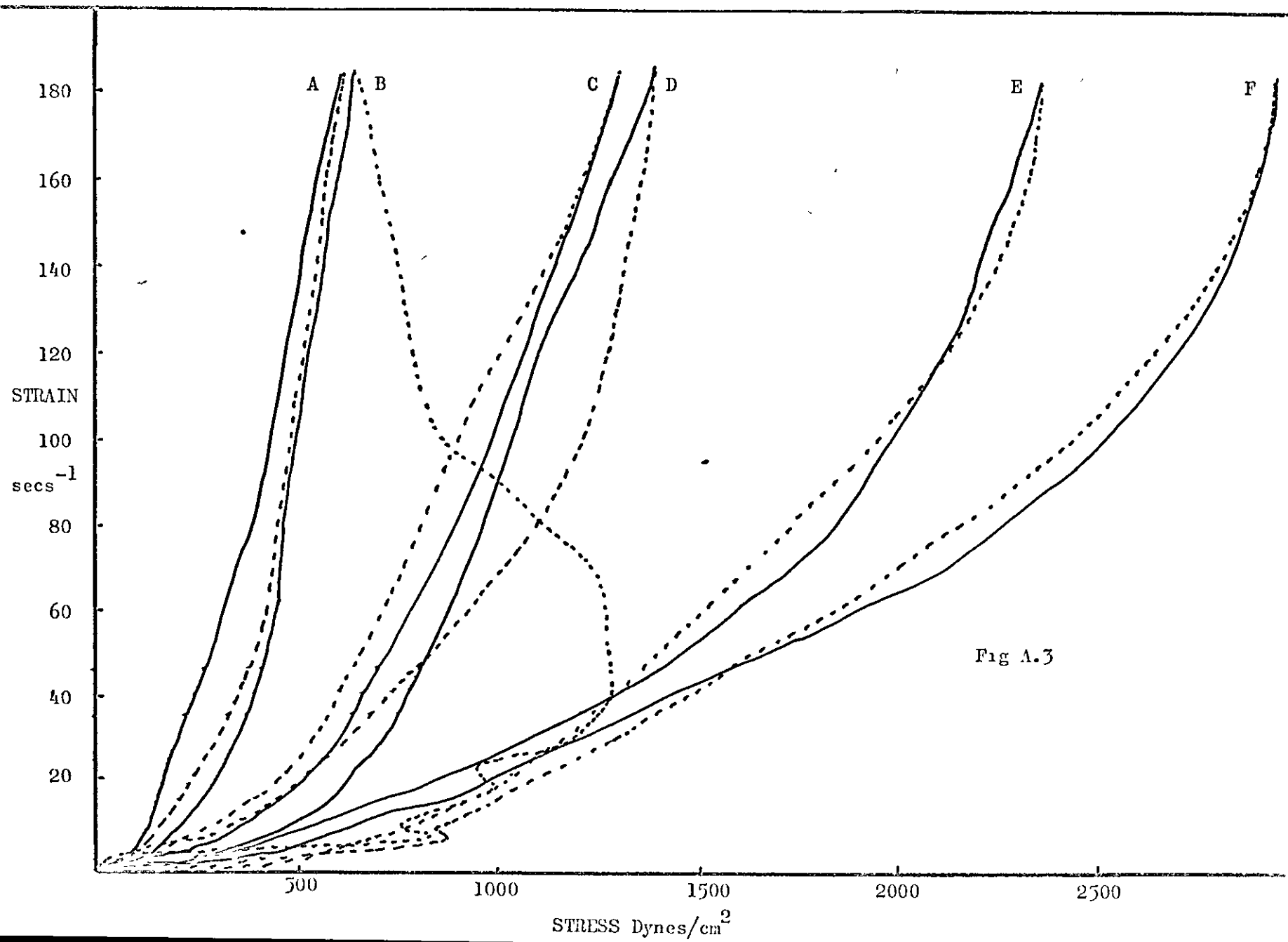
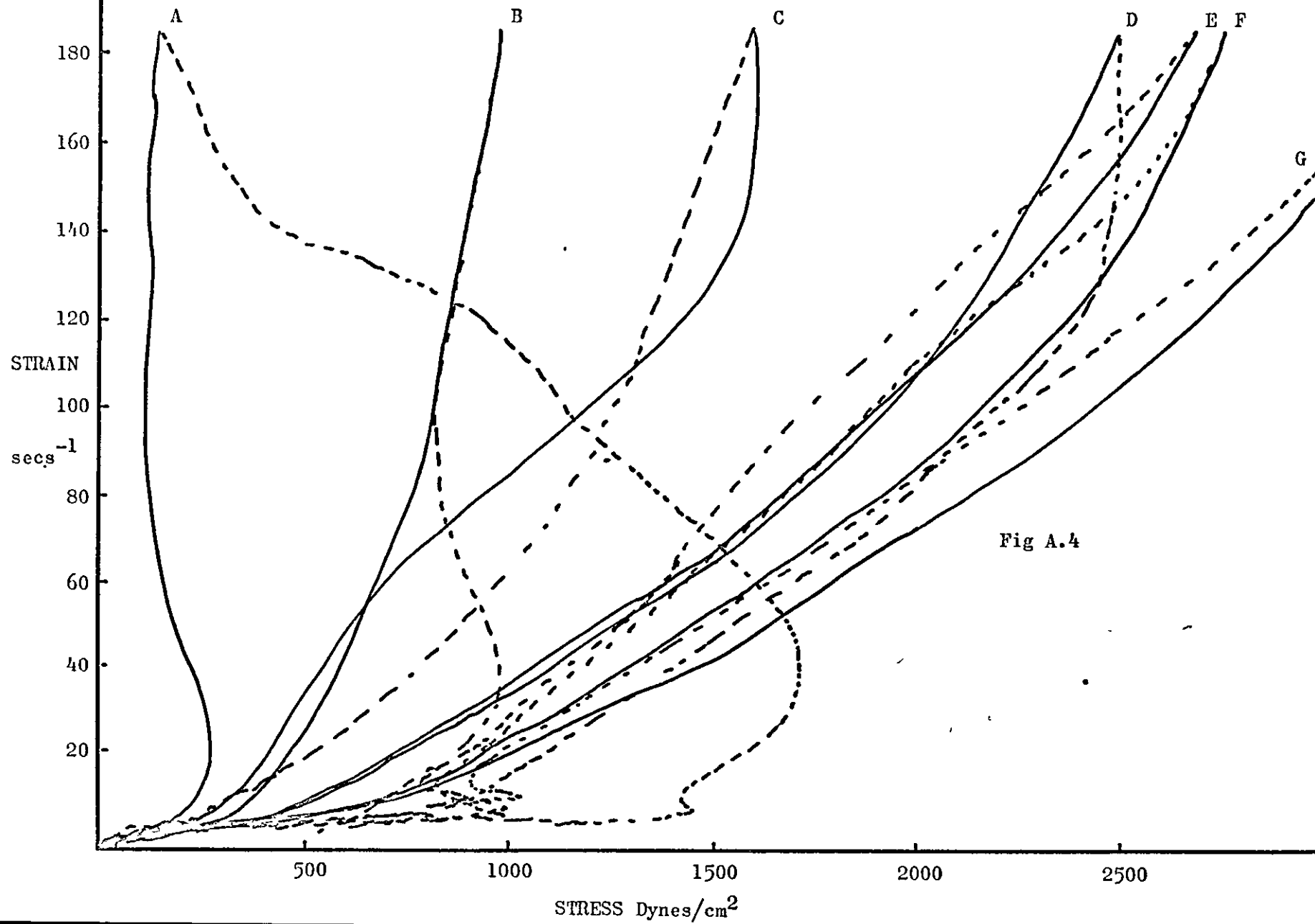
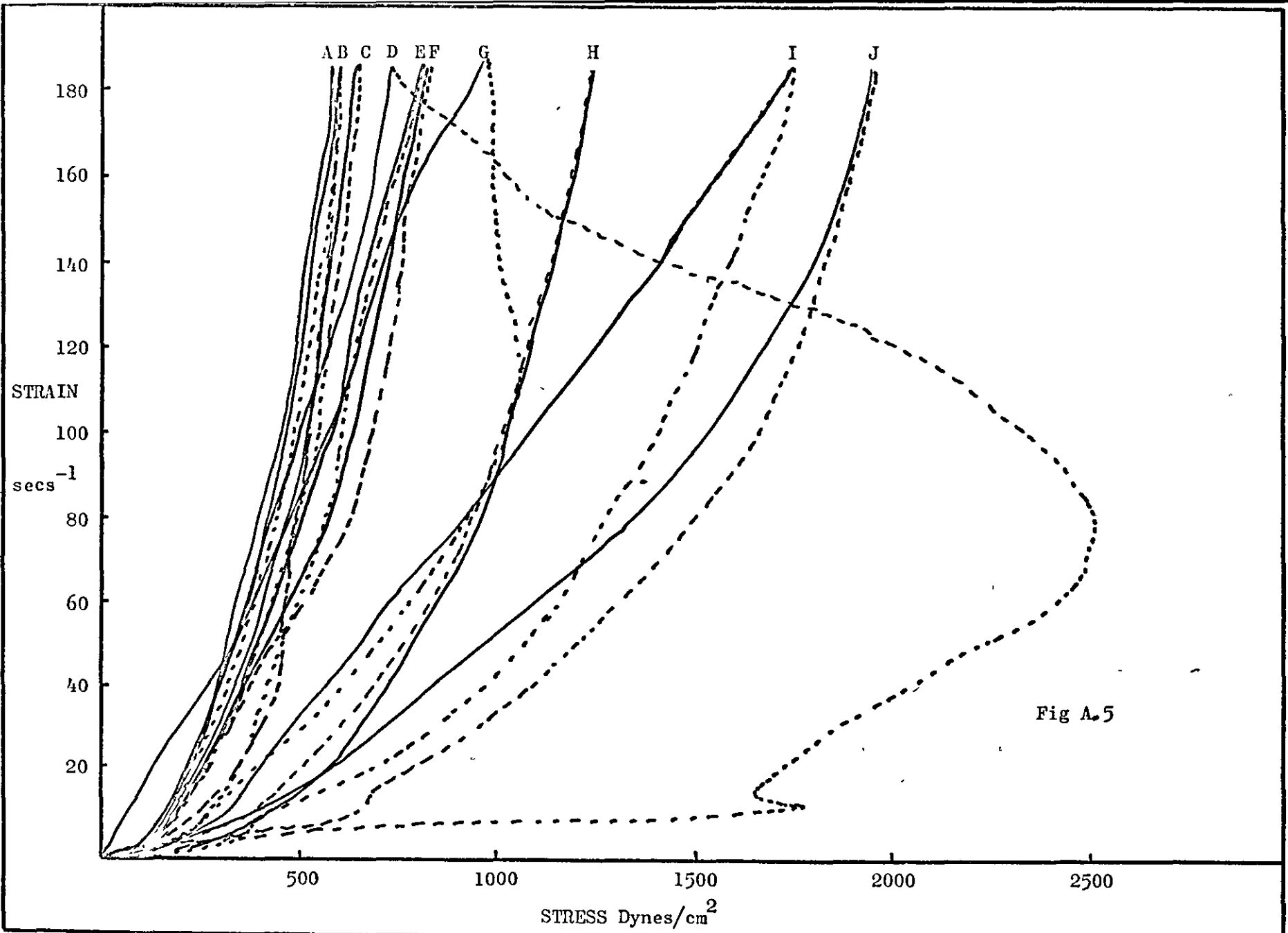
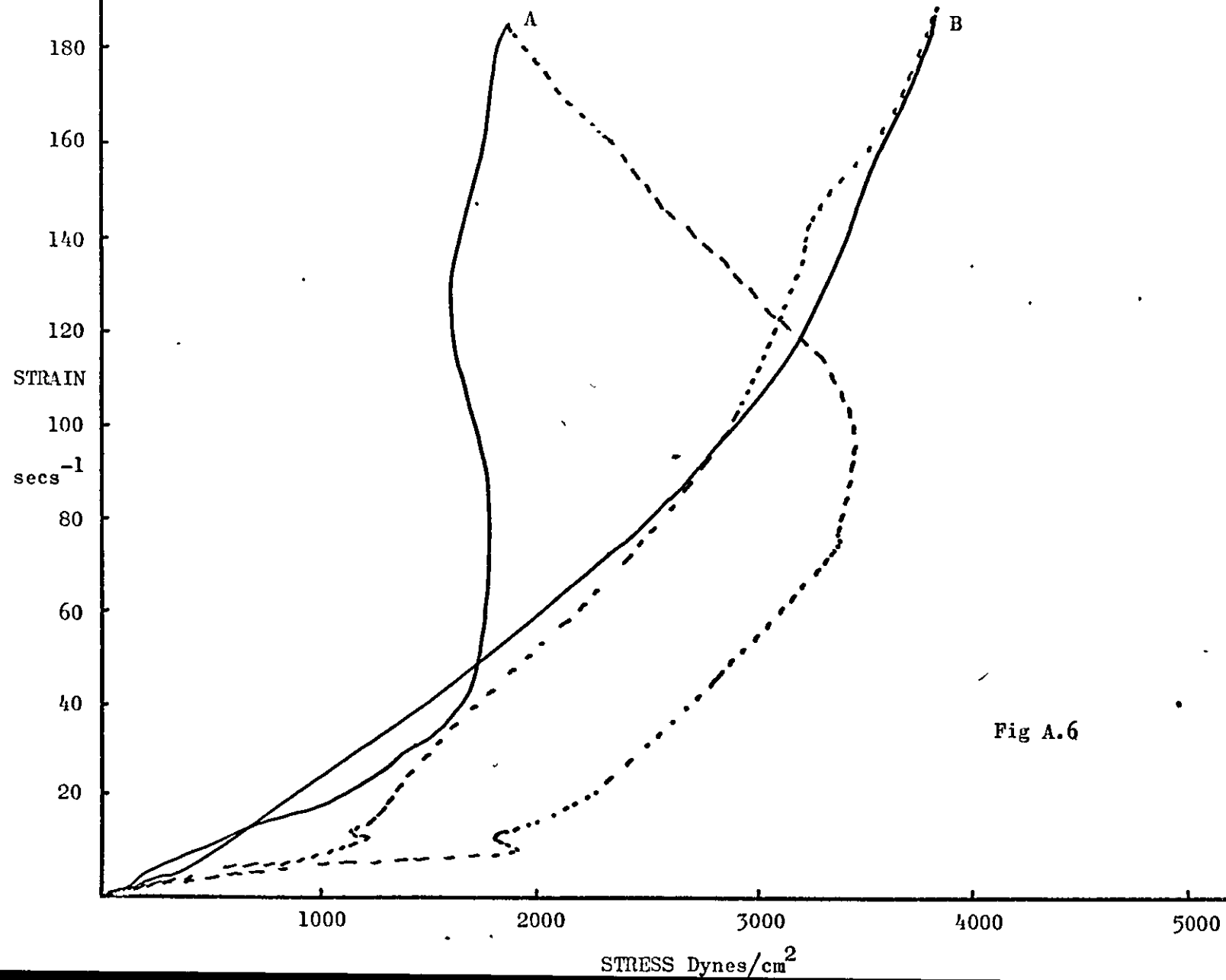


Fig A.3







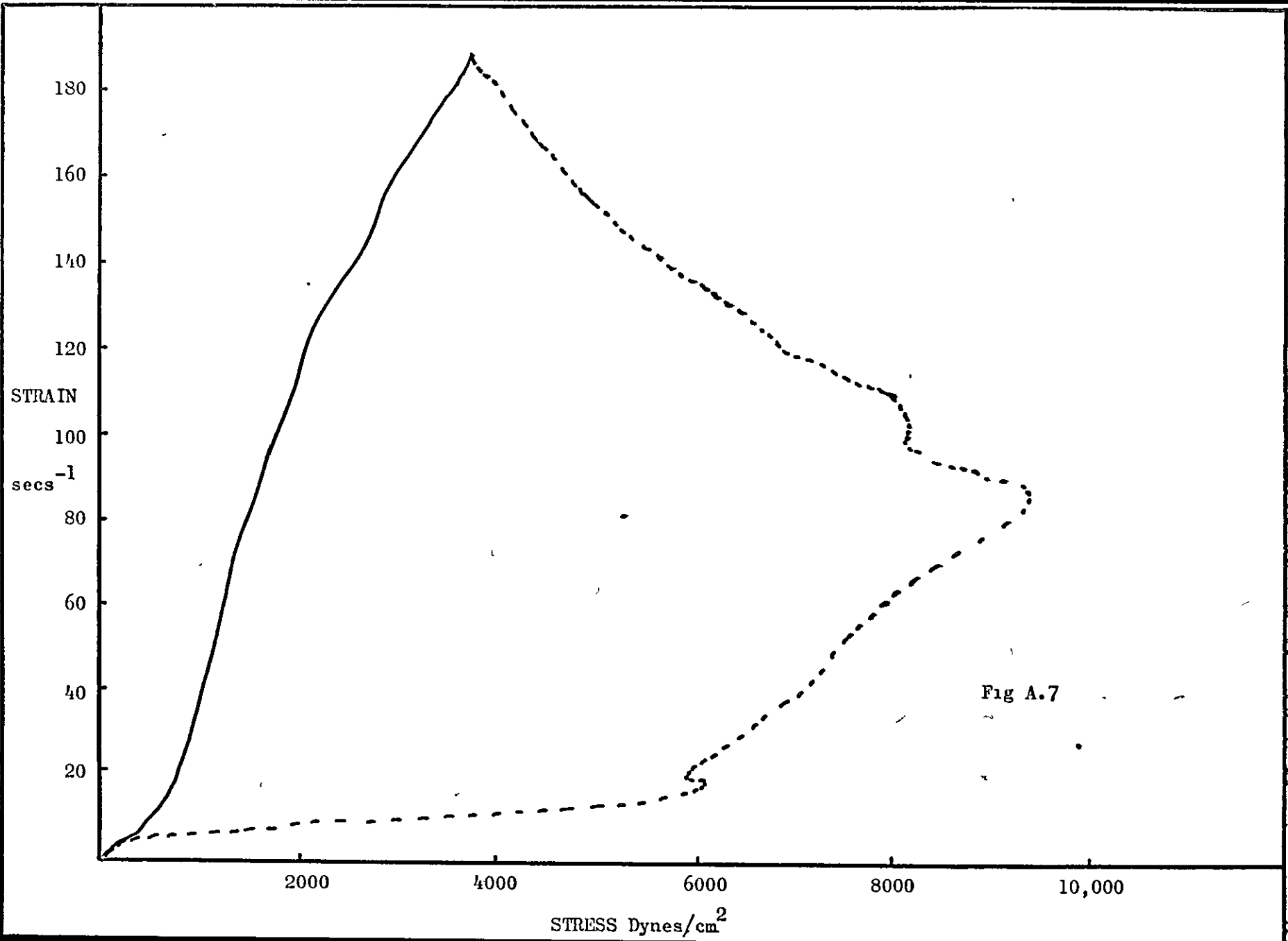
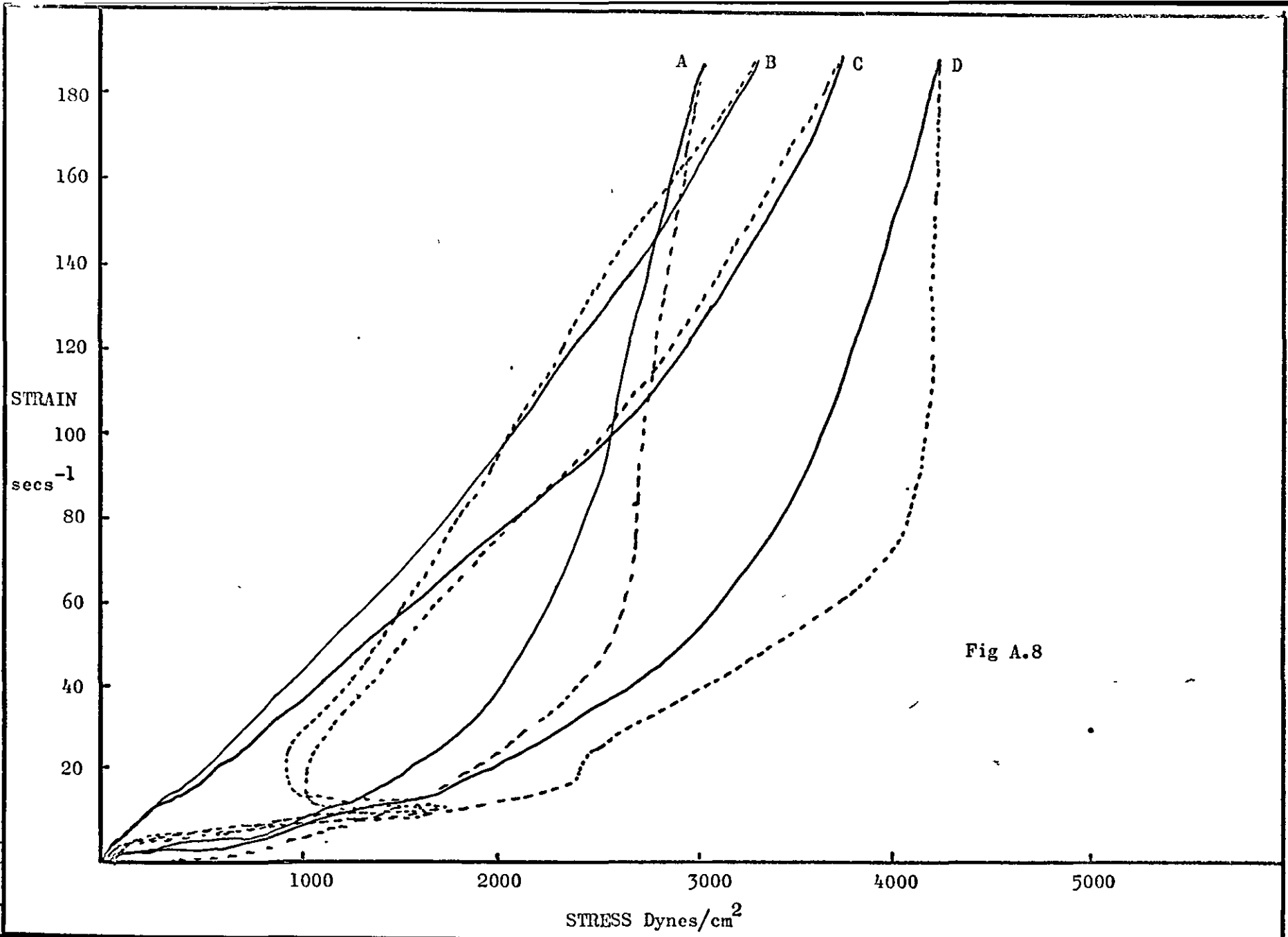


Fig A.7



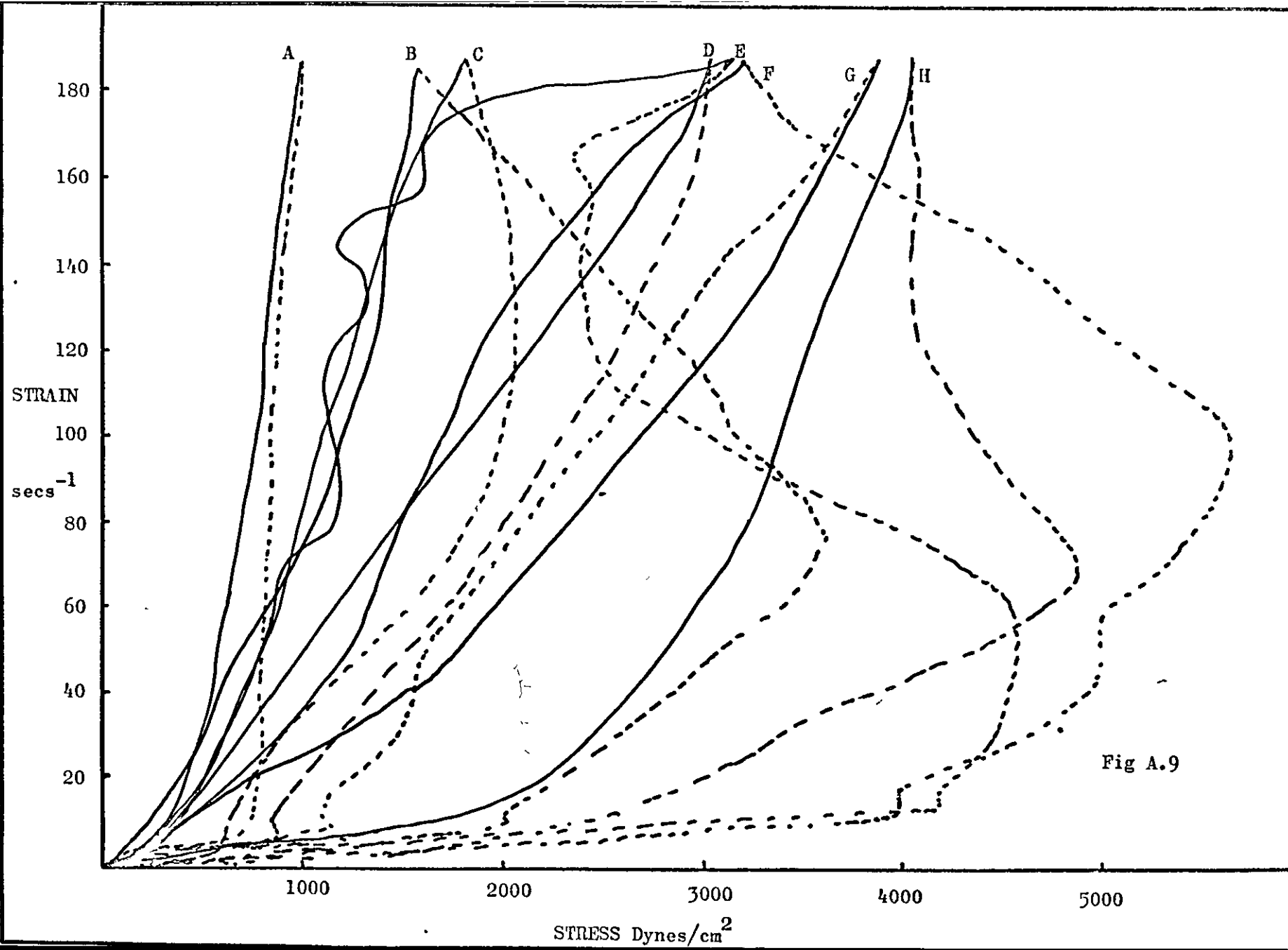


Fig A.9

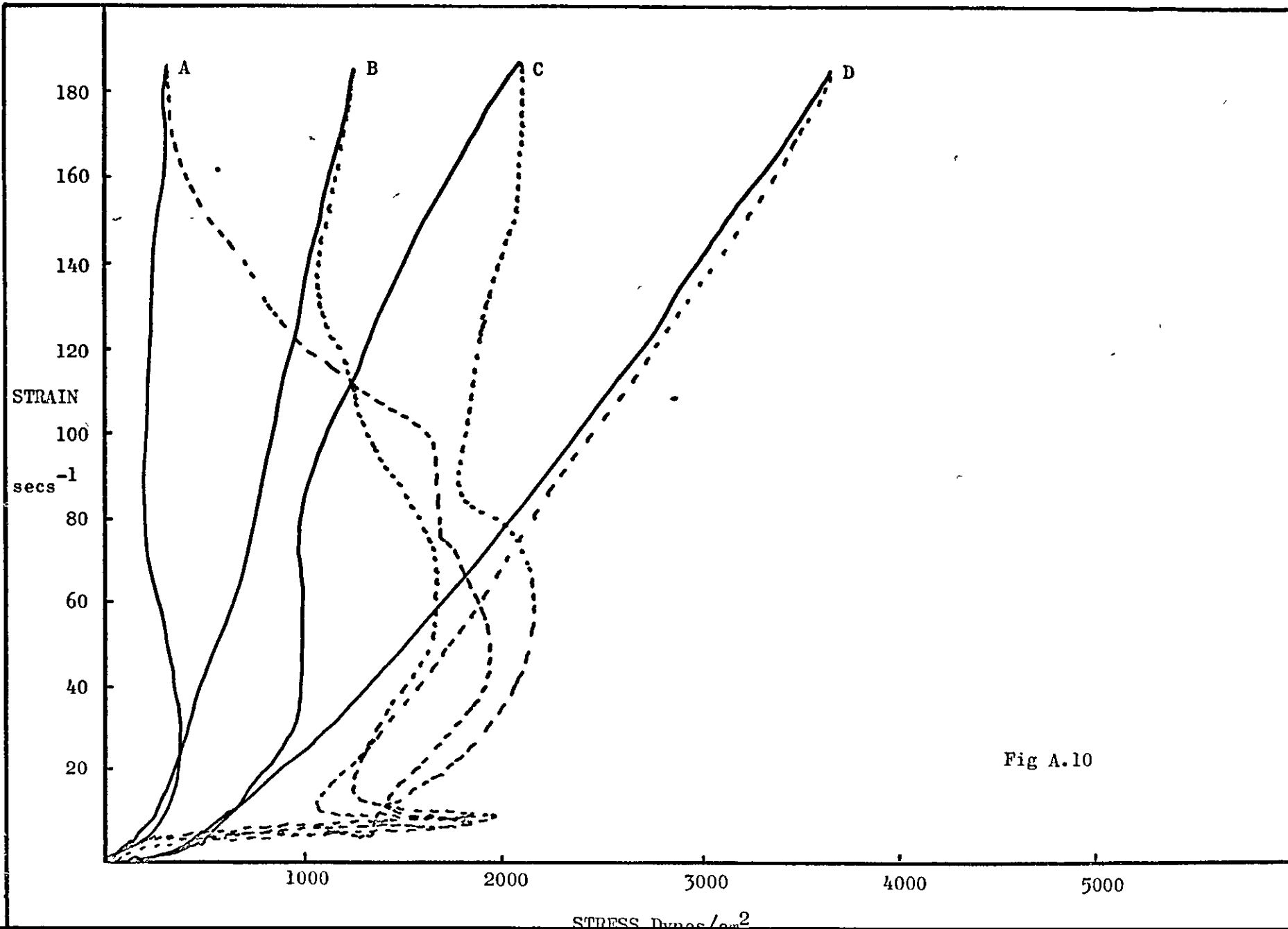


Fig A.10

