TABLE I
Wiley Melting Points °C.[a]

Sample No.[b]	Tube 1	Tube 2	Tube 3	Tube 4	Tube 5	Tube 6	Stand. dev.	Ave.	Hand-operated bath
1	43.0	42.9	43.5	43.6	43.4	43.6	0.306	43.3	43.1
2	40.8	41.0	40.9	40.9	40.6	40.8	0.134	40.8	41.2
3	47.9	47.7	48.0	47.9	48.0	48.0	0.118	47.9	47.4
4	41.7	41.5	41.5	42.0	41.6	41.2	0.265	41.6	42.1
5	45.1	44.6	45.1	44.7	45.2	44.7	0.262	44.9	44.5
6	43.3	42.9	43.1	43.1	42.9	43.4	0.205	43.1	43.6

[a] Typical set of determinations. [b] Samples represent emulsified and non-emulsified shortenings.

heater are turned on. The analyst then needs only return to the apparatus when the temperaure of the solution within the tube approaches the end-point temperature and make the readings. This is one advantage of the apparatus since the analyst's time can be spent doing other things while most of the heating and stirring phase of the determination is being performed automatically.

Discussion

Testing of Apparatus. In order to determine the accuracy and reproducibility of results when using this bath, the Wiley Melting Points were determined on several sets of six shortening samples, which had been done by the hand-stirring procedure some months before. One determination on each sample of each set was made each day for six days. Each day the sample position was changed in the apparatus so that no two determinations on any one sample were obtained from the same position in the mechanical bath.

The comparison between these two methods (Table I) show differences well within the analytical error of the Wiley Melting Point test. Also the slight deviations shown between separate runs of any one sample, when using the mechanical bath alone, indicate that the reproducibility of results from the mechanical bath are equal to or better than results that one expects with the hand-stirring procedure.

Advantages of Apparatus. The advantages of this apparatus over the hand-stirring technique for the Wiley Melting Point determination are as follows:

1. With this mechanically stirred bath, more determinations can be run at one time by one operator. The number of tests was limited to six in this apparatus so that more constant surveillance of several samples having nearly equal Wiley Melting Points could be more accurately managed.
2. Less operating time is required in making a determination since the analyst needs only start the stirring apparatus to begin the heating and stirring phase and return to read the end points. The time between can be spent doing other things.
3. Being mechanical and self-operating, the apparatus eliminates the arduous and tiring stirring-operation for the analyst and also eliminates human variations in the stirring phase between two or more different analysts. These variations are often very evident when using the hand-stirring technique. With this apparatus steady, even agitation is continually applied to all samples.
4. A constant, steady even rate of heating is applied to the heating bath and thus to the sample discs, a condition which minimizes error in determining accurate end-points.

Summary

A mechanically stirred Wiley Melting Point bath apparatus is described, which makes the Wiley Melting Point more accurate and reproducible, permits more determinations to be run at one time, and is less time-consuming than the hand-agitation procedure of the A.O.C.S. Method.

Acknowledgments

It is a pleasure to acknowledge the cooperation of the Mechanical Development Laboratories of the Research and Development Department for their advice and construction of the test unit. Most of the analytical data reported were obtained by Mrs. Violet Hoffman.

[Received August 8, 1957]

The State of Dispersion of Detergent Additives in Lubricating Oil and Other Hydrocarbons[1]

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THE STATE of dispersion of detergents in hydrocarbon solvents has long been a subject of interest. Only within recent years however has appreciable experimental evidence become available on the detailed nature of such dispersions. A recent article by Singleterry (10) who, with his coworkers at the Naval Research Laboratory, has made highly important contributions to this subject over the past several years, adequately summarizes the present state of knowledge. The available evidence indicates that soaps and detergents commonly exist in hydrocarbon solvents in the form of micelles. These micelles usually contain less than 50 molecules but, in some cases, may contain up to several thousand. It is the purpose of the present paper to demonstrate in greater detail the state of dispersion in which detergent additives are

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[1] Presented before the Division of Petroleum Chemistry Symposium on Additives in Lubricants, Atlantic City A.C.S. Meeting, September, 1956.

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normally present in commercial lubricating oils and other hydrocarbon solvents. This will be done by using evidence obtained from ultracentrifugation, viscosity measurements, and electron microscopy.

The detailed study of such micellar solutions is experimentally difficult, and conclusions reached by any single method are usually based on assumptions which are subject to some uncertainty. It is clearly desirable that these solutions should be studied by all available methods. Much of the published data on the state of solution of soaps in hydrocarbons has been obtained by cryoscopic or ebullioscopic methods. Many micellar weights are however too large to be readily measurable by these techniques. Such measurements moreover give a number of average micellar weight which may be quite misleading if low molecular weight impurities are present or if a significant amount of molecularly dissolved soap is present. Other methods that have recently been applied to the study of these systems include measurements of the depolarization of the fluorescence of solubilized dye (1), viscosity and flow birefringence measurements (13), X-ray scattering (6), and ultracentrifugation (5). A previous paper from this laboratory has shown that, in some cases, it is possible to observe simple detergent micelles and larger aggregates of micelles in lubricating oil with the electron microscope (7).

Most of the published data on this subject have been obtained on soaps and detergents that were relatively pure chemical entities. These materials, while similar in type to the detergent additives normally used in lubricating oils, are generally more nearly homogeneous in molecular structure. While the importance of studies of such pure materials is obvious, it is also desirable that detergents of the type actually used in lubricating oils be studied directly, where possible. Data on a pure detergent (Aerosol O.T.), which is not normally used in lubricating oil, are included in this study for purposes of comparison.

Experimental

Materials and Methods. For the ultracentrifugation and viscosity measurements the following solvents were used: n-decane and n-dodecane supplied by Humphrey-Wilkinson Inc., and distilled under reduced pressure in a spinning-band column. Cuts having the same refractive index were combined to obtain heart cuts of each of these solvents. The refractive indices and densities of these solvents were found to be in good agreement with the best literature values. The isooctane (2,2,4-trimethylpentane) used as solvent in the Aerosol O.T. work was Phillips Pure Grade (99 mole % minimum). This solvent was dried with P_2O_5 and distilled through a short Vigreaux column; initial and final cuts were discarded. Oil A was a western paraffin base lubricating oil having a density of 0.8701 and a viscosity of 0.468 poise at 25.0°C.

The Aerosol O.T. (di-2-ethylhexyl sodium sulfosuccinate) was purchased from the American Cyanamid Corporation. This material is said to be 99% pure. A concentrated solution of Aerosol O.T. was made in isooctane and dried by refluxing for 2 hrs., removing water and some isooctane with an azeotrope head. The solution was then centrifuged at 30,000 times gravity to remove insoluble material. Dilutions were made with dry isooctane.

The calcium petroleum sulfonate used was supplied by O. L. Harle of this laboratory. This material was obtained from a commercial concentrate slightly thinned with mixed hexanes by repeated extraction with isopropyl alcohol, followed by vacuum drying at 100°C. The product was a friable, resinous, amber-colored solid. The average molecular weight of this material was about 940. (The average molecular weight of the original sulfonic acid was determined to be about 450.) The apparent specific volume was 0.909 ml./g. in n-decane and n-dodecane.

Lead alkylbenzenesulfonate was obtained as a dry, oil-free product by repeated extraction of an oil concentrate with methanol followed by vacuum drying at 100°C. The dry sulfonate was a brown, resinous solid. The lead alkylbenzenesulfonate was originally made from acid obtained by sulfonation of an alkylbenzene of approximately 440 molecular weight. The alkyl groups are derived from polypropylene. Absorption spectra indicate that the original alkylbenzene was predominately p-dialkylbenzene (75–85%). The calculated molecular weight of the lead alkylbenzenesulfonate was approximately 1,245. The apparent specific volume of this material was found to be 0.800 ml./g. in n-dodecane.

The essential similarity of the extracted dry detergents to the material present in the original concentrates was established by ultracentrifuging dilute solutions of the original concentrates in the same hydrocarbon solvents used for the dry detergents. The sedimentation rates and patterns obtained were quite comparable to those found for dry detergents.

Solution densities were determined at 25.0 ± 0.03° C., using a 10-ml. pycnometer. Viscosity measurements were made at 25.0 ± 0.01°C., using a calibrated Ostwald-type viscometer.

For the ultracentrifugation work a Spinco Model E analytical ultracentrifuge was used. Sedimentation velocity measurements were ordinarily made at 59,780 r.p.m. At this speed the centrifugal field is about 250,000 times gravity. The centrifuge was equipped with heating coils which permitted operation at elevated temperatures. Calculations of sedimentation constants were made, using standard procedures (11).

Small corrections ($<10\%$, except for Oil A) were applied for change-of-solvent viscosity with pressure and for variation of temperature from 25°C.

Ultracentrifugation and Viscosity Measurements

The ultracentrifuge offers unique advantages in the study of detergent dispersions in hydrocarbon solvents. Not only can average micellar weights be determined, but something can be learned at the same time about the distribution of micellar sizes. Color of the solution does not interfere with the determination of particle weights, provided only that the solution will transmit enough light for photographic recording of the sedimenting boundary. The presence of small amounts of low-molecular-weight impurities or of large particles does not materially affect the accuracy of the determination.

From photographs of the sedimenting boundary taken periodically a sedimentation rate can be calculated. The sedimentation rate is governed by a balance established between the centrifugal force acting on the particles and the frictional force resisting the motion of these particles through the solvent. Minimum-particle weights can be calculated from the observed sedimentation rate when the densities of solute and solvent, the viscosity of the solvent, and the centrifugal field are known. For this purpose the particles are assumed to be unsolvated spheres, and Stoke's law is used.

For particles which are not spherical or which are solvated, the frictional constant is greater than for unsolvated spheres. Frictional constants for use in calculations of micellar weights were calculated from viscosity data. For rigid unsolvated spheres, which are large with respect to the solvent molecules,

$$\left(\frac{\eta_{sp}}{\phi}\right)_{\phi \to 0} = 2.5, \text{ according to the Einstein equation}$$

where η_{sp} = specific viscosity and ϕ = volume fraction of solute. Deviations from the value 2.5 are usually attributed to either solvation or to deviations from a spherical shape. If however, as seems to be the case with many sulfonate-type detergents (13), the micelle changes in shape with concentration, direct extrapolation of viscosity, and sedimentation data to infinite dilution is not very useful. The interference existing between particles in moderately concentrated solutions makes interpretation of viscosity and sedimentation data somewhat difficult. This interference is to a considerable extent taken into account in an empirical equation developed by Eilers (2). This equation has been used by Van der Waarden (13) in the interpretation of his data on the viscosity of concentrated metal naphtha sulfonate solutions in hydrocarbon solvents. The equation has the following form:

$$\eta_r = \left(1 + \frac{1.25\,V\phi}{1\text{-}1.35\,V\phi}\right)^2$$

where η_r = relative viscosity

V = voluminosity

$$= \frac{\text{hydrodynamically effective volume of solute}}{\text{volume of dry solute}}$$

ϕ = volume fraction of dry solute

In the case of Aerosol O.T. in isooctane where the micelles are thought to be roughly spherical, the voluminosity is close to unity and does not change appreciably with concentration over a wide range. This indicates that micelle shape and extent of solvation do not change appreciably with concentration. This is shown in Figure 1. For sulfonate detergents however, as Van der Waarden shows, this is frequently not the case. Information about micellar shape or degree of solvation must be obtained for specified concentrations. If the micelles are assumed to be solvated spheres, Eilers' equation can be used to calculate the approximate extent of solvation at a given concentration. If it is assumed that at the relatively low (*i.e.*, <3.5 vol. %) concentrations studied, the concentration dependence of η_{sp}/ϕ for suspensions of randomly oriented ellipsoids is similar to that for spheres, the Eilers' voluminosity can be used to calculate the extrapolated value of η_{sp}/ϕ at infinite dilution. This quantity can be related to the axial ratios of assumed possible micelle shapes. The equations used in this study to calculate length-diameter ratios for ellipsoids are those of Simha (9). Tables calculated by Svedberg (11) from Perrin's equation were used to obtain frictional coefficients from length-diameter ratios. Alternatively the particles can be assumed to be solvated spheres and micellar weights calculated on this basis. The micellar weights thus obtained do not differ greatly from those obtained by assuming nonspherical shapes for the detergents studied.

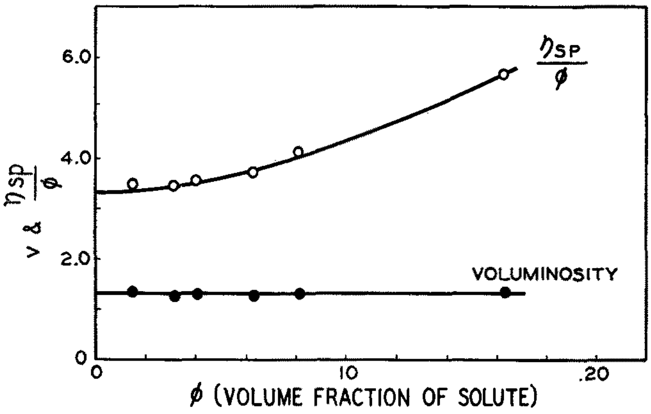


FIG. 1. Aerosol O.T. in isooctane (25.0°C.).

Sedimentation constants should also be extrapolated to infinite dilution before being used to calculate micellar weights. This is not normally difficult experimentally for particles of the size and shape of most micelles. If however the particle size and shape change with concentration, direct extrapolation of the sedimentation constants is not meaningful. In this study it was assumed that extrapolation of individual sedimentation constants obtained at various concentrations for the sulfonate detergents should be similar to that determined experimentally for Aerosol O.T. (The Aerosol O.T. micelle does not appear to change markedly in size or shape over the observed concentration range.) For purposes of extrapolation it was assumed that Aerosol O.T. and the sulfonate detergents could be treated identically at equal-volume concentrations. Figure 2 shows the experimental extrapolation of Aerosol O.T. sedimentation constants in isooctane.

Results and Discussion

From the data presented in Figures 1 and 2 and the measured specific volume of Aerosol O.T. in isooctane solution (0.877 ml./g.) the micellar weight can be calculated to be 11,800, assuming the micelle to be

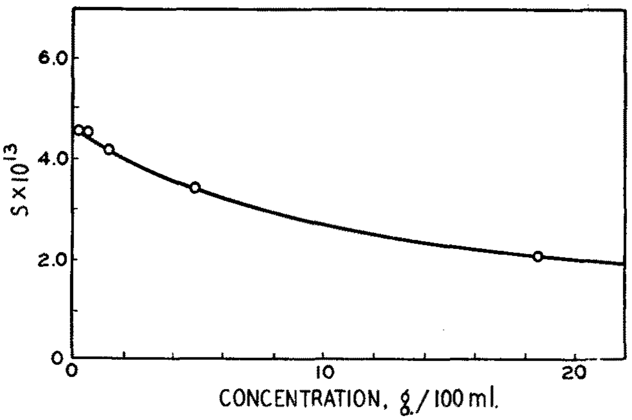


FIG. 2. Aerosol O.T. in isooctane (25.0°C.).

TABLE I

Calcium Petroleum Sulfonate in n-Decane (25°C.)

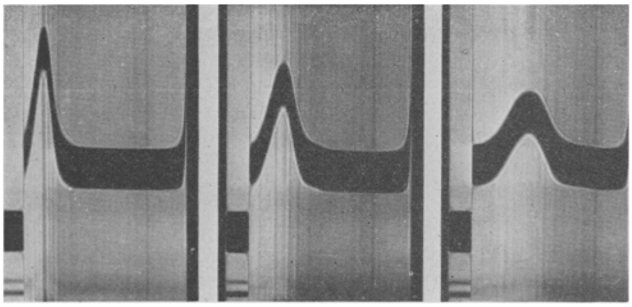
Concentration, Wt. %	Experimental		V^a	Calculated for unsolvated prolate ellipsoids				
	S x 10^{13}	η_{sp}/ϕ		L/d^b	Length Å	Diameter Å	Micellar weight	Molecules per micelle
5.0	4.35	18.0	4.92	9.3	272	29.2	80,400	86
3.4	4.04	11.1	3.71	7.5	210	28.0	57,200	61
1.0	3.84	8.6	3.29	6.8	177	26.0	41,200	44

[a] From Eilers' equation.
[b] From Simha's equations for prolate ellipsoids.

an unsolvated prolate ellipsoid. A 6% correction was applied to the solvent viscosity to correct for the pressure existing in the cell during centrifugation. This result corresponds fairly well with a micellar weight of 14,000 reported by Mathews and Hirschhorn (5) for Aerosol O.T. in dodecane. These authors however did not extrapolate the observed sedimentation constant to infinite dilution and applied a pressure correction which appears too large. The viscosity data are consistent with a possible micellar shape ranging between an unsolvated prolate ellipsoid 23.3 Å in a diameter and 60.4 Å in length and a solvated sphere containing 26% by volume of bound solvent (V = 1.35) approximately 35.7 Å in diameter. The micellar weight calculated for such a solvated sphere excluding bound solvent) is 12,160. An unsolvated disk shape (oblate ellipsoid) does not appear possible because, to fit the viscosity data, the thickness of the disk would have to be much less than twice the molecular length. The close agreement of the diameter calculated for the prolate ellipsoid with twice the length of the Aerosol O.T. molecule lends a certain amount of support to this model. Analysis of the sedimentation patterns shows no change in apparent diffusion constant with time, indicating that the micelles are essentially monodisperse. No evidence was found for the existence of larger aggregates in solution.

Sedimentation patterns for calcium petroleum sulfonate in n-decane are shown in Figure 3. The peak represents the sedimenting boundary. The area under the peak is proportional to the amount of sedimenting material and the refractive index difference between the solute and the solvent.

Table I presents the experimental results and calculated micellar weights for calcium petroleum sulfonate in n-decane, assuming unsolvated prolate ellipsoids. A basically rodlike shape appears to be the most reasonable possibility for these micelles. If, as did Van der Waarden, we assume an unsolvated, platelike shape, the calcium petroleum sulfonate micelle has a thickness of only 10 Å to 11 Å. This is unreasonably small, being less than even a single molecular length. If, on the other hand, we assume a spherical shape, we must have an unreasonably high degree of solvation (at 3.4 weight percentage, V = 3.7, corresponding to a sphere composed of 27% dry detergent and 73% bound solvent by volume). The calculated diameter of such a solvated sphere is moreover much greater than twice the molecular length.



26 minutes 42 minutes 73 minutes

FIG. 3. Ultracentrifugation patterns for calcium petroleum sulfonate in n-decane (3.4 wt. %).

Table II gives micellar weights and dimensions calculated for calcium petroleum sulfonate, assuming solvated spheres and unsolvated oblate spheroids. X-ray diffraction data obtained on a dry sample of this detergent show a diffuse, long spacing of 28.2 Å. This probably corresponds to twice the average molecular length, assuming the two hydrocarbon tails to be folded together. A solvated disk shape is, of course, still conceivable, but if the thickness of such a disk is assumed equal to twice the molecular length, it becomes necessary as in the case of a spherical model to assume an unreasonably large amount of solvation; the extent of solvation increases with increasing detergent concentration. The close agreement between the calculated diameters for unsolvated prolate ellipsoids and the X-ray long spacing is encouraging. Minor modifications in the calculated values for micellar dimensions could, of course, easily be made by assuming a shape somewhat different from a prolate ellipsoid (*e.g.*, a cylindrical rod) or by assuming some solvation. The micellar weights given would not however be materially altered by such assumptions. From the data of Tables I and II it can readily be seen that the micellar weight decreases markedly on dilution. This conclusion is independent of any assumptions about shape because both the sedimentation constant and the voluminosity decrease on dilution. Figure 4 shows a possible typical micelle consistent with the data presented for calcium petroleum sulfonate in n-decane at 3.4 weight percentage. It is also possible however that the rodlike shape results from a linear aggregation of roughly spherical micelles.

TABLE II

Calcium Petroleum Sulfonate in n-Decane (25°C.)

Concentration wt. %	Calculated for solvated spheres			Calculated for unsolvated oblate ellipsoids		
	Micellar weight	$D_o{}^a$ (Å)	$D_s{}^b$ (Å)	Micellar weight	Thickness (Å)	Diameter (Å)
5.0	97,300	65	111	95,400	10	165
3.4	66,600	58	89	65,200	11	131
1.0	46,800	51	77	46,300	11	111

[a] D_o = minimum diameter of detergent core.
[b] D_s = total diameter of solvated sphere.

Analysis of the shape of the sedimentation patterns obtained in n-decane at 3.4 weight percentage shows that, although only one fairly sharp peak is present, the micelles are not uniform in size but show a very marked size distribution. Sedimenting boundaries tend to be deceptively sharp for polydisperse,

TABLE III

Calcium Petroleum Sulfonate in n-Dodecane

Temperature, °C.	Concentration, wt. %	Experimental		V	Calculated for unsolvated prolate ellipsoids				
		$S^a \times 10^{13}$	η_{sp}/ϕ		L/d	Length (Å)	Diameter (Å)	Micellar weight	Molecules per micelle
25.0	5.0	2.58	10.2	3.23	6.7	208	31.0	70,000	74
75.0	5.0	3.46	6.9	2.34	5.1	117	23.0	20,700	22
75.0	2.5	—	5.1	1.91	4.1	—	—	—	—
75.0	1.25	—	4.1	1.58	3.0	—	—	—	—

[a] In all tables S is experimental sedimentation constant corrected to the given temperature but not extrapolated to infinite dilution.

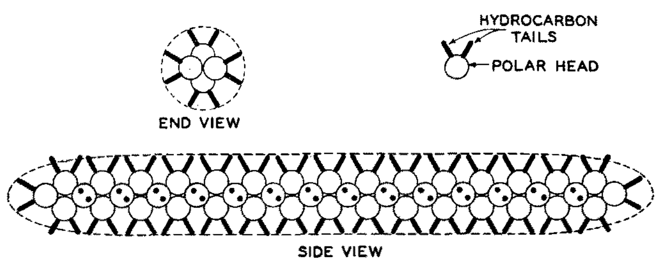


FIG. 4. Possible calcium petroleum sulfonate micelle in n-decane.

rodlike particles because the frictional constant increases with increasing particle length

To estimate the degree of polydispersity, apparent diffusion coefficients calculated from the standard deviation of the sedimentation patterns after various sedimentation times were extrapolated to zero time, using the method of Baldwin and Williams (12). The extrapolated diffusion coefficient thus obtained was 6.25×10^{-7} sq. cm./sec. From the slope of the plot of apparent diffusion coefficient against time the standard deviation of the sedimentation constant distribution can be calculated (12). The standard deviation thus obtained was 0.99×10^{-13}. This must be regarded as only approximate because concentration effects are ignored. If the sedimentation constant distribution is assumed to be Gaussian and the sedimenting micelles are assumed to be rodlike with an average diameter of 25 Å, it can be calculated that approximately 16% of the calcium petroleum sulfonate is present as micelles of less than 85 Å in length containing 29 or less molecules per micelle while another 16% is in the form of micelles of greater than 325 Å in length containing 120 or more molecules per micelle.

Table III shows the effect of temperature on the voluminosity and calculated micellar weights for calcium petroleum sulfonate in n-dodecane. The micellar weight can be seen to be markedly lower at the higher temperature. At a concentration of 1.25 weight percentage at 75°C. the average micelle probably contains less than a dozen molecules.

The state of dispersion observed apppears to be quite stable. No change in viscosity could be detected after one and one-half years for a 5 weight percentage solution of the calcium petroleum sulfonate in n-dodecane.

Direct measurement of micellar weight in lubricating oils is not feasible by most conventional methods. In the ultracentrifuge the high viscosity and density of most oils make the sedimentation rates of simple micelles too low to be measurable. The situation is further complicated by the wide range of micellar weights and shapes of the oil molecules. This leads to a nonuniform distribution of molecular types in the ultracentrifuge and, in a prolonged run, produces a badly curved base line for the sedimentation patterns. To a considerable extent these difficulties can be circumvented through the use of a synthetic boundary cell. The design and function of this cell have been described by Pickels, Harrington, and Schachman (8). This device permits a layer of pure solvent to run in above the detergent solution while the centrifuge is in operation. The boundary formed between the solvent and the solution, being strongly stabilized by the centrifugal field, is quite sharp. Very small displacements of this boundary can be accurately measured, and a sedimentation constant can be determined in a shorter time than would otherwise be possible.

Even with the synthetic boundary cell, sedimentation constants usually cannot be accurately determined for the micelles in most detergent lubricating oils, owing to the extremely slow sedimentation rate, although the existence of small micelles can be demonstrated in these oils. In the case of lead alkylbenzenesulfonate however, the solute density is sufficiently high relative to that of lubricating oil so that readily measurable sedimentation rates are obtained. Table IV gives results obtained from ultracentrifugation and viscosity measurements for lead alkylbenzenesulfonate in n-dodecane and in light lubricating oil (Oil A). These results show that the micellar shapes and sizes are fairly similar in this lubricating oil and in n-dodecane although the micelles appear to be somewhat smaller in the lubricating oil. The viscosity data indicate that the micellar shape is relatively constant over a wide concentration range. This contrasts sharply with the behavior of petroleum sulfonates.

The agreement between the calculated micellar diameters and the diffuse, X-ray, long spacing of 23.8 Å obtained on a sample of the solid lead alkylbenzenesulfonate is fairly good. This long spacing is quite close to twice the calculated molecular length.

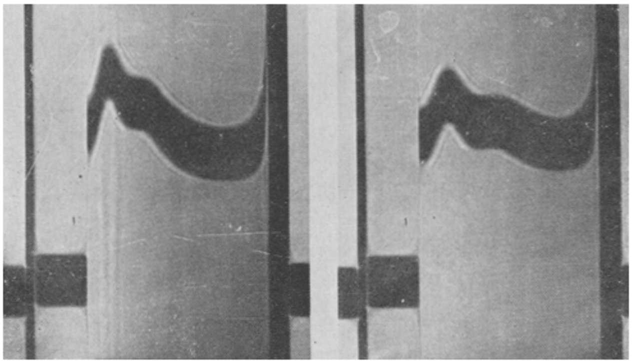
There can be little doubt that, in many or most cases, detergent additives exist in lubricating oils in the form of small micelles which have at least one dimension approximately equal to twice the molecular length. It is not safe to assume that detergents exist in hydrocarbon solution solely in the form of such micelles. Under some circumstances calcium petroleum sulfonate appears to contain two rather well-defined particle sizes. Ultracentrifugation in kerosene of the same sample studied in n-decane and n-dodecane gave two distinct peaks. The smaller fast peak sedimented at two and one-half times the rate of the slow peak. The fast peak appears to be due to an aggregate at least four times as large as the average micelle represented by the slow peak. It seems likely that this larger aggregate is due to interaction of the detergent with certain constituents of the kerosene.

Basic petroleum sulfonates are widely used at present as detergent additives. In some instances these basic sulfonates may actually be definite compounds.

TABLE IV

Lead Alkylbenzenesulfonate (25°C.)

Solvent	Concentration, Wt. %	Experimental		V	Calculated for unsolvated prolate ellipsoids				
		S x 10^{13}	η_{sp}/ϕ		L/d	Length (Å)	Diameter (Å)	Micellar weight	Molecules per micelle
n-Dodecane............	5.0	—	8.2	2.58	5.5	—	—	—	—
n-Dodecane............	2.5	3.81	7.6	2.77	5.9	177	30.0	62,400	57
Oil A....................	10.0	—	7.6	2.12	4.6	—	—	—	—
	5.0	—	6.5	2.19	4.8	—	—	—	—
	2.5	—	5.4	2.00	4.4	—	—	—	—
	1.25	—	5.3	2.04	4.4	—	—	—	—
	2.0	0.0532	—	—	—	124	28.3	39,300	36



44 minutes 58 minutes

FIG. 5. Ultracentrifugation patterns for basic calcium petroleum sulfonate in n-dodecane.

In general, the basicity is variable between rather wide limits, and it does not appear that a simple basic salt is formed. It appears instead that the excess base is in some way solubilized or incorporated by the detergent micelles.

Figure 5 shows the sedimentation patterns obtained on centrifuging a basic calcium petroleum sulfonate concentrate in n-dodecane. Two distinct peaks are evident. If the same shape and density are assumed for the particles represented by each peak, the fast peak corresponds to a five-fold increase in particle weight over the slow peak.

While the ultracentrifuge sometimes shows us that detergent additives in solution contain more than one distinct species of particle, it cannot tell us much about the nature of the larger aggregates. The electron microscope, on the other hand, frequently permits observation of the extremely small particles present in detergent lubricating oils. There is admittedly some question as to whether the state of aggregation seen with the electron microscope accurately represents the condition existing in the original oil. In general, the electron micrographs obtained have been entirely consistent with present independent knowledge of these colloidal systems. In many detergent oils the micelles are apparently too small or too lacking in contrast to be visible with the electron microscope. In other cases not only can individual micelles be seen, but larger aggregates are also in evidence. Long fibers, approximately two molecular lengths in diameter, have previously been shown to coexist with short, rodlike micelles in a detergent oil (7). Figures 6 to 9, inclusive, show other types of particles which appear characteristic of certain samples of commercial detergent oils in electron micrographs. Figure 6 shows a detergent oil sample which appears to contain both rodlike micelles and spherical particles of various sizes. The spherical particles are generally significantly greater in diameter than the rods, which appear to have minimum diameters of about 50 Å. Some of the thicker rods appear to be linear aggregates of spherical particles.

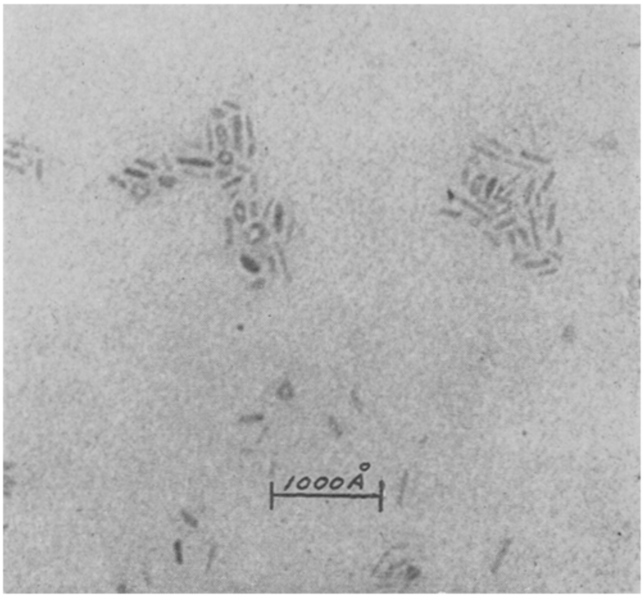


FIG. 6. Detergent oil "B." 135,000×.

Figure 7 shows a detergent oil sample which apparently contains fairly large, spherical particles of various sizes. The general appearance of micrographs of this oil suggests that of an extremely fine emulsion. The various aggregates of the spherical particles also

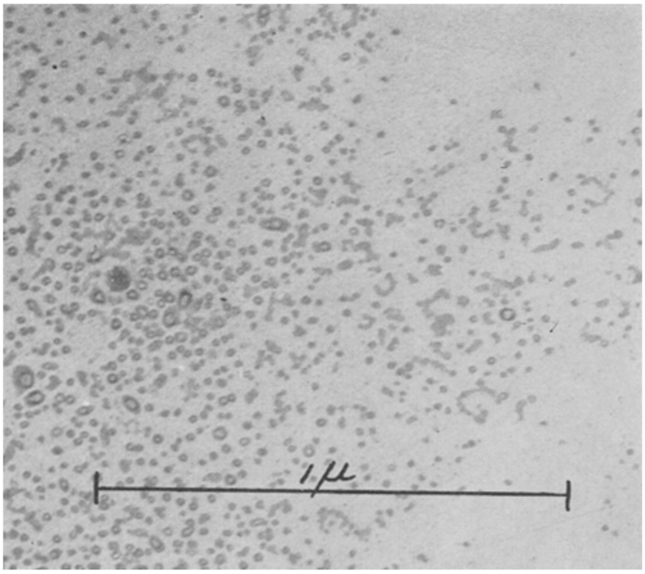


FIG. 7. Detergent oil "C." 62,000×.

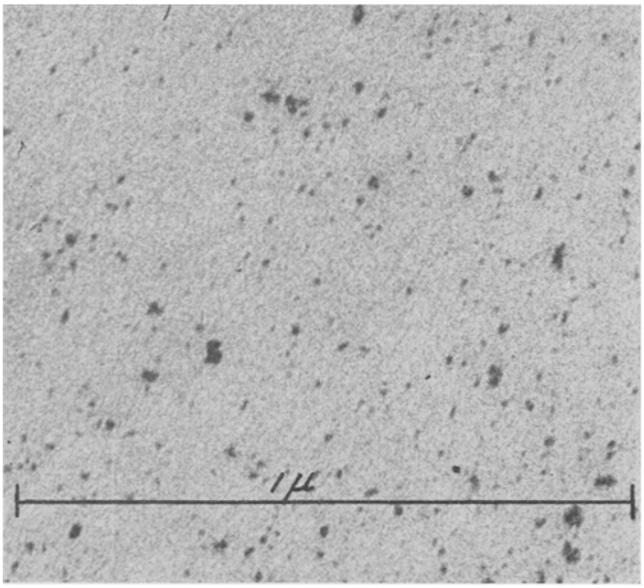


FIG. 8. Detergent oil ''D.'' 82,000×.

evident could easily have been formed during drying of the oil film in the electron microscope.

Figure 8 shows another detergent oil which appears to contain larger aggregates in addition to small, simple micelles.

Figure 9 shows, at high magnification, a detergent concentrate containing large amounts of a solubilized inhibitor. Small micelles and larger aggregates can both be seen in this electron micrograph. This material gave a clear solution in oil but showed two distinct peaks in the ultracentrifuge.

Ultracentrifugation and viscosity studies show that certain sulfonate-type of detergents exist in hydrocarbon solution in the form of small micelles ordinarily containing fewer than 100 molecules per micelle. The data indicate that these micelles are in some cases rodlike in shape and in other instances nearly spherical. Studies of detergent lubricating oils with the electron microscope have previously shown that the micelles existing in lubricating oil solutions of calcium cetyl phosphate and calcium alkyl phenate are quite comparable in size and shape to those found here for the sulfonates (7). These results are consistent with the findings of Singleterry *et al.* (10, 1) for the alkali and alkaline earth aryl stearates. The results obtained do not however support the conclusions of Van der Waarden (13), who has interpreted his viscosity data on naphtha sulfonates in terms of a platelike, micellar shape. Van der Waarden's data are however equally interpretable on the basis of a rodlike micelle. Recalculation of his data on the same basis as for the data presented here gives length-to-breadth ratios for unsolvated micelles ranging from 3.5 to 10. These values are in good agreement with those found for calcium and lead sulfonates in the present paper. As recalculated, Van der Waarden's data support the picture of rodlike micelles varying in length with concentration. It is not possible however to calculate micellar weights from these data.

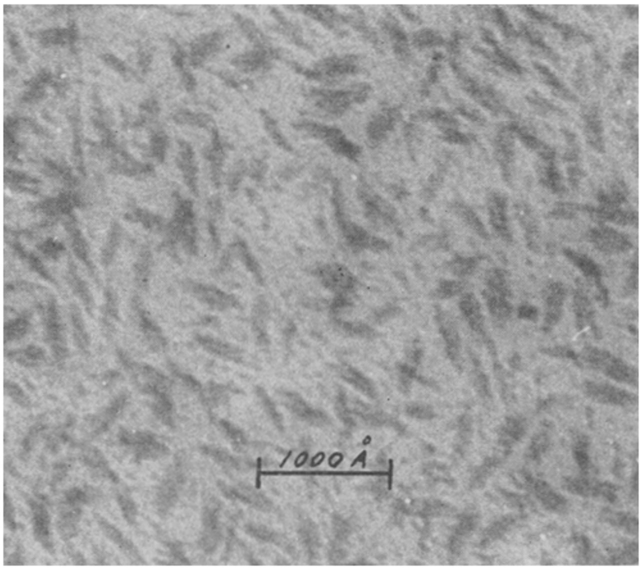


FIG. 9. Detergent concentrate ''E.'' 170,000×.

In addition to the micelles existing in detergent solutions, there must also exist a finite concentration of molecularly dispersed detergent. The work of Singleterry *et al.* (1, 4) has shown that the critical concentrations for detergents similar in type to those used in lubricating oils are extremely low, ranging between 10^{-6} and 10^{-7} molar. Above the critical micelle concentration the additional detergent nearly all appears in micellar form; and the concentration of molecularly dissolved detergent increases only very slightly.

Micelle formation in hydrocarbon solvents appears to be due principally to interaction of the polar heads of the detergent molecules, probably due either to ionic attraction or to specific coordination bonding between atoms. It is reasonable to suppose, as previous workers have done, that geometrical considerations are a major factor in preventing indefinite growth of the micelles with ultimate separation of a second phase. It does not appear justifiable however to attribute micellar dimensions entirely to the molecular geometry. The fact that micellar weights can change with concentration, solvent, and temperature indicates that statistical considerations and solute-solvent interactions play an important role in determining the limiting micellar size.

Evidence has been presented in this paper and elsewhere (7) that larger aggregates may exist in hydrocarbon solution simultaneously with small simple micelles. No completely satisfactory explanation of these aggregates can be made at present. Such aggregates have to date only been found in cases where other polar compounds are known or can reasonably be expected to be present. These cases are not trivial however because the detergent additives normally used in lubricating oils are not usually free from trace amounts of such polar compounds. It appears that solubilization of polar compounds by the detergent micelles may, in some cases, lead to the formation of larger aggregates. Mathews and Hirschhorn (5) have shown that, when water is solubilized by Aerosol O.T. in n-dodecane, the water appears to be held in swollen micelles ranging up to 99 Å in diameter. These swollen micelles are thought to consist of a spherical or near spherical water core surrounded by a monolayer of detergent molecules. Other polar compounds may be solubilized in a similar manner. Solubilized polar material may also result in an aggregation of existing micelles to form long, threadlike or fiberlike structures.

Honig and Singleterry (3) have concluded that sodium phenyl stearate in benzene is organized into three types of structure: a) long polymeric chains of anhydrous soap held together by ionic forces; b) a small, compact micelle which exists in the presence of a fraction of a mole of various polar additives per mole of soap; and c) an extensive but loosely bonded structure formed through a bridging between small micelles by an excess of certain polar additives. Extended structures of Types 1 and 3 postulated by these authors could explain some of the larger aggregates present in detergent oils. Much further work remains to be done however before a complete explanation of these structures can be given.

Summary

Ultracentrifugation and viscosity data indicate that the sulfonate type of detergents normally exists in hydrocarbon solvents as small micelles approximately two molecular lengths in diameter, ranging in shape from nearly spherical to rodlike. The micellar size is shown, in the case of calcium petroleum sulfonate, to change with concentration and temperature. Analysis of the sedimentation patterns shows that, while Aerosol O.T. appears essentially monodisperse, calcium petroleum sulfonate shows a marked distribution of micellar weights. Ultracentrifugation and electron microscopy show that larger aggregates sometimes exist in solution together with small micelles. These aggregates may result from association of various polar compounds with the detergent micelles.

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[Received April 8, 1957]

Bleaching of Drying Oils by Ionizing Radiation

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EXPOSURE OF DRYING OILS to ionizing radiation changes a number of properties. These include color, drying characteristics, iodine number, molecular weight, refractive index, viscosity, and hexabromide number, alkali resistance and gas proofness of varnishes from the oils (1, 2). One of the most striking of these changes is bleaching of the oil. This effect was mentioned as early as 1927 when linseed and perilla oils were made almost water-white by electrons from a cathode ray tube (1). Bleaching was again reported in 1956 after the development of nuclear reactors and electron accelerators stimulated a study of the effects of ionizing radiation on tung oil. After exposing the oil to neutrons, *gamma* radiation, or electrons, a color decrease was noted and described briefly (2).

The destruction by ionizing radiation of carotenoids, one of several pigment classes found in drying oils (3), was previously reported in several other systems. The carotenoids were studied in connection with the retention in irradiated foods of the biological activity of β-carotene and vitamin A. *Beta* and *gamma* radiation destroyed the carotenes in butter (4, 5) and dehydrated butter fat (6). Mackinney found that bleaching of the carotenoids in carrot root oil required more *gamma* radiation than those in corn oil (7). Pure β-carotene (6–8) and lycopene (7) in hexane were destroyed with small amounts of ionizing radiation. Lycopene in methyl oleate or methyl linoleate was destroyed by nearly the same dose as in hexane. In contrast, methyl stearate solutions of lycopene were slowly bleached under similar conditions (7). Selected drying oils were therefore irradiated, and their degree of bleaching was compared with those above. The radiation requirements, the effect of environment, and the mechanism of bleaching were emphasized.

Experimental

The oils used were commercial products. Nonbreak safflower and soybean oil and nonbreak bleached linseed oil were obtained from the Pacific Vegetable Oil Corporation. The tall oil fatty acids were purchased as Unitol ACD from the Union Bag-Camp Paper Corporation. The oleic acid was USP special, light quality.

Three sources of ionizing radiation were used. *Gamma* radiation was obtained from cobalt-60 at a rate of 3.1×10^5 reps[1]/hour (9). A "traveling wave" linear accelerator (10) provided 6 Mev electrons at a dose rate of 3 Megareps/minute. Electrons from a 2-Mev Van de Graaff accelerator (11) were also used, especially for large-scale runs.

Most irradiations were done with 6 Mev electrons and a sample thickness less than the penetration of the beam (1.3 in.). This provided a constant radiation level throughout the sample. The oil was contained in a beaker equipped with a side arm just above and at a 45° angle to the liquid level to allow introduction of helium. The oil was maintained at room temperature by immersion of the beaker in circulating cold water or by giving the radiation in increments. Large portions of oil were stirred with a magnetic stirrer and bleached, using 2 Mev electrons from the Van de Graaff. Samples exposed to the cobalt source were sealed in glass ampoules with a small air space.

The total radiation (dose) was determined by the exposure time at a constant radiation level (dose rate). The dose was measured by its known relationship to the color change in an irradiated chip of cobalt glass (12). The dose rate was constant during an

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[1] A rep (roentgen equivalent physical) corresponds to an energy absorption of 93 ergs/g. of sample and a Megarep to 93×10^6 ergs/g.