

# PARTICLE SIZE AND ANISOMETRY IN DILUTE DISPERSIONS OF LITHIUM STEARATE IN HYDROCARBONS

BY M. J. VOLD,<sup>a</sup> D. L. BHATTACHARYA,<sup>b</sup> AND D. V. RATHNAMMA<sup>c</sup>

(*Indian Institute of Science, Bangalore-3*)

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## ABSTRACT

A technique has been developed for the preparation of dispersions of lithium stearate suitable for consideration as assemblies of rigid lath-shaped particles. The particles tend toward a length/width ratio of 10 and a thickness of only 80–100 Å regardless of length or width, up to lengths of the order of one micron. Change in particle size or shape by recrystallization is negligibly slow in benzene and in *n*-heptane at room temperatures. This is a consequence of the low solubility which has been estimated electron microscopically as of the order of  $10^{-8}$  moles per litre in benzene at 30° C. The particles show preferential end-to-end contacting in the formation of flocs and yield a sediment whose volume is much larger than can be ascribed to random packing of primary particles.

The electron microscope studies here reported are part of a program intended to help to unravel the several geometrical, energetic, and kinetic factors involved in the rheological behaviour of lubricating greases. A further fundamental objective is to contribute to the development of an experimental means of studying particle interactions based on observations of sedimentation or subsidence phenomena.

Bondi and colleagues<sup>1</sup> were the first to point out the relationship between particle anisometry (length to width ratio of fibres) and grease consistency. Subsequently Moore and Cravath<sup>2</sup> developed a semi-quantitative relation between consistency and working time based on the hypothesis that working ruptured the fibres without shredding them. Leet<sup>3</sup> found a linear relation between consistency and length/width ratio for many greases. However Hotten<sup>4</sup> concluded that particle size was a more important factor than particle shape in determining grease consistency. R. D. Vold<sup>5</sup> and colleagues studied the role of particle shape and orientation. Renshaw<sup>6</sup> also showed that both size and shape and probably also particle orientation are important in one and the same grease and also pointed out clearly that the shape and size of aggregates of primary particles could be as important as the shapes of the primary particles themselves.

<sup>a</sup> Permanent Address: Department of Chemistry, University of Southern California, Los Angeles 7, Calif., U.S.A.

<sup>b</sup> Department of Metallurgy.

<sup>c</sup> Department of General Chemistry.

Concurrently with this work R. D. Vold, Coffey and Baker<sup>7</sup> showed that in calcium stearate greases the primary particles formed three-dimensional network structures whose porosity was directly related to grease consistency. The network structure was confirmed, for sodium soap greases, by Peterson and Bondi<sup>8</sup> by means of stereo-electron micrographs of a soap aerogel prepared from a grease directly upon the specimen holder of the microscope. M. J. Vold<sup>9</sup> suggested trying to account for the very large sedimentation volumes of lithium stearate suspensions prepared by dilution of greases in light hydrocarbons on the basis of network formation.

These two sets of observations lead to the hypothesis that the principal role of particle size and shape is in helping to fix the number of interparticle contacts that occur.

No special cognizance seems to have been taken in previous work of the fact which is apparent in many electron micrographs, particularly of lithium and some sodium greases, that the fibres have a lath-like or ribbon structure. Since any attempt to calculate the density of contact points will have to take this fact into account, it seemed desirable as a first objective in this study to measure not only length/width but also length/width/thickness ratios of the particles under study.

In view of the fact that sedimentation experiments often have a duration of many weeks, while Robert and Grenon<sup>11</sup> observed extensive modification of shape in sodium stearate fibres in hydrocarbons over a few hours, a second object was to investigate the dimensional stability in dispersions of lithium stearate. Although no reliable measurements exist for either one, the solubility of both sodium and lithium stearate in hydrocarbons at room temperature is known to be low. It proved possible to make a rough estimate of the solubility of lithium stearate in benzene at 30° C. of *ca*  $10^{-8}$  moles/litre which is low enough to account for the observed absence of appreciable recrystallization.

#### EXPERIMENTAL PART

*Materials.*—Lithium stearate was prepared by neutralizing a solution of stearic acid in aqueous ethanol with Riedel-Haen lithium hydroxide and drying the washed precipitate to constant weight at 105° C. Most of the experimental work was done using a technical triple pressed acid having an iodine number of 6 and an equivalent weight of 290. The high equivalent weight was shown to be due to alcohol soluble unsaponifiable matter, the recovered acid having an equivalent weight of 285. Benzene was purified by repeated treatment with concentrated sulphuric acid, alkali washing and distillation. *n*-Heptane (May & Baker Limited, England) and medicinal white oil were used without purification.

*Preparation of Suspensions.*—Pastes of 2 grams of dry lithium stearate and 18 grams medicinal white oil were heated to 230° C. (in sealed tubes) and maintained at this temperature, with occasional agitation, for 6 hours. The clear solution was cooled quickly by plunging the tube into an ice-salt mixture at -15° C. The resulting grease was diluted with 180 ml. of the desired hydrocarbon solvent,

dropwise at first, accompanied by vigorous stirring, and then more rapidly. After it had been shown that no large comminution of particles resulted, the reduction of any residual grease lumps was accomplished by 10 minutes agitation in a Waring Blendor running at about 10,000 r.p.m. The one per cent. dispersion was freed of paraffin oil by repeated centrifugation, decantation, and re-dispersion of the sediment in fresh solvent. It was then analysed (by evaporation of solvent from a weighed portion). Other dispersions were prepared by diluting this stock.

*Electron Microscopy.*—For measurements of particle size, drops of 0.1% dispersion were placed on Formvar covered specimen mounts, which (for the Philips Metalix microscope are metal strips containing a single slit roughly  $3 \times 0.1$  mm. and first examined directly without shadowing. The deposited crystallites are so thin that no evidence of melting under the beam was generally observed, despite the low melting point ( $224^{\circ}$  C.). Melting was conspicuous for the more absorbing copper stearate examined (in other work) under the same conditions. After surveying the entire specimen, three areas were selected for photographs on the basis of obtaining the largest number of clearly resolvable particles, and a comparison photograph made of Dow polystyrene latex No. 580-G. (sphere diameter 2590 Å).<sup>11</sup> At least two specimens were examined for each suspension. The dimensions of length and width were determined by measurements either from the projected negative or enlarged prints. The third dimension was obtained by measuring similarly the lengths of shadows, after deposition of a 10 Å film of Pt-Ir alloy at a 1:5 angle. For length and width, statistically valid averages could readily be achieved by counts of a few hundreds of particles. The shadows were too short for very precise measurement. However an occasional dust particle (which would presumably be isometric) was found with a shadow roughly five times its diameter so that taking the thickness as 1/5 the approximate shadow length is certainly correct as to order of magnitude.

The estimate of solubility is less certain. Loeffler and König<sup>12</sup> have developed a procedure for determining the concentration of a solution electronmicroscopically by spraying it on the specimen screens, measuring the dimensions of the small number of crystals formed as each droplet evaporated, and estimating the drop size from the area of the ring produced on the supporting film. The solubility of lithium stearate is too low to employ this neat procedure, since a droplet of 1 micron diameter would be expected to contain only a few molecules of dissolved material. Hence a substantial volume of saturated solution (.05 c.c.) was deposited in 20 drops (from a fine hypodermic syringe) and the total amount deposited on the entire slit surface estimated. To prepare a saturated solution, a six months old 0.1% dispersion was centrifuged (at 12,000 r.p.m.) for two hours. That this is sufficient to remove suspended particles is implied by the fact that evaporating an entire c.c. of benzene so treated left generally only a few, (in one case not even one) dust particles on the screen. Depletion of the saturated solution by adsorption on the glass surface of the syringe was avoided by prolonged soaking in six successive portions of the solution. The specimen holder was mounted on three

needle points. Each drop spread just to the edges of the metal strip and was allowed to evaporate completely before the next was applied. Flocculation of the depositing crystallites occur to give a very non-uniform deposit. Hence the total quantity of material was estimated by a two stage count. The fraction of the slit covered with deposit was estimated from photographs at low magnification. Although 16 photographs would be required to cover the slit, usually only four to seven contained any clumps. Each clump was then examined under high magnification, and the number of particles per unit area counted. These were taken to have the same average dimensions as the particles in the suspensions. This assumption is not easily justified but appears reasonable by inspection of the photographs, although the particles in the clumps were generally overlapped so badly as to make dimension counts impractical. Of the numerous uncertainties involved this one is the most likely to give a consistent error (positive and hence the result, which at best is correct only in order of magnitude, is probably too high rather than too low. A further fact making the reported figure an upper limit is that of the impurities in the technical lithium stearate used, the unsaturated soaps might well be more soluble than the stearate itself.

#### RESULTS AND DISCUSSION

*Particle Dimensions.*—Figs. 1 (A) and 1 (B) are typical of the unshadowed fields from which counts of length and width were made. It can be seen that the particles are very thin since many are sharply visible beneath others overlapping them. There are very few examples of bent crystallites. Most objects which at first seem to be curled, ribbon-like crystals are seen on close inspection to be made of discrete rods in end-to-end aggregates. The results of the counting experiments are summarized in Table I. It can be seen that the description of all the suspensions as assemblies of rigid rods  $0.6 \mu$  long with a width one tenth as great is valid within 20%. Since each suspension (except C) represents preparation from a new sample of dry soap, the technique employed can be said to lead to reproducible particle size and the size of the primary particle formed by crystallization may be said to be static in hydrocarbon dispersions media. Fig. 1 (C) shows that the same particles dispersed in a hydroxylic solvent (ethanol) have undergone considerable change, becoming shorter and, judging from the contrast only, probably thicker as well. The tendency of these particles to form chain-like aggregates rather than isometric clumps is also well illustrated by this print.

Differential distribution curves of particle lengths for suspensions D and E of Table I are shown in Fig. 2. The distributions are quite broad and quite comparable in the two cases, in accord with the idea that the primary particles formed in the initial crystallization have not changed greatly in either solvent.

Photographs of the type used in the solubility estimate are shown in Fig. 3 (A, B). Two experiments are tabulated in detail in Table II. The entries are all self-explanatory apart from the figure of  $3.0 \times 10^{-16}$  grams per particle. The mean particle length and width are taken as  $0.6$  and  $0.06 \mu$  based on Table I together

TABLE I  
Length and width of lithium stearate particles

Suspension	Number of particles counted	Length ( $\mu$ )	Width ( $\mu$ )	L/W <sup>a</sup>
A. Benzene suspension, 3 days old, manually dispersed	50	0.65	0.064	10
	(5)	(0.67)	(0.061)	(11)
	67	0.50	0.052	9.6
B. Benzene suspension, 6 weeks old, blender dispersed	76	0.42	0.04	10.6
	62	0.50	0.05	10
C. Suspension A, 2 months old	21	0.80		
	28	0.79		
	22	0.72		
D. Benzene suspensions, 3 days old, Blender dispersed	50	0.56		
	25	0.66		
	45	0.52		
	30	0.46		
	50	0.44		
	70	0.56		
E. Heptane suspension, 3 days old, Blender dispersed	60	0.43	0.063	7.5
	28	0.72	0.062	11.5
	26	0.77	0.068	11.3
	16	0.78		
	16	0.67		
	40	0.58		
	50	0.50		
F. Heptane suspension, 2 months old, Blender dispersed	50	0.72		
	50	0.75		
	25	0.69		
	40	0.69		
	25	0.74		

<sup>a</sup>. In several cases it was verified that the ratio of average length to average width and the average of individual length/width ratios are indistinguishable.

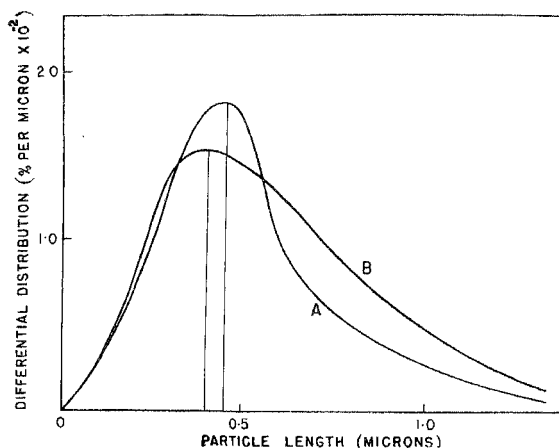


FIG. 2.

TABLE II

*Electron microscopic determination of the solubility of lithium stearate at 30° in benzene*

	A	B
c.c. saturated solution taken .. ..	0.05	0.05
c.c. per total slit area .. ..	$1.25 \times 10^{-8}$	$1.25 \times 10^{-8}$
Particle laden area (cm. <sup>2</sup> ) .. ..	$4.7 \times 10^{-5}$	$2.05 \times 10^{-5}$
Particle per sq. cm. clump $\times 10^{-9}$ .. ..	0.93 1.05	1.35 1.74
Mean grams/particle .. ..	$3.0 \times 10^{-16}$	$3.0 \times 10^{-16}$
Solubility moles/litre .. ..	$3.9 \times 10^{-8}$	$2.6 \times 10^{-8}$

with the assumption of a slow nucleation rate and comparable concentrations of nuclei, which is admittedly a dubious assumption. The mean thickness was taken to be 83 Å as discussed below. The result,  $ca 3 \times 10^{-8}$  is substantially lower than for typical inorganic precipitates such as AgCl ( $ca 10^{-5}$ ) or BaSO<sub>4</sub> ( $ca 10^{-5}$ ),

which exhibit Ostwald ripening, and comparable with that of AgI ( $1.2 \times 10^{-8}$ ) sols of which can also be kept unchanged for months.

Fig. 4 (A, B) shows typical electron micrographs of shadowed specimens. In virtually all cases where the shadow corresponds to a thickness of over 100 Å the particle is obviously lying on edge as in the lower left corner of Fig. 4 (B) or lying on a heap of particles as in the upper corner of Fig. 4 (A). Many shadows, even of fairly wide fibres, are even shorter than this. Apparently the laths are generally of the order of 75–100 Å thick regardless of their width. The *c*-axis x-ray spacing is probably 83 Å, rather than 40–42 Å as is commonly reported,<sup>13, 14</sup> and it has been shown<sup>5</sup> that these planes lie parallel to the lath surface. The extreme thickness is in accord with the finding that the corresponding x-ray lines are extremely weak and broad for greases.

These suspensions of lithium stearate in hydrocarbons are bluish white when freshly shaken, but flocculate visibly within a few minutes and settle under gravity to yield very high sediment volumes. Starting with 0.1 volume per cent. suspensions, the particles come to occupy a limiting volume of the order of 600 c.c. per gram of dry material. It is intuitively reasonable that the random packing volume of anisometric particles should be substantially greater than that of isometric ones also the magnitude of the increase does not appear to be easily calculable. However Chomse<sup>15</sup> has determined empirically that for rods with  $l/w$  of the order of 10 the increase is of the order of only a factor of 5. Hence the very large volumes observed here are believed due to the building of an expanded network with preferential end-to-end contacts, the volume of which is determined by the number of contacts required to support the structure against gravitational compaction. The thickening action of the particles in forming greases from hydrocarbon oils is correspondingly determined by the number of such contacts per unit volume, together with their strength.

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## LEGEND FOR FIGURES

FIG. 1. Characteristic Particle Shapes in Suspensions of Lithium Stearate (unshadowed).

- A. 0.1% technical lithium stearate in benzene.
- B. 0.1% technical lithium stearate in *n*-heptane.
- C. 0.1% technical lithium stearate in ethanol.

All the particles were prepared by quick cooling a 10% solution of lithium stearate in medicinal white oil.

- FIG. 2. Differential Distribution curves of Particle Lengths in Suspensions of Lithium Stearate. A. Benzene suspension. B. *n*-Heptane suspension of particles crystallized under the same conditions from medicinal white oil.
- FIG. 3. Data for Estimation of the Solubility of Lithium Stearate in Benzene. A. Typical appearance of the deposited residue at low magnification. B. Typical appearance of the deposited residue at high magnification. In A the total clump area is measured. In B the number of particles per unit area of clump is counted.
- FIG. 4. Characteristic appearance of Shadowed Particles of Lithium Stearate. 10 A Pt-Ir deposited at an angle of  $\tan^{-1} \theta = 0.2$ . A. Original suspension in Benzene. B. Original suspension in *n*-Heptane. Fig. 4 (B) shows in its left-hand lower corner one of the rare examples of a bent fibre. Most of the crystallites are rigid laths. The magnification mark (M) on the prints corresponds to one micron for the particles and to 2000 Å for the shadows.



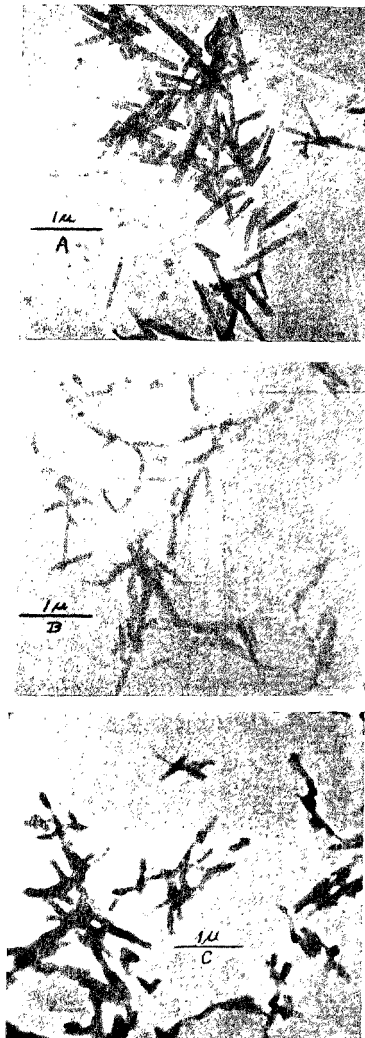


FIG. 1

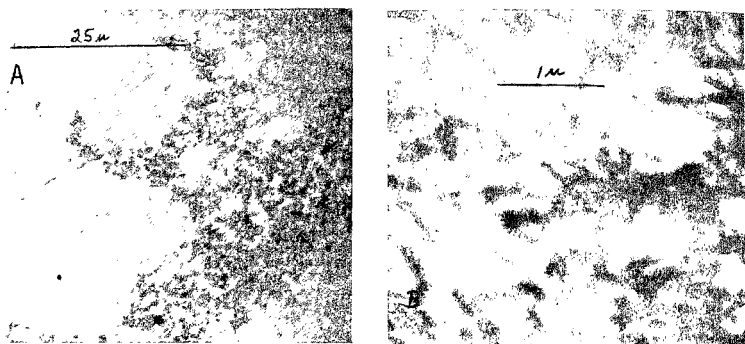


FIG. 3

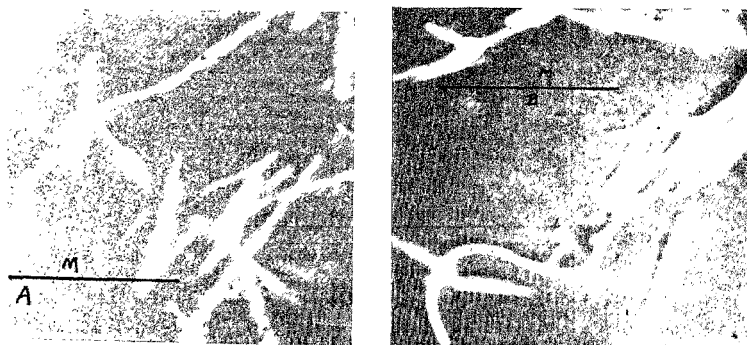


FIG. 4