PROPERTIES OF ORGANIC SOLUTIONS OF HEAVY METAL SOAPS

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Contents

I. Introduction

This review deals with some of the physico-chemical properties of systems containing an organic solvent and a soap of a heavy metal; systems based on the soaps of the alkali and of the alkali earth metals are only considered incidentally.

The systems range from true solutions to colloidal dispersions, gels and pastes and their properties are conveniently discussed under the headings of physical properties, electrical properties and mechanical properties. Wherever possible these are interpreted in terms of the micellar theory of soaps.

The review covers the period of about 25 years since the middle 1930's and includes a section on commercial lubricating greases, which are essentially mineral or vegetable oils thickened with soaps. However, the properties of oil–soap systems are profoundly affected by even trace quantities of additives and impurities and it is therefore impossible to correlate the properties of the commercial products with those of the systems based on pure chemicals.

It is emphasized that it is difficult to prepare the soaps of the heavy metals in a pure state; systematic work on their pure solutions dates only from the late 1930's, when the carboxylates of a number of the metals in groups 1, 2, 3, 4, and 8 of the periodic table were prepared, in certain cases, for the first time (11, 47, 67, 76, 77).

II. Preparation of Heavy Metal Soaps

A. SOAPS BASED ON CARBOXYLIC ACIDS

The classical method of aqueous metathesis was employed. This involves treating an aqueous solution of the appropriate sodium or potassium soap with a solution of a metal salt, filtering off the precipitate, washing with ethanol and acetone and drying. Copper and lead dodecanoates and octadecanoates can be obtained from the acetates (77); zinc, cadmium, magnesium and aluminum, etc., carboxylates can be obtained from the corresponding chlorides (65, 87).

In the latter case it is necessary to add approximately twice the amount of aluminum trichloride required to complete the precipitation of the fatty acid as the disoap, wash with water, extract with anhydrous acetone and dry over phosphorus pentoxide.

Another method of preparation (47) for the carboxylates of such metals as copper, silver, barium, mercury, lead, iron, cobalt and nickel is to treat the hydroxide of the metal with the fatty acid in alcoholic solution

$$M(OH)_2 + 2RCOOH \rightarrow M(COOR)_2 + 2H_2O \qquad (1)$$

removing the water either by heating *in vacuo* or by

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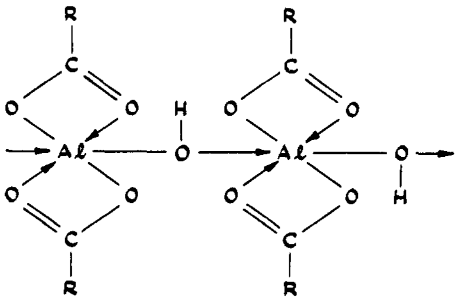
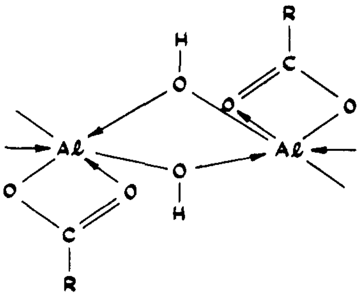


ALUMINIUM
DISOAP $Al(OH)(COOR)_2$



ALUMINIUM
MONOSOAP $Al(OH)_2COOR$

Fig. 1.—Structures of aluminum soaps.

washing with anhydrous solvents. However, due to the fact that many of the heavy metal soaps are extremely sticky, which makes it difficult to filter them and to extract unreacted fatty acids adequately, a better procedure is to dissolve the metal oxide in the molten fatty acid, wash with hot ethanol, dissolve in petroleum ether and evaporate to dryness *in vacuo.* This method has been employed for the soaps of mercury, lead, iron and the alkali earths (47).

It is necessary to control accurately the amount of water that is present during the preparation of certain heavy metal soaps if they are to be obtained as discrete compounds of identifiable composition. Treating magnesium chloride with sodium octadecenoate (oleate) in aqueous solution (68) yields a white, crystalline precipitate of $Mg(C_{18}H_{33}O_2)_2 \cdot 2H_2O$ which, even after drying for 4 weeks in a desiccator, is only moderately soluble in benzene. But if the product is refluxed in perfectly dry benzene and then recrystallized, a yellow, glassy product is obtained, $Mg(C_{18}H_{33}O_2)_2$, which is readily soluble in benzene (76).

However, the formation of such well defined hydrates is uncommon. When aluminum sulfate is treated with sodium dodecanoate in aqueous solution it is possible, by suitable variation of the experimental conditions, to obtain a range of compounds with compositions varying between aluminum hydroxy didodecanoate, $Al(OH)(COOR)_2$, and aluminum hydroxide. These contain various proportions of adsorbed or bonded water, which it is very difficult to remove.

Considerable work has been done (78) on the purification and identification of the products; there is now good evidence for the existence of disoaps of aluminum and some evidence for the existence of monosoaps with the structures given in Fig. 1 (28).

To avoid problems of purification and identification, it is convenient, particularly in the preparation of aluminum soaps, to carry out the reactions in anhydrous solvents. An aluminum alkoxide (which is prepared by treating metallic aluminum with, for example, isopropyl alcohol, *sec*-butyl alcohol or *m*-cresol) is dissolved in anhydrous benzene, the purified fatty acid is added and the soap recovered by evaporation and purified by washing with anhydrous dioxane. The reaction is presumed to be (69)

$$Al + 3R'OH \rightarrow Al(OR')_3 + 3H \tag{2}$$

$$Al(OR') + 2HCOOR \rightarrow Al(OR')(COOR)_2 + 2R'OH \tag{3}$$

By this procedure aluminum alkoxide soaps have been prepared containing between 1.4 and 2.0 fatty acid groups per atom of aluminum. They are converted to the hydroxy soaps by treating with water.

$$Al(OR')(COOR)_2 + H_2O \rightarrow Al(OH)(COOR)_2 + R'OH \tag{4}$$

The existence of aluminum trisoaps was for many years a subject of controversy. Originally it was claimed that they could be produced by aqueous metathesis, but this now seems unlikely (2). Aluminum tridodecanoate can be prepared (27) by treating trimethylaluminum with pure dodecanoic acid in dry benzene, and trituration with dry, light petroleum ether. The product is a yellow amorphous powder, m.p. 94°, containing 9.9% Al_2O_3 (theoretical 8.1%).

A method of more general application (26, 58) is to treat 1 mole of freshly distilled aluminum isopropoxide with 3 moles of the doubly distilled fatty acid in dry benzene, reflux at 150°, distil off the residual benzene at reduced pressure and then heat the residue for 1 hour at 200° and 0.2 mm. pressure. This method is suitable for the soaps of aluminum, zirconium, titanium and other tri- and tervalent metals.

B. SOAPS BASED ON OTHER ACIDS

Heavy metal soaps based on acids other than the straight chain monocarboxylic acids that have been studied in solution include half-esters of dicarboxylic acids, xenyl carboxylates, alkyl sulfates and sulfonates and alkyl aryl sulfonates, as well as soaps of naphthenic acids, so called "mahogany acids" and other commercial materials which, because of their complex and generally unknown compositions, are not included in the present review.

Barium and lead 2-ethyl hexyl sebacates are obtained

(44), respectively, as a white porous solid and as a faint yellow glass (m.p. 80–81°) by adding 100% excess of an aqueous solution of the sodium soap to a solution of barium or lead nitrate, stirring for 2 hours, dissolving the precipitate in benzene and repeatedly extracting, first with barium or lead nitrate solution and then with water at a pH of 4.0, finally evaporating to dryness at reduced pressure.

Calcium xenyl octadecanoate is prepared (86) by dissolving xenyl octadecanoic acid in aqueous isopropyl alcohol, neutralizing with sodium carbonate, and then adding calcium chloride solution at a pH of 10.5. The gummy precipitate is freed from water by centrifuging, dissolved in benzene, refluxed under nitrogen and dried *in vacuo*.

Magnesium, calcium, and barium sulfonates are obtained (97) as white to yellowish powders by neutralizing an aqueous solution of the appropriate sulfonic acid with the solid oxide or hydroxide, extracting with ether and evaporating to dryness *in vacuo*. And barium dinonylnaphthalenesulfonate is prepared similarly (42) from dinonylnaphthalenesulfonic acid.

III. PHYSICAL PROPERTIES OF THE SOLUTIONS

A. SOLUBILITY

The soaps of the heavy metals are soluble in a wide variety of organic solvents and yield liquids, gels and dispersions with characteristic colloidal properties. The solubility depends on the temperature, on the metal involved and on the solvent employed. But the nature of the acid radical, its carbon chain length, degree of unsaturation, etc., are also of considerable importance.

A homologous series of zinc soaps (57) was only slightly soluble in toluene, xylene, nitrobenzene, etc., at room temperature, but at temperatures above about 85° there was a sudden and substantial increase in solubility. The critical solution temperatures increased with the chain length of the fatty acid concerned (Table I). But above the critical solution temperatures the solubilities of the soaps also increased with the chain lengths of the acids. These findings are in agreement with qualitative observations on other homologous series (47, 64, 67).

It is well established that unsaturation in the fatty acid radical increases the solubility; the octadecenoates (oleates) of the heavy metals are, without exception, more soluble than the corresponding octadecanoates (stearates). But there is little reliable information available on the part played in solubility by the metallic portion of the molecule. Nickel and manganese dodecanoates appear to be more soluble in toluene than calcium, cadmium, lead and silver dodecanoates (64); magnesium carboxylates appear to be more soluble in benzene than the corresponding cadmium soaps (67).

TABLE I (57)

CRITICAL SOLUTION TEMPERATURES OF ZINC SOAPS IN ORGANIC SOLVENTS

Solvent	Decanoate	Dodecanoate	Tetra-decanoate	Octa-decanoate
Toluene	86.0°	90.8°	93.0°	97.0°
Xylene	89.0	93.7	96.0	98.5
Octadecanol	...	...	108.0	104.0
Dodecanoic acid	...	...	114.0	113.0
Nitrobenzene	...	111.0	113.0	112.0

B. THE MICELLAR THEORY OF SOAP SOLUTIONS

The physical properties of solutions of heavy metal soaps in organic solvents can be interpreted in terms of the micellar theory, a micelle being here defined as an aggregate of three or more soap molecules existing in the liquid in thermodynamically stable equilibrium. While this theory was early applied to data on soaps and other amphipathic compounds in aqueous solution (32, 52, 60), it is only recently that attempts have been made to apply it quantitatively to heavy metal soaps in non-aqueous solvents.

Micelles can be detected in a liquid in a number of ways; if several techniques are employed in conjunction it is possible to obtain information on the number of molecules per micelle and on their shapes and sizes under specified conditions of temperature, concentration, etc. For example, cryoscopic measurements on dilute solutions of magnesium, zinc and aluminum dioctadecenoates in benzene (75) have shown that these soaps are still in the micellar form at concentrations below about 10^{-4} molar. In the range 10^{-2} to 10^{-4} molar the micelles appear to contain about three molecules.

Somewhat higher values are obtained for the numbers of molecules per micelle in a series of metal soaps based on saturated monocarboxylic acids (57, 64). These were studied in toluene, isopropyl alcohol and pyridine solution and micellar molecular weights were calculated from ebullioscopic data, obtained with a modified form of the Cottrell apparatus. The micellar molecular weights were found to increase with the concentration of the soap (Table II (57)).

However, extrapolation of the values to infinite dilution revealed a correlation between the number of molecules per micelle and the chain length of the fatty acid radical, the former rising as the latter decreased. Some typical data for a series of zinc soaps in toluene are given in Fig. 2 (64).

TABLE II (57)

EFFECT OF CONCENTRATION ON MICELLAR MOLECULAR WEIGHTS

Zinc dodecanoate			Zinc octadecanoate			Copper octadecanoate		
C^a	M	N	C	M	N	C	M	N
0.653	2310	4.98	0.938	3460	5.47	1.038	4040	6.41
1.335	2840	6.13	1.690	3400	5.38	1.647	4220	6.70
1.935	3040	6.56	2.650	3530	5.58	2.580	4470	7.10

[a] C = concn. in g./100 g.; M = micellar molecular wt.; N = no. of molecules/micelle.

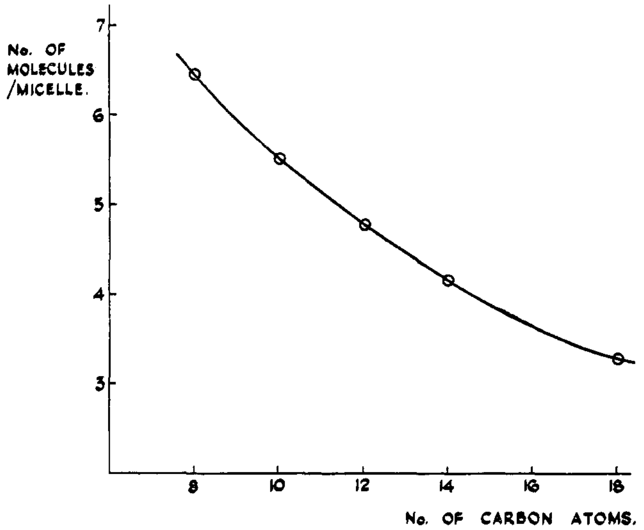


Fig. 2.—Effect of carbon chain length on number of molecules per micelle; zinc soaps in toluene (64) (reproduced by permission of the *Journal of the Chemical Society*).

Both viscosities and osmotic pressures have been used for the determination of micellar molecular weights. Sheffer (82) measured the viscosities and osmotic pressures at 30° of dilute benzene solutions of aluminum disoaps from the octanoate to the octadecanoate. The measurements were made in Ostwald-type viscometers and Fuoss and Mead osmometers; for the latter the number average molecular weight is given by the expression

$$\frac{\Pi}{C} = \frac{RT}{M_n} + \frac{RT}{v_1 d_2{}^2} ({}^1/{}_2 - \mu_1) C \qquad (5)$$

where v_1 is the partial molar volume of the solvent, d_2 is the density of the solute (taken as 1.02 to 1.07 (67)), M_n is the number average molecular weight, Π is the osmotic pressure, C the concentration and μ_1 is a constant for each soap–solvent system. It was found that in the concentration range 10^{-3} to 10^{-4} molar, the micelles of these soaps contained between 500 and 1000 molecules, a figure substantially higher than that obtained for aluminum dioctadecanoate (75) or for the carboxylates of the mono- and divalent metals (57, 64) over the same concentration range.

This tendency on the part of aluminum soaps to form larger micelles than the soaps of mono- and divalent metals is due presumably to the fact that they contain hydroxyl groups which, through hydrogen bonding, facilitate aggregation of the individual molecules. The observation that the micelles of the octadecenoate soaps are smaller than those of the soaps based on saturated monocarboxylic acids is consistent with their greater solubility in most organic solvents.

A method which recently has been applied with success to the determination of micellar volumes of heavy metal soaps is fluorescence depolarization (41, 86). This depends on the fact that when an oil-soluble dye, such as Rhodamine B, is added to a solution in which micelles are present, there is a marked enhancement in the fluorescence of the dye when the solution is illuminated with light of a particular wave length, *e.g.*, 546 mμ. This fluorescent emission is polarized by an amount p, given by the expression

$$p = (I_z - I_x)/(I_z + I_x) \qquad (6)$$

in which I_x and I_z are the intensities of fluorescence observed in planes normal to the x- and z-axes, respectively, when the light entering the solution in a direction parallel to the x-axis has its electric vector oriented parallel to the z-axis.

From observations of the degree of polarization of the emitted light and by substitution into eq. 7, originally derived by Perrin (70), it is possible to obtain an estimate of the volume, V, of the micelles

$$V = \left(\frac{1}{p_0} - \frac{1}{3}\right)\frac{\tau RT}{\eta}\left(\frac{pp_0}{p_0 - p}\right) \qquad (7)$$

In this equation η is the viscosity of the solution, T is its absolute temperature, p_0 is the polarization of an immobilized dye molecule and is determined experimentally (for Rhodamine B, p_0 is approximately 0.5), τ is the average life of the dye molecule when in the excited state and is obtained by comparing the efficiency of the fluorescence process in the system under study with the efficiency in a system for which τ has been measured by other means. The volume, V, that is obtained is that of a sphere which, hydrodynamically, would be equivalent to the micelle. If measurements also are made of the viscosity (34) or streaming birefringence (18) of the system, an estimate can be made of the shapes of the micelles and the two sets of data then yield a value for the number of molecules per micelle.

Using these techniques it has been shown that the number of molecules per micelle for calcium xenyl octadecanoate in benzene varies between about 20 and about 1000 depending on the amount of water present in the system. In contrast, the dinonylnaphthalenesulfonates of magnesium, calcium, barium, zinc and aluminum contain between 9 and 14 acid residues per micelle (43).

Geometrical factors play an important role in controlling the shapes and sizes of the micelles of the heavy metal soaps in organic solvents. It can be shown that not more than 50 molecules can be accommodated in a spherical micelle if the volume of each molecule is taken as 500 Å.^{3} and its length as 20 Å. The micelle itself must be spherical if it contains less than 50 molecules; otherwise the polar core would be inadequately shielded from the surrounding liquid by the non-polar tail groups of the molecules.

The presence in the core of dipole–dipole interaction forces causes a spherical micelle to deform into a prolate or oblate spheroid when more than about 50 molecules are present. But the former is more commonly observed since there is less thermodynamic free energy associated with a prolate spheroid than with an oblate spheroid of equal volume. The ratio of the major axis to the minor axes of the micelle will increase with the number of molecules that it contains; the final stage is a rod-shaped micelle in which the ratio of the axes can vary from about 5 (36) to about 80 (82) or more if, for example, traces of water also are present.

C. CRITICAL MICELLE CONCENTRATION

The concept of a critical concentration below which the micelle dissociates into individual molecules has not been extensively applied to systems of the type now being considered. This is because the critical micelle concentrations, if they exist at all in such systems, are extremely low. Most of the methods (60) available for their determination are insensitive and yield equivocal results. An exception is the fluorescence dye method (already discussed) which has been applied successfully to the determination of critical micelle concentrations as low as 10^{-3} to 10^{-5} molar (43, 44) and even, in some cases, to 10^{-7} molar (41, 42).

At the critical micelle concentration

$$nS \rightleftarrows S_n \tag{8}$$

where S_n and S refer to the soap micelle and to the monomer, respectively, and n is the number of molecules per micelle.

Dissociation of the micelle into individual molecules will occur if, in the process, the total free energy of the system is decreased. An estimate can be made of the magnitude of the decrease if a simple geometrical model is adopted for the micelle and if certain assumptions are made about the shapes, sizes and physical properties of the individual molecules of the soap.

In one such treatment (75) it is assumed that each soap molecule consists of a spherical head group, radius R, containing a dipole, which is joined to one or more cylindrical tail groups of length L and radius r, consisting of the hydrocarbon portion of the fatty acid residue. If half the surface of the head group is covered by tail groups, the exposed surface of each head group is $2\Pi R^2$, while the exposed surface of each tail group is $2\Pi rL$. When the molecules are in the micellar form, which is assumed to be spherical, the head groups are completely shielded from the solvent, but when they are individually dispersed the whole of the exposed surface of the heads and of the tails is in contact with solvent.

It is assumed that three main factors contribute to the energy change which occurs when a micelle dissociates.

First there is a change in the interfacial energy of the molecules. For n of these in the micellar state the interfacial energy is

$$E_{\text{micelle}} = 2\Pi rLn\gamma_{\text{tt}} + 2\Pi R^2 n\gamma_{\text{hh}} + X \tag{9}$$

where γ_{tt} is the cohesional energy of the tails, γ_{hh} is cohesional energy of the heads and X is a term which allows for the fact that a certain proportion of the hydrocarbon surface is in contact with the solvent. After dissociation the interfacial energy becomes

$$E_{\text{monomer}} = 2\Pi rLn\gamma_{\text{ts}} + 2\Pi R^2 n\gamma_{\text{hs}} \tag{10}$$

where γ_{ts} is the interfacial energy between a tail group and the solvent and γ_{hs} is the interfacial energy between a head group and the solvent. The change, ΔE, in interfacial energy then may be written

$$\Delta E = 2\Pi rLn(\gamma_{\text{ts}} - \gamma_{\text{tt}}) + 2\Pi R^2 n(\gamma_{\text{hs}} - \gamma_{\text{hh}}) - X \tag{11}$$

The second factor which contributes to the energy change is dipole–dipole interaction. For n dipoles in the micellar state (indicated by the subscript m), the interaction energy W_{m}, may be expressed by

$$W_{\text{m}} = n\mu_{\text{m}}^2/\gamma_{\text{m}} \tag{12}$$

where μ is the dipole moment and γ is the polarizability of the soap. When the same number are uniformly dispersed in a non-polar solvent, the total dipole interaction energy is (14)

$$W = \frac{n\mu^2(\epsilon_{12} - 1)}{3\gamma} \tag{13}$$

where ϵ_{12} is the dielectric constant of the solution. Thus the change, ΔW, in dipole interaction energy which occurs on dissociation is

$$\Delta W = \frac{n\mu^2(\epsilon_{12} - 1)}{3\gamma} - \frac{n\mu_{\text{m}}^2}{\gamma_{\text{m}}} \tag{14}$$

The third factor which is involved is hydrogen or similar bonding, which is believed to arise in the micelle as a result of the complex structures of heavy metal soaps. Denoting the change in hydrogen bonding energy between the micellar and monomeric forms by ΔH, the total energy change, ΔE_{t}, which occurs when the micelle dissociates is

$$\Delta E_{\text{t}} = \Delta E + \Delta W + \Delta H \tag{15}$$

Although it is possible to ascribe fairly precise values to the dimensions of the head and tail groups of the molecules (1, 46), to the numbers that are associated into micelles and to the latter's polarizabilities and dipole moments, the values of the remaining parameters are not known with sufficient accuracy for it to be possible to solve equation 15 quantitatively. Nevertheless, by making a number of further assumptions, it can be shown that ΔE_{t} has an order of magnitude somewhere between 10^{-13} and 10^{-14} erg for soaps having a carbon chain of 10 or more atoms. Since this is comparable to the kinetic energy of an average molecule at room temperature, the micellar form of the soap has approximately the same stability as the monomeric form. As a result the micelles continue to exist even at extremely low concentrations.

This treatment is not claimed to be more than semi-

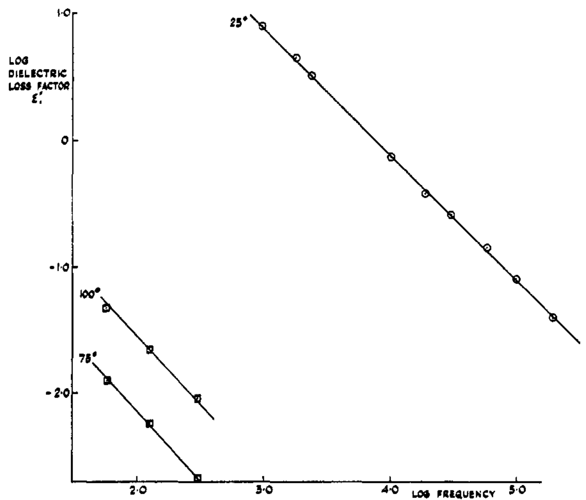


Fig. 3.—Effect of frequency on dielectric loss factor (65, 66): □, 0.31% solution of lead octadecanoate in liquid paraffin; ○, 0.31% solution of calcium octadecanoate in toluene.

quantitative and it is clearly open to a number of criticisms. For example, in cases where the micelle contains only a few molecules there may be insufficient tail groups available to shield the head groups completely from the surrounding liquid and equation 11 is only approximately obeyed. On the other hand, when the micelle contains hundreds or even thousands of soap molecules, geometrical considerations show that it cannot be spherical. The expression for the dipole–dipole interaction in the micellar form (equation 12) is strictly valid only for the case of two dipoles under particular conditions; its applicability to a micelle containing many dipoles is questionable.

Despite these shortcomings the analysis is useful since it gives some indication of the nature and magnitude of the forces involved in micelle stabilization in organic solvents.

D. SOLUBILIZATION

The ability of the heavy metal soaps to solubilize compounds such as oil-insoluble dyes, acids of high molecular weight, certain alkali soaps, water, etc., which would normally be insoluble in organic solvents, is due to the presence of the micelles. In this respect the heavy metal soaps in organic solvents behave analogously to the alkali metal soaps in water, which solubilize at least a proportion of a water-insoluble compound by enclosing its molecules in the cores of the micelles (45, 53). This enclosure causes the micelles to swell; for example, when a trace of water is added to benzene solutions of certain xenyl octadecanoates the number of molecules per micelle increases by a factor of about 10 (4, 41, 86). The change in size frequently is accompanied by a change in shape and this can have a pronounced effect on the physical and mechanical properties of the system as a whole. Thus aluminum alkoxide soaps, which when perfectly dry dissolve in benzene, etc., to form clear, limpid liquids, exhibit a marked increase in viscosity when small amounts of water are added and eventually develop a gel structure (55, 74). This is believed to be due to a change in the shapes of the soap micelles from small spheres to long flexible rods or threads, which can then interlink to form a three dimensional network having strongly elastic properties.

Other of the mechanisms of solubilization, which operate in aqueous soap systems, may also contribute to solubilization in non-aqueous systems. There is evidence (5, 36) that the solubilization of carboxylic acids and of their sodium soaps by soaps of the heavy metals may involve the formation of mixed micelles in which the molecules of the polar–non-polar additive are oriented between those of the heavy metal soap. This slightly increases (or may even sometimes slightly decrease) the size of the micelles, but has little or no effect on their shape.

IV. ELECTRICAL PROPERTIES OF THE SOLUTIONS

A. CONDUCTANCE AND DIELECTRIC LOSS

Investigations have been made of the electrical properties of the solutions of heavy metal soaps in organic solvents, the subject being of interest to electrical engineers and others concerned in the transmission of electric power.

When mineral or other insulating oils are maintained at a high temperature and under electric stress in contact with metals such as copper, iron and aluminum in cables, transformers, capacitors, etc., small amounts of the metal soaps are produced in solution which adversely affect the insulating properties of the oil by raising its specific conductance, σ, and its dielectric loss factor, ϵ'' (91).

These quantities have been measured over a range of temperatures and frequencies using dilute solutions of a number of heavy metal soaps in a variety of solvents (9, 63, 65, 66, 77). The data show that in many cases the dielectric loss is inversely proportional to the frequency, provided the measurements are made at low frequencies ($<10^4$ cycles/sec.) when relaxation effects associated with dipoles or dipolar aggregates do not arise (20). The whole of the loss is then due to direct current conductivity, the carriers being micellar ions whose ionic charge is localized in the interior of the aggregates. For these systems the specific conductance can be related to the dielectric loss factor by equation 16

$$\sigma = 5.5 \times 10^{13}\epsilon'' f \text{ ohm}^{-1} \text{ cm.}^{-1} \qquad (16)$$

where f is the frequency in cycles/sec. at which the measurements have been made. Typical data on systems exhibiting this type of behavior are reproduced in Fig. 3 (65, 66) and Table III (63, 65, 66) gives values

TABLE III (63, 65, 66)

EQUIVALENT CONDUCTANCES OF SOAP SOLUTION

Soap	Solvent	Concn., molar	Temp., °C.	Equiv. conductance, ohm^{-1} cm.^{2}
Magnesium octadecenoate	Toluene	0.004	25	2.00×10^{-5}
Calcium octadecanoate	Nujol	.032	200	4.54×10^{-6}
Calcium octadecenoate	Toluene	.004	25	4.01×10^{-4}
Zinc octadecanoate	Nujol	.031	100	1.87×10^{-8}
Zinc octadecenoate	Toluene	.004	25	7.50×10^{-7}
Copper octadecanoate	Nujol	.033	100	1.02×10^{-8}
Copper octadecenoate	Toluene	.004	25	3.25×10^{-6}
Lead octadecanoate	Nujol	.003	100	2.35×10^{-7}
Lead octadecenoate	Toluene	.004	25	7.50×10^{-6}
Aluminum didodecanoate	Toluene	.057	25	5.00×10^{-7}
Aluminum tridodecanoate	Toluene	.016	25	6.51×10^{-6}

of the equivalent conductances of a number of metal soaps under conditions when equation 16 holds.

There are circumstances, however, when even at these low frequencies, equation 16 fails. This is shown in Fig. 4, where it is seen that there is considerable departure from linearity in the plot of log ϵ'' against log f for both calcium and lead octadecanoates in liquid paraffin at 90° and for aluminum didodecanoate in toluene at 25°.

For every soap–solvent system there is a particular temperature (in the above cases 90 and 25°, respectively) below which the soap commences to precipitate from solution. The precipitate may consist of a very small, slow settling particles, which impart an opalescent appearance to the liquid, or of large, flocculated particles, which settle rapidly, leaving a clear, supernatant layer. In other cases, *e.g.*, aluminum soaps and certain metal octadecenoates, the precipitate may take the form of a stable, transparent gel in which the particles of the soap are of colloidal dimensions.

The onset of precipitation has a pronounced effect on the dielectric loss of the system, which frequently rises to a maximum value at the precipitation temperature, Fig. 5 (66). This is interpreted as due to a second mechanism coming into operation in addition to the d.c. conduction.

The observed dielectric loss factor, ϵ''_{obs}, is regarded as consisting of two parts (17)

$$\epsilon''_{\text{obs}} = \epsilon''_{\text{dc}} + \epsilon''_{\text{x}} \qquad (17)$$

where ϵ''_{dc} is due to direct current conduction and is given by equation 16 and ϵ''_{x} is the loss arising from the heterogeneous nature of the dielectric.

Considering this as a system of small, spheroidal particles in a surrounding continuum, the dielectric loss factor, ϵ''_{x}, can be expressed by (84)

$$\epsilon''_{\text{x}} = \frac{\epsilon'_1 N w \tau}{1 + w^2\tau^2} \qquad (18)$$

where

$$\tau = \frac{\epsilon'_1(n-1) + \epsilon'_2}{4\Pi\sigma_2} \qquad (19)$$

and

$$N = \phi \frac{n^2\epsilon'_1}{\epsilon'_1(n-1) + \epsilon'_2} \qquad (20)$$

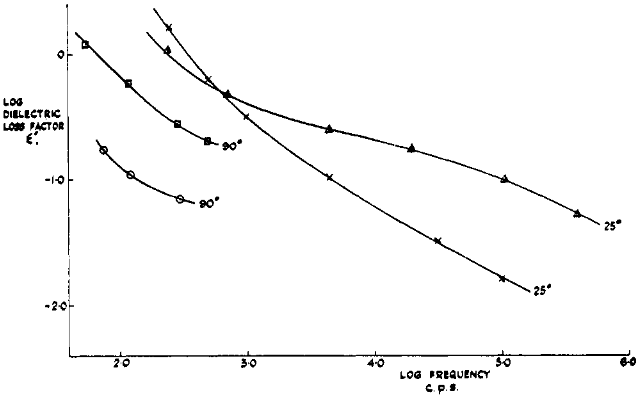


Fig. 4.—Effect of frequency on dielectric loss factor (63, 66): ○, 0.31% solution of lead octadecanoate in liquid paraffin; □, 2.45% solution of calcium octadecanoate in liquid paraffin: △, 0.44% solution of aluminum didodecanoate in toluene; ×, 4.86% solution of aluminum didodecanoate in toluene.

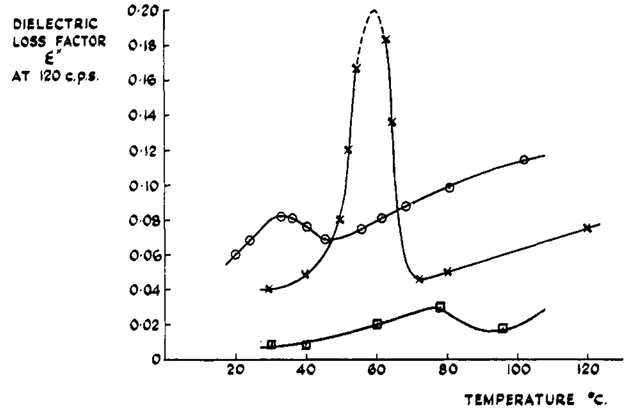


Fig. 5.—Effect of temperature on dielectric loss factor at 120 cycles per second (66): □, 3.84% solution of copper octadecanoate in xylene; ×, 3.39% solution of lead octadecanoate in xylene—cooling rate 1° per minute; ○, 2.43% solution of zinc octadecanoate in liquid paraffin.

ϵ'_1 and ϵ'_2 are the dielectric constants of the continuous and disperse phases, respectively, σ_2 is the latter's conductance, w is the angular frequency and ϕ is the volume fraction of the disperse phase.

It has been seen earlier that a prolate spheroidal soap micelle is a more probable form than an oblate spheroidal one. A prolate spheroid (with axes a, b and c) in which $a > b = c$ has a value of n given by

$$n = \frac{a^2}{b^2(\ln(2a/b) - 1)} \qquad (21)$$

All the quantities in equation 17 to 21, with the exception of n, are now known and it is therefore possible to calculate the ratio of the axes of the spheroidal particles of the soap with reasonable accuracy.

This type of analysis has been applied to solutions of metal soaps in liquid paraffin, toluene and xylene; the value obtained for the axial ratio, a/b (where $b = c$), of lead octadecanoate in liquid paraffin at 90°, the temperature of maximum loss, is ~17 (66).

B. DIPOLE MOMENTS

Measurements have been made of the dielectric constants of solutions of the heavy metal soaps at higher frequencies, up to 10^6 cycles/sec., in order to derive values for the dipole moments of the soaps (6, 7, 67, 74, 75). It is customary, when the dilute solution method is being employed (88), to use benzene as the solvent. However, at ordinary temperatures relatively few of the soaps of the heavy metals are sufficiently soluble in benzene for dielectric constants, densities and refractive indices to be measured over a range of concentrations; this explains why, with minor exceptions (7, 67), the bulk of the published results refer to the octadecenoates of the heavy metals, these being more readily soluble in benzene than the soaps based on the saturated acids.

The dipole moments can be calculated from the experimental data in several ways. Using the Debye equation

$$P_{12} = P_1c_1 + P_2c_2 = \frac{(\epsilon_{12} - 1)}{(\epsilon_{12} + 2)} \frac{M_1c_1 + M_2c_2}{d_{12}} \qquad (22)$$

in which P denotes the polarization, c the mole fraction, ϵ the dielectric contant, M the molecular weight and d the density, with the subscripts 1, 2 and 12 referring, respectively, to the solvent, solute and solution, the values of P_2 are extrapolated to infinite dilution to give $P_{2\infty}$, which is then substituted into equations 23 to 25.

$$\mu P = P_{2\infty} - P_{\mathrm{D}} \qquad (23)$$

$$P_{\mathrm{D}} = 1.05 \frac{(n_2^2 - 1)}{(n_2^2 + 2)} \frac{M_2}{d_2} \qquad (24)$$

$$\mu = 0.012812[293(P_{2\infty} - P_{\mathrm{D}})]^{1/2} \qquad (25)$$

n is the refractive index for the sodium D line, and T is the temperature at which the measurements have been made.

An alternative (and generally more convenient) method is to use equation 26

$$P_{2\infty} = M\left[\frac{2\alpha\nu_1}{(\epsilon_1 + 2)^2} + \frac{(\epsilon_1 - 1)}{(\epsilon_1 + 2)}\right](\nu_1 + \beta) \qquad (26)$$

in which ν is the reciprocal of the density, α and β are the limiting values of $\partial\epsilon/\partial\omega$ and $\partial\nu/\partial\omega$ at zero concentration and ω is the weight fraction; then substitute as before into equation 23 to 25. Other methods that have been used for determining $P_{2\infty}$ for soaps include those of Hoecker (35), Guggenheim (29) and Hedestrand (33).

Besides the differences arising from the methods used in the extrapolation itself, there are other reasons why the values of the dipole moments obtained by different workers differ from each other, in some cases by quite large amounts, as shown in Table IV. Some workers have taken M as the formula molecular weight of the soap, others as its micellar molecular weight at very low concentrations. In some cases n has been taken as the refractive index of the solid soap; in others it has been derived from solution data, using the expression

$$\frac{(n_1^2 - 1)}{(n_1^2 + 2)} \nu_1\omega_1 + \frac{(n_2^2 - 1)}{(n_2^2 + 2)} \nu_2\omega_2 = \frac{(n_{12}^2 - 1)}{(n_{12}^2 + 2)} \nu_{12} \qquad (27)$$

The figure of 1.05 in equation 24, which is based on the assumption that the atomic polarization is 5% of the electronic polarization, is not necessarily applicable to the soaps of the heavy metals and other values have been used. Of greater significance is the fact that the soaps employed by the different investigators often have differed considerably in their chemical composition. The aluminum dioctadecenoate used in reference 67 contained about 2.0 molecules of octadecenoic acid per atom of aluminum, that in reference 74 about 2.2 molecules. Moreover, the various specimens undoubtedly have contained different amounts of adsorbed or bonded water, which would affect the values of the dipole moments. Despite this, it is posible to arrive at some general conclusions from the data in Table IV.

TABLE IV

DIPOLE MOMENTS

Metal soap	Dipole moment, D.
Magnesium hexadecanoate	3.32 (67)
Magnesium octadecanoate	3.67 (67)
Magnesium octadecenoate	2.96 (67), 1.66 (6), 2.19 (74), 4.28 (75)
Calcium octadecenoate	4.49 (6)
Zinc octadecenoate	0.29 (6), 1.97 (75)
Copper octadecenoate	1.20 (6)
Lead octadecenoate	4.29 (6)
Cadmium octadecanoate	4.80 (67)
Cadmium octadecenoate	4.37 (67)
Nickel octadecenoate	2.67 (6)
Chromium tri(?)octadecenoate	4.32–4.63 (7)
Iron tri(?)dodecanoate	1.70–2.33 (7)
Iron tri(?)octadecanoate	3.03–3.46 (7)
Iron tri(?)octadecenoate	2.69–2.90 (7)
Aluminum dibutanoate	3.24 (67)
Aluminum dipentanoate	3.44 (67)
Aluminum didodecanoate	4.06 (67)
Aluminum ditetradecanoate	4.42 (67)
Aluminum dihexadecanoate	5.22 (67)
Aluminum dioctadecanoate	5.49 (67)
Aluminum monoöctadecenoate	2.20 (74)
Aluminum dioctadecenoate	2.59 (36), 4.35 (75), 4.29 (67), 2.56–3.11 (48)
Aluminum tri(?)octadecenoate	3.08–3.90 (7)

Considering the three homologous series of the magnesium and aluminum disoaps (67) and of the iron tri(?)soaps (7), it is seen that the dipole moments increase with the chain lengths of the fatty acids involved. Normally in an homologous series, the dipole moments rapidly attain a constant value which is characteristic of the polar grouping. In the above cases, however, the dipole moments have been calculated on the basis of the formula molecular weights of the soaps. There are no reliable data available on their micellar molecular weights at low concentrations, but since it is known generally (64, 82) that micellar molecular weights decrease as the carbon chain of the soap is increased, it may be inferred that the micellar molecular weights would increase along the homologous series less rapidly than the formula molecular weights. Employment of the former in the calculations would thus tend to equalize the dipole moments of successive members and reconcile the behavior of the soaps with that of other homologous series.

Considering next the octadecenoates of the heavy metals to see whether there is any correlation between the dipole moment and the nature of the metal concerned, none is immediately apparent. Metals in the same vertical column of the periodic table might be expected to exhibit a gradual increase in dipole moment as their atomic number increased, since the ability of the elements to form covalent bonds increases from top to bottom and from left to right across the periodic table. While the dipole moments of calcium and cadmium and of aluminum octadecenoates are greater than that of magnesium octadecenoate, the moment of the zinc soap is abnormally low. Moreover, the moments of the iron and nickel soaps are certainly not greater than that of the aluminum soap.

The absence of a correlation presumably is due to the dipole moment being a vector quantity whose magnitude is also a function of the geometry of the soap molecules. Data on the molecular shapes of the majority of the soaps listed in Table IV are not available. But since coördination compounds generally exhibit a variety of shapes, *e.g.*, planar, tetrahedral, trigonal, bipyramidal, octahedral, etc. (22, 83), depending on the coördination number of the particular metal concerned, it may be assumed that the different soaps will also have fundamentally different structures. This explains the apparent lack of pattern in the values of the dipole moments.

V. MECHANICAL PROPERTIES OF THE SOLUTIONS

A. VISCOSITY

Heavy metal soaps in organic liquid exhibit a wide range of rheological properties. At low concentrations and high temperatures they are mobile liquids whose viscosities are approximately Newtonian. They become increasingly viscous and non-Newtonian as the concentration of the soap is increased and the temperature is reduced; in many instances the solutions also develop elastic properties. Further increase in concentration and decrease in temperature leads to precipitation of the soap, frequently in the form of a viscoelastic gel, in which the soap exists as long interlinked, thread-like micelles. In other cases the soap is precipitated as a paste or pseudo-gel consisting of crystalline, or microcrystalline particles (47).

Measurement of the viscosity of a series of aluminum carboxylates in benzene solution at 25° using an Ostwald viscometer (2, 28) showed that there was a steady increase in the viscosity as the chain length of the fatty acid was increased. This can be shown by extrapolating the specific viscosity, η_{sp} to zero concentration, Application of the Staudinger equation

$$(\eta_{sp}/c)_{c \to 0} = KM \qquad (28)$$

in which K is approximately 2×10^{-4}, yields values for the molecular weights of the soaps, M, in the region of 300 to 400, indicating that they are monomeric at extreme dilution, a finding which is at variance with that of other investigators (75, 82).

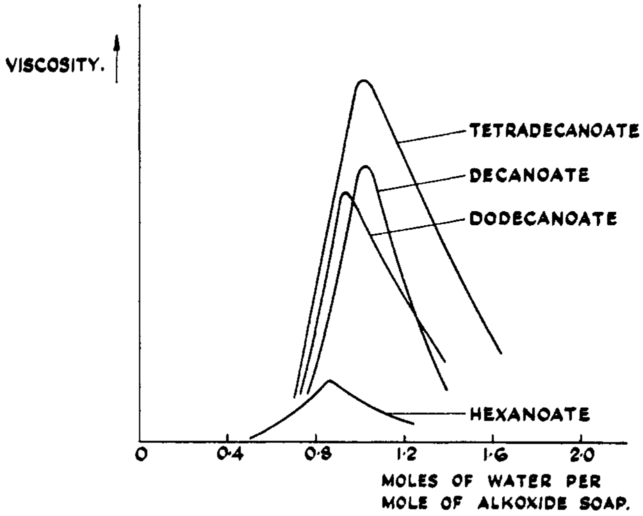


Fig. 6.—Effect of added water on viscosities of approximately 1% solutions of aluminum disoaps in benzene.

A 1 to 2% solution of aluminum didodecanoate in benzene is markedly non-Newtonian, the viscosity decreasing by a factor of 10 as the rate of shear is increased from about 20 to about 400 sec.$^{-1}$. But pronounced changes in the viscosity occur on the addition of small amounts of other materials. Cresol, phenols and petroleum ether reduce the viscosity; but if water is present in the proportion of about 1 mole of water to 1 mole of the alkoxide soap, there is a considerable increase in viscosity, as shown in Fig. 6 (55). This is ascribed to the formation of hydrogen bonds which facilitate interlinking of the soap micelles to form a network structure (26, 54, 55).

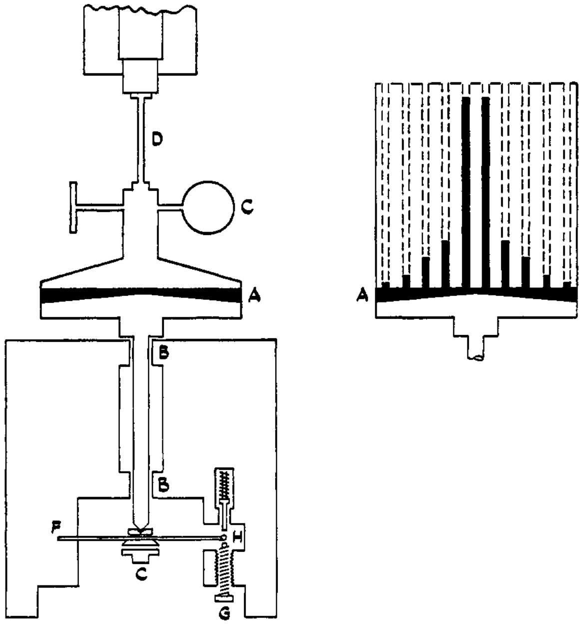
B. VISCOELASTICITY

While the viscosity yields some information on the strain which develops when a particular mechanical stress is applied to the system, the viscosity concerns only two terms of a general relationship between stress and strain, applicable to many rheological bodies. This can be formulated

$$\Pi_0 P + \Pi_1 \dot{P} + \Pi_2 \ddot{P} + \ldots = \sigma_0 S + \sigma_1 \dot{S} + \sigma_2 \ddot{S} + \ldots \qquad (29)$$

where P is the stress, $\dot{P}$, etc., are the time derivatives of stress, S is the strain, $\dot{S}$, etc., are the time derivatives of strain and Π and σ are mechanical constants for the system. The Newtonian viscosity

$$\eta = (P/S) \qquad (30)$$



KEY

A	CONICAL GAP.
B	BEARINGS.
C	CAPACITY GAUGES.
D	TORSION WIRE.
F	SPRING.
GH	SPRING, SENSITIVITY CONTROL.

Fig. 7.—Roberts–Weissenberg rheogoniometer.

and the Hookian elasticity

$$G = (P/S) \tag{31}$$

are particular cases of this general stress–strain relationship.

There are various experimental methods that can be used in principle for determining the values of the constants in equation 29, thereby enabling a full description to be given of the rheological properties of the material in question. They include sinusoidal techniques, transient techniques, techniques based on laminar flow, high stress techniques, etc. (24, 39, 92). The goniometry of continuous laminar shear, *i.e.*, the measurement of the distribution of stresses and strains within the flowing material at every instant of time and at every point in space around the full solid angle of directions, has been usefully applied to the study of the rheology of organic solutions of the heavy metal soaps (72, 79, 81).

An apparatus, termed the Roberts–Weissenberg rheogoniometer, is employed (Fig. 7) (39, 40, 99). It consists of a slide (not shown) which is mounted vertically on a steel base, both being part of a precision lathe which is driven by a variable speed motor.

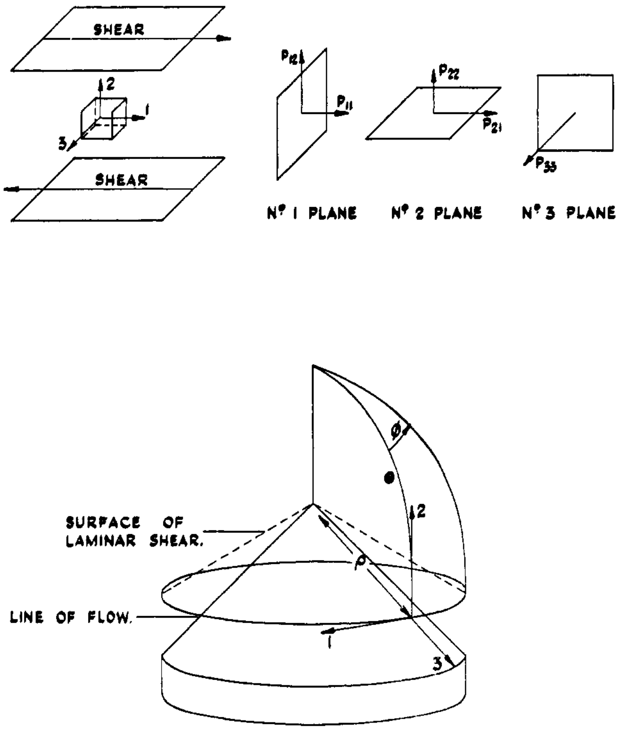


Fig. 8.—(a) Resolution of pressures at a point in laminar shearing motion. (b) Coördinate system.

The material to be tested is contained in the gap (A) between a stationary upper plate and a conical lower plate which can either be rotated continuously or subjected to an oscillatory movement with a variable amplitude, or given a continuous rotation on which is superimposed the oscillatory motion. The gap itself is conical and by having the angle of the cone less than 4°, the rate of shear at all points in the gap is kept constant to within ±2%.

The upper plate can take two forms. In the earlier design it consisted of a crown glass cylinder fused to a rectangular prism of the same material, through which passed ten equally spaced capillary tubes with a diameter of 3 mm. In the later design the upper plate is prevented from moving in a vertical direction, though it is free to rotate horizontally, while the lower plate is now attached to the driving motor *via* a diaphragm which leaves it free to move slightly in a vertical direction, though still ensuring a rigid rotational movement.

The flowing liquid exercises at any point and across any one plane a pressure whose components normal and tangential to the plane may be individually measured. Each point in the plane is located in the flow pattern by spherical polar coördinates whose origin is the apex of the conical gap and the planes themselves are oriented at each point by means of trirectangular coördinates of which the number 1 direction is taken along the streamlines of flow, the number 3 direction is perpendicular to it and in the plane of shear, with the number 2 direction perpendicular to 1 and 2 (Fig. 8).

The P_{22} pressure at any point is obtained directly from the height of the liquid in the capillary (in the earlier design) or from the total downward force exerted on the lower plate (in the later design). The P_{33} pressure at the same point is measured by balancing it against the pressure exerted by a Newtonian liquid such as mercury, and if P_{33} is then measured at various radii, r, from $r = 0$ at the center of the gap to $r = R$ at the periphery, a value is obtained for $\partial P_{33}/\partial \ln (r/R)$

Substitution into the classical equation for the equilibrium or forces

$$\frac{\partial P_{33}}{\partial \ln (r/R)} + 2P_{33} - (P_{11} + P_{22}) = 0 \qquad (32)$$

yields P_{11} at the point in question.

The P_{12} pressure at this point, which is numerically equal to P_{21}, is measured by balancing the tangential stress exerted on the upper plate against a calibrated spring. Employing the relationship

$$\eta = P_{12}/\dot{S}_{12} \qquad (33)$$

where $\dot{S}_{12}$ is the rate of shear in the gap, gives the apparent viscosity, η, of the liquid.

Its mechanical properties now can be expressed in terms of four parameters, defined by equations 34–37 (100, 101).

$$\gamma \equiv (P_{12})^2/(P_{11} - P_{22}) \qquad (34)$$

$$\mathrm{C} \equiv (P_{11} - P_{22})/P_{12} \qquad (35)$$

$$\tau \equiv (P_{11} - P_{22})/P_{12}\dot{S}_{72} \qquad (36)$$

$$\eta_{\max} \equiv \sqrt{1 + [(P_{11} - P_{22})/2P_{12}]^2} \qquad (37)$$

γ, which has the dimensions of dynes/cm.^{2}, is termed a modulus of rigidity; τ, which has the dimensions of seconds, is termed a relaxation time; C is a dimensionless quantity which may be thought of as a measure of the amount of energy directly recoverable when the stress is rapidly withdrawn from the elastic liquid undergoing continuous shear; $\eta_{\max}$ is an idealized viscosity which would be obtained if the directions of the stress and strain in the plane of shear coincided exactly and if the whole of the tangential stress were thus effective in overcoming the viscous resistance.

Measurements made on a 3% (72) and on a 7% (39, 81) solution of aluminum didodecanoate in petroleum ether have shown that the apparent viscosity of the material falls as the rate of shear is increased, but that the value of $\eta_{\max}$ remains sensibly constant up to rates of shear of about 10 sec.$^{-1}$ (Fig. 9). As the rate of shear is increased up to 30 sec.$^{-1}$ γ and τ fall to about half their initial value, but C increases by a factor of about four (similar results have been obtained on solutions of polymethyl methacrylate in toluene and on sodium and potassium octadecenoate soaps in aqueous electrolytes (71)).

C. GEL STRUCTURE

Attempts have been made to interpret these results in terms of the micellar structures of the soap gels (50, 51). The micelles are assumed to be interlinked at a number of junction points, which are continually breaking and reforming. Defining a junction point age distribution function by the statement that $N(t)dt$ is the number of junction points in unit volume of the gel which are formed in the interval t and still exist at the end of it, it is found that the second-order moment, N_2, can be related to the measured quantities γ, C and $\dot{S}_{12}$ by the expression

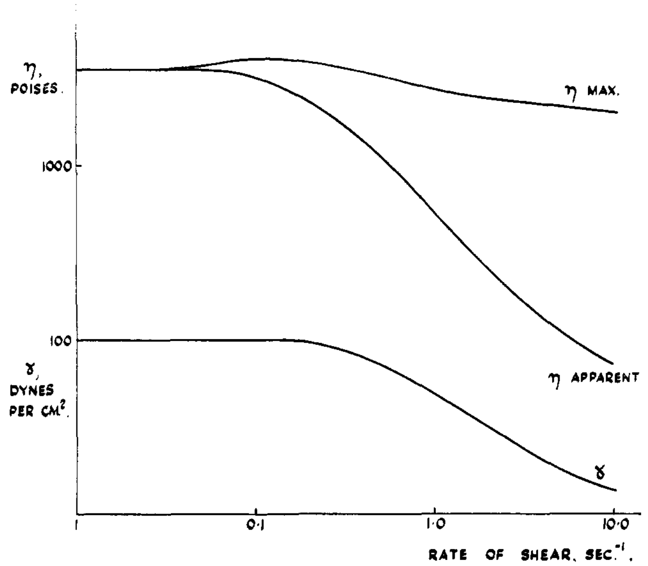


Fig. 9.—Viscosity and elasticity as a function of the rate of shear; 7% solution of aluminum didodecanoate in petrol with ethoxy ethyl alcohol (39) (reproduced by permission of the Academic Press).

$$\gamma C^2 = skTN_2(Tc)\dot{S}_{12}^2 \qquad (38)$$

where N_2 is a function of the temperature T and the concentration c, and is measured in sec.^{2} cm.$^{-3}$, s is approximately 1 and kT is about 4×10^{-14} erg at room temperatures.

Applying this expression to the data on the 3% solution of aluminum didodecanoate, it is found that N_2 is 10×10^{13} sec.^{2} cm.$^{-3}$ when the rate of shear is 10 sec.$^{-1}$ and 5×10^{13} sec.^{2} cm.$^{-3}$ when the rate of shear is 20 sec.$^{-1}$ (72).

If it is now assumed that the dissociation of junction points takes place exponentially with time and that there is a single relaxation time λ, one can write

$$N_1(Tc) = \lambda N_0(Tc) \qquad (39)$$

$$N_2/N_1 = 2\lambda \qquad (40)$$

in which N_1 is the first-order moment of the junction point age distribution function and N_0 is the zero-order moment. Since the latter has the dimensions of cm.$^{-3}$, it can be identified as the actual number of junction points per unit volume of the gel at any instant of time.

Although the parameter τ, as measured on the rheogoniometer, has the dimensions of seconds, it has not

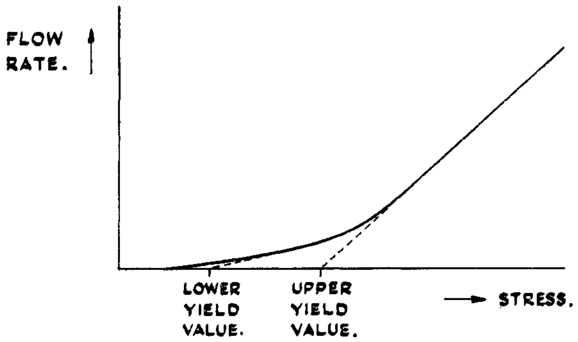


Fig. 10.—Flow curve of a grease.

been established that τ and λ are the same or, indeed, that there is necessarily any connection between them and it is not, therefore, possible to calculate N_0 from the above experimental data. However, it should be possible, in principle, to obtain a value for λ by subjecting the system to vibrational testing, either in the latest design of rheogoniometer (80), or in other types of vibrational equipment (24, 92) and this would yield valuable information on the detailed structure of the soap gel.

VI. Heavy Metal Soaps in Greases

A. GREASES

A grease consists of a mineral oil which has been gelled or thickened by the addition of a soap. Most commercial greases are based on the soaps of the alkali and alkali earth metals and of those of lead and aluminum. But greases containing soaps of other heavy metals such as zinc, mercury, manganese, iron, cobalt and nickel have been prepared and used for a variety of purposes (12, 48, 49).

The grease usually contains between 5 and 25% of one or more of the soaps; other materials which are frequently incorporated include water, glycerol, naturally occurring waxes, esters and glycerides of fatty acids, inorganic fillers, oxidation and corrosion inhibitors, etc. This wide variation in their chemical composition is reflected in the diversity of the physical properties of commercial greases.

Greases are employed primarily as lubricants and, to a lesser extent, as protective coatings. The properties which are of particular interest and which have therefore received the greatest attention are the rheological properties (10, 15, 19, 38, 56, 89, 90), texture (8, 23, 95), thermal and chemical stability (89, 96), adhesion characteristics (25) and ability to withstand wear under both normal and extreme conditions of pressure and temperature (13, 59, 62, 89, 93, 94).

B. RHEOLOGICAL PROPERTIES

The rheological properties are measured on a variety of instruments. They include viscometers, plastometers, penetrometers, elastometers, etc. (12, 61, 85, 89). But the different instruments frequently are measuring fundamentally different properties of the material and it is not surprising that the results obtained often appear contradictory. One grease may be more viscous than another, but its penetration figure may also be higher. The apparent anomalies extend to measurements made on instruments which are of the same general design.

Using a plunger viscometer with a variable gap width it was found that the viscosity of an aluminum based grease increased by up to 30% when the gap width was increased from 0.0042 to 0.0624 cm. (15). In addition, the viscosities were found to depend on the nature of the materials (brass, steel, glass) from which the plunger and cylinder of the viscometer had been constructed. These results can be explained by postulating a modified form of "plug flow" in which the properties of the grease in the boundary layer differ from those of the material in bulk.

The immediate past history of a grease has a pronounced effect on its rheological properties. Quite different results are obtained on so called "worked" and "unworked" samples. The age of the grease is also relevant and in many cases there is a slow change in rheology, frequently extending over periods of weeks or months. For these reasons considerable emphasis is now placed on the test procedures to be adopted and on the equipment to be used for measuring the rheological properties of the commercial products (12, 89).

It is convenient to present the rheological properties of a grease in graphical form. Plotting the rate of flow against the applied stress generally yields curves of the type shown in Fig. 10. This shows that many greases approximate to Bingham bodies. They exhibit a lower yield value which is usually between a few hundred and a few thousand dynes/cm.^{2} and an upper, or Bingham, yield value, generally between 10^4 and 10^7 dynes/cm.^{2}.

At stresses well above the yield points the viscosities of most greases decrease regularly with stress, eventually reaching the viscosity of the relevant base oil. The plots of log η *versus* log $\dot{S}$ are usually linear, or nearly linear, for rates of shear between about 10^{-2} and 10^3 sec.$^{-1}$, the slopes of the lines frequently falling between -0.3 and -1.0 (10, 15, 19).

The departure of many greases from ideal Bingham behavior is not expected in view of the very wide variation which is possible in the detailed structure of the gel. Some greases have a fibrillar structure; others are pseudo-gels or pastes, consisting of small crystals of the soap suspended in the base oil (48). The texture of the grease, *e.g.*, its smoothness, appears to be intimately related to its microscopic structure. This can be studied conveniently by means of the electron microscope, though special methods are required for the preparation of the specimens (16, 23, 95).

C. THERMAL AND CHEMICAL STABILITY

The thermal and chemical stability of a grease can be assessed in a number of ways (89). Its tendency to syneresis is measured by pressing a cylindrical column of the grease against a metal gauze and weighing the quantity of oil that separates in seven days. Its stability toward oxidation is determined by heating it at 99° in a bomb, which is pressurized with oxygen at 7.7 kg./cm.^{2} and recording the decrease in oxygen pressure with time.

The effects of metals such as copper, aluminum and steel on the grease are determined by aging tests; corrosion tests, tests for water resistance and for losses by evaporation, etc., are also included in the specifications of commercial greases.

D. AS LUBRICANTS

The effectiveness with which a grease will act as a lubricant depends on various properties, including its rheology, chemical stability, ability to adhere to metal surfaces, to withstand physical changes or denaturation arising from the high temperatures and pressure to which it may be subjected during its service life. While some assessment of its potentialities can be made by measuring these properties individually, it is necessary also to include lubrication tests with machines and gear systems of various types (21, 37, 89, 98).

In the Rolling bearing performance test (89) the grease is used to lubricate the bearing of a standard test rig for a period of 500 hours under selected conditions of temperature, speed and applied radial load, measuring the amount of wear that is caused to the bearing and the changes that occur in the color, texture and hardness of the grease. Electron microscopy has been used in this connection (59) to show the way in which the fiber structure of a lime-based grease broke down during the course of the test.

Of particular interest in many instances is the ability of the grease to function as an extreme pressure lubricant (73), whereby one or more components of the grease react chemically with metal surfaces at the points of incipient seizure to form an anti-welding layer. The lead soaps of 12-hydroxyoctadecanoic acid and of various naphthenic acids have been used as ingredients of extreme pressure lubricating greases (12); other lead soaps that have been employed are obtained by treating about 6 parts by weight of litharge with about 12 parts of Menhaden (fish) oil and about 2.5 parts of sodium hydroxide, the grease being formed by dissolving the product in 80 parts by weight of mixed mineral oils.

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