THE METAL SOAPS AND THE GELATION OF THEIR PARAFFIN SOLUTIONS.

BY A. S. C. LAWRENCE.

Systematic work on gels in dispersion media other than water is almost entirely lacking. Some interesting cases have been reported. Camphoryl-phenyl-thio-semicarbazide [1] and dimethyl-5 amino-anilo-3, 4 diphenyl-cyclopentene-1, 2 dione,[2] dissolved in hot non-polar solvents gelate on cooling. Concentrations of less than 1 per cent. are sufficient to show the phenomenon. These gels are not, however, stable as crystal growth occurs on standing. Calcium acetate [3] and sodium benzoate [4] are examples of a more complex type. Gels are formed by these salts when precipitated from strong aqueous solution by alcohol. A number of soaps have been reported to gelate in non-polar or slightly polar solvents such as paraffins, toluene and chloroform. In several cases, however, the name " gel " has been misapplied to pastes of micro-crystals suspended in liquid which have been described as " opaque

[1] E. Hatschek, *Koll. Z.*, 1912, **11**, 158 ; 1930, **51**, 44.
[2] W. Hardy, *P.R.S.*, 1912, **87**, 29.
[3] H. Henstock, *Trans. Faraday Soc.*, 1933, **29**, 1101.   [4] *Ibid.*, 1934, **30**, 560.

gels." A true gel is optically empty in the sense that individual particles cannot be detected ultramicroscopically although a weak Faraday-Tyndall cone is usually visible. Any substance separating from solution in sufficiently small particles may form a plastic paste holding the solvent.[5] In such systems, crystal growth occurs with consequent segregation although this process may be retarded greatly by the plasticity. Some gels appear to be permanently stable (see p. 674).

Previous Observations on Soaps.

Koenig prepared palmitates and stearates of copper, nickel and cobalt, and found that they dissolved in hot benzene, toluene, heptane, chloroform and carbon tetrachloride and set to gels on cooling.[6] McBain and McClatchie [7] examined the behaviour of a number of soaps in xylene and observed gelation in some cases. Table I shows their results. It is obvious that there is no regularity in the appearance of the phenomenon.

TABLE I.

	Palmitates.	Stearates.	Oleates.
Soluble at b.p. . . .	Cu	Zn	—
Separates without gelation on cooling	Fe_{ous}	—	—
	Tl_{ous}	—	—
	Pb	—	—
Soluble at b.p. . . .	Th	Na	K
Gelates on cooling . . .	Ag	Al	Na
	Li	—	Al
	Na	—	—
	Ca	—	—
	Cr	—	—
	Al	—	—
Insoluble at b.p. . . .	K	—	Ferric
	Ba	—	—
	Na	—	—

Boner has prepared a number of metallic soaps and recorded their behaviour when dissolved in various oils.[8] In paraffin, gelation occurred with aluminium, cadmium, cobalt, magnesium and nickel but not with barium, calcium, cerium, chromium, copper, lead, manganese, mercury, strontium, silver, tin and zinc compounds. The soaps used were not pure substances, being prepared from commercial doubly pressed stearic acid and from lard fatty acids. Whitby [9] has described paraffin gels of silver stearate; aluminium soaps in benzene have been examined, the myristate showing the greatest viscous anomaly.[10]

Present Work.

The work described in this paper consists of a systematic examination of dispersions of soaps in Nujol. Nujol was chosen as dispersion medium as

[5] P. Thomas, *Rev. Gen. Colloides*, 1929, **7**, 295.
[6] A. E. Koenig, *J.A.C.S.*, 1914, **36**, 951.   [7] *J. Physik. Chem.*, 1932, **36**, 2567.
[8] C. J. Boner, *J. Ind. Eng. Chem.*, 1937, **29**, 58.
[9] G. S. Whitby, *Coll. Symp. Mon.*, 1926, **4**, 213.
[10] W. Ostwald and R. Riedel, *Koll. Z.*, 1935, **70**, 67.

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a non-polar solvent with conveniently high-boiling point. Sodium soaps of the common fatty acids were examined first. On heating with Nujol, they swell somewhat as the temperature rises and then, in the neighbourhood of 200°, dissolve suddenly to clear mobile solution. On cooling, this sets to clear gel just below the dispersion temperature. On further cooling, opacity develops and the mechanical properties are modified. The thermal conductivity of the gels is very small so that cooling curves provide a simple and exact method for observing the setting-points. Fig. 1 shows results for the sodium soaps. The sharpness of the break at the gelation point depends upon the size and shape of the container. A boiling tube half full w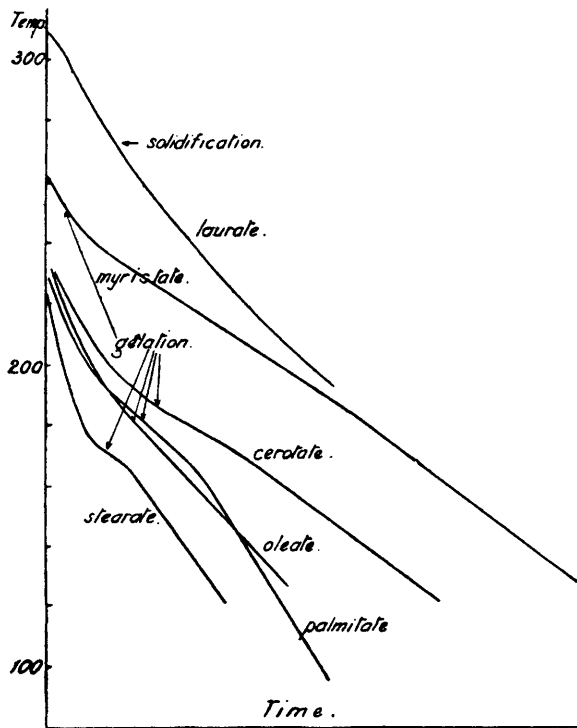as found to be most convenient. Sodium laurate is distinct from its higher homologues in that it separates from Nujol solution as an oil which solidifies at a lower temperature. No gelation therefore occurs. The lower members are insoluble in Nujol at its boiling-point (c. 340). Experiments were then made to determine the effect of the cation and a number of stearates were prepared. It was then noticed that the mechanical properties of the gels were parallel to those of the solid soaps. Measurements were made of the melting-points of the soaps used. On cooling the isotropic liquid, an intermediate plastic form appears with certain cations. This on further cooling

FIG. 1.—Cooling curves of 1 per cent. solutions of sodium soaps of the saturated fatty acids in nujol.

undergoes a sharp transition from clear horny to brittle opaque solid. The appearance of opacity in gels was then found to be a discontinuous change accompanied by loss of " body." The discontinuity of this change can be observed only in small specimens cooled very slowly to preserve uniformity of temperature or in very dilute systems. In the latter case, segregation of the soap occurs below the transition point.

The preparation of a certain number of the soaps of the common fatty acids has been described but very few have been obtained in a state of purity.[11] Many of these substances are in the plastic state at room temperature so that purification by crystallisation is difficult

[11] A book—*Metallseifen*, H. J. Braun (Leipzig, 1932)—has been published but it merely illustrates the extreme paucity of the information available.

and incomplete. Owing to lack of recognition of this plastic state, melting-points recorded are in many cases seriously incorrect, since they are no more than the temperature at which the substance attains some arbitrary viscosity value required for flow in the melting-point apparatus used. Even in those soaps which do not pass through a plastic stage, the liquid just above the melting-point may have a very high viscosity so that melting-point determinations depending upon observation of flow give results which are too high. The error is increased by the very low thermal conductivity of the substances. Lead stearate has been studied more than any other metallic soap owing to its use in the analytical separation of saturated from unsaturated acids. The melting-points recorded are: 113-114, 115-116, 125.[12] My value for a pure specimen examined in bulk is 106°. The peculiar transformations of the soaps are described in the next section and, after that, their preparation and purification. This order is chosen because the purificiation depends upon the physical condition of the soap more than on any other factor.

The Physical State of the Soaps.

There are four possible stages through which a soap may pass :
(1) Isotropic liquid of low viscosity.
(2) Very viscous liquid : this stage may also show a small elasticity.
(3) Soft crystalline.
(4) Hard fully crystalline.

In a few cases all four stages occur when the molten substance is cooled. More usually (3) or (2) is omitted. A small number of soaps exhibit no anomalous stage, passing directly from (1) to (4). Class (4) may include more than one form. The transitions (1) to (3) and (3) to (4) are abrupt physical changes but from (1) to (2) is not. It is, however, convenient to have a measure of the rate at which the viscosity varies with temperature and in this work this was made by observing, as the " melting-point," the temperature at which the substance no longer drops from the thermometer. This separation into classes is arbitrary in that there is probably continuity from viscous true liquid → viscous elastic liquid → soft crystalline. Also the two forms, (3) and (4), of ammonium soaps are very different from the two corresponding forms of the alkali soaps. The soft crystalline variety of the latter is certainly closer to class (2) while those of ammonia are closer to class (4).

The Smectic Form.

Vorlander showed in 1910 that the sodium soaps underwent a transition in the neighbourhood of 220° C. to an intermediate form which at a higher temperature melted to isotropic liquid.[13] Friedel named the layer type of liquid crystal " smectic " on the assumption that soaps were typical examples of this class of liquid crystals.[14] This, however, is not so. They do not show the properties of characteristic substances such as ethyl p-azoxy benzoate—focal conic structure, Grandjean's terraces nor "gouttes à gradins." The thallous soaps [15] do show the

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[12] See Table III.   [13] Ref. a, Table V.
[14] He took smectic to mean " soap-like " from the Greek σμεγμα. The Greeks, however, did not have soap and the verb σμαω means I smear. The Latin word " sapo " is of German origin, and Pliny states that soap was introduced to the Romans from the Gauls.
[15] K. Herrmann and A. H. Krummacher, $Z.$ $Crystallog.$, 1932, **81**, 317.

characteristic properties of smectic substances (Fig. 2) but no other soaps known do so. The alkali soaps might be classed as smectic substances in which the viscosity normal to the layers was very large. This suggestion cannot be upheld because at higher temperatures the viscosity of the soaps is reduced to a value small enough for layer flow or for the development of focal conic structure if there is no common orientation. The general name " plastic " will be used for the intermediate form in the soaps. This name is not quite free from objection in that plastic is frequently taken to mean a non-crystalline paste with a definite yield point. Some of the soaps described here as plastic are probably liquids of very high viscosity and no rigidity. The point, however, requires further investigation and will be mentioned again later in connection with gels.

It was observed that soaps, when in the plastic stage, could be drawn out into threads and that in some cases the threads had a high birefringence whereas the substance in bulk had little or none. It appears that two separate factors apply. The very high viscosity—approaching the consistency of pitch at room temperature—allows the substances to be drawn into threads. These are birefringent only if the substances contain some micro-crystals of class (3) or (4). When fully transformed, the viscosity is too high for drawing. The mixture of liquid with the crystals allows the slip necessary for orientation. The crystallites are microscopic needles. The birefringent threads given by lead oleate and magnesium stearate show parallel extinction and give good X-ray pictures.[16] Lead oleate is biaxial and gives a spacing of 46·5 A. Nickel oleate forms fibres which are not birefringent : these give only a side spacing of 4·7 A. This substance does not pass through the soft crystalline stage and is plastic at room temperature.

Results.

The following tables give the results for the soaps used in this work. Those marked with a † have not been prepared before. Few of the others have been obtained pure. The temperature T_1 is that at which the molten substance no longer drops from the thermometer. T_2 is the temperature at which the substance becomes hard crystalline solid. It cannot be observed by the usual methods and the following procedure was found to be the best. About 0·25 gm. of the substance was cooled (if necessary by solid CO_2) and broken into small pieces. It was then warmed in a test tube in a suitable bath until the transition temperature T_2 was reached. Below this, a piece of the substance rubbed against the side of the tube crumbled and did not adhere. Above T_2 it flowed under the pressure and adhered very tenaciously to the glass. By taking the specimen up and down past the transition, its value is easily determined within 1°. Optical methods were discarded owing to the microcrystalline form of the solids. The opacity which develops on solidification is slight and the change in appearance under the microscope is less than those due to thermal contraction. X-ray examination of aluminium stearate gave a spacing of 41 A. so that the angle of tilt of the molecules must be between 50° and 60°. The crystallites contained only a few thousand molecules.[17]

Fig. 12 shows the variation of melting-point with length of fatty acid in the few series for which figures are available. Most of these are normally melting substances. Zinc is the only metal found forming a normally melting oleate.

Nickel soaps decompose when heated above 200°. A black powder is formed. This is not the oxide since it dissolves in amyl alcohol and pyridine. Mercury soaps decompose suddenly with considerable evolution of heat when heated, the stearate at 230, and the laurate at 210° and the oleate at 235°. Metallic mercury is formed and a product which is soluble in alkali hydroxide solution. Its melting-point is 40·5 and is a mixture of anhydride and acid.

TABLE II.—Soaps passing through Plastic Stage.

	T_1.	T_2.	Previously Recorded m.p.
Stearate—			
Sodium . . .	291	163	220, 305 [a]
Potassium . .	270	138	—
† Rubidium . .	360	185	—
† Cæsium . .	340	105	—
Silver . . .	180	130	205 [b]
Aluminium [18] . .	280	90	—
Calcium . .	decomp. without melting *c.* 350°		—
Magnesium . .	240	109	132 [b]
Cobalt . . .	200	—	73-75 [c]
Nickel . . .	240	10	80-86,[e] *c.* 100 [r]
Copper . . .	111	80	115-120,[e] *c.* 125 [r]
Manganese . .	200	80	—
† Uranyl . .	82·5	70	—
Ferric . . .	115	23	—
Chromium . .	*c.* 75	35	—
Oleates—			
Sodium . . .	245	140	232-235 [f]
Potassium . .	—	—	—
Silver . . .	—	—	— [b]
Lead . . .	40	— 16	*c.* 80 [h]
Mercury . .	*c.* 0	— 80	*c.* 80,[h] *c.* 50 [r]
Nickel . . .	100	— 1	102-103 [g]
Cobalt . . .	235	— 17	18-20,[r] 19
Copper . . .	136	13	below 100 [r]
† Magnesium . .	203	90	—
Aluminium . .	100	*c.* —70	—
Barium . . .	decomposes without melting *c.* 350°		—

TABLE III.—Soaps not passing through Plastic Stage.

Stearate of	M.p.	Trs. for Dimorphous Salts.	Previous m.p.
Lithium . .	136	78	221 [b]
† Ammonium . .	107	50	— [u]
Thallous . .	163	128	—
Lead . . .	106	none	115,[r] 125,[d] 113 [e]
Zinc . . .	118	none	130 [r]
Mercurous . .	117·5	none	112·2 [r]
† Thorium . .	73	none	—
† Beryllium (co-ordination) .	35	none	—

Zinc oleate is a normal substance melting at 60° (previously recorded 70°).[r]

[18] Monostearate.

TABLE IV.—AMMONIUM SOAPS.

	M.p. to Soft Crystals.	M.p. to Liquid.	Previously Recorded m.p.
Acetate . . .	—	—	113 [i]
Propionate . .	—	—	c. 45 [j]
Butyrate . .	—	—	70-85 [k]
Valerate . .	—	—	—
† Caproate . .	⎧ No soft	48	—
† Caprylate . .	⎱ crystalline	70	—
Laurate . .	⎰ form	36	c. 75 [i]
Myristate . .	80·5	50	75-90 [i]
Palmitate . .	86·5	52	—
† Stearate . .	107	50	—
⎰ Oleate . .	?	51	—
† ⎱ Elaidate . .	—	50	—
† Diethylamine stearate . .	—	27	—
† Triethanolamine stearate . .	—	40	—

TABLE V.—SODIUM SALTS OF FATTY ACIDS.

		T_1	T_2.	Previous.
Formate . .	C 1	—	—	253
Acetate . . .	2	—	—	323 [l]
Propionate . .	3	—	—	—
Butyrate . .	4	—	—	210, 310 [a]
Valerate . .	5	220	—	210, 335 [a]
Caproate . .	6	—	—	225, 350 [a]
Caprylate . .	8	344	217	225, 355 [a]
Pelargonate . .	9	250	—	218, 242 [a]
Caprate . . .	10	—	—	220, 318 [a]
Laurate . . .	12	324	200	220, 310 [a]
Myristate . .	14	299	203	240, 330 [a]
Palmitate . .	16	259	155	c. 270 [f]
Stearate . . .	18	270	162	220, 305 [e]
Arachidate . .	20	—	—	—
† Cerotate . .	26	360	112	—
⎰ Oleate . .	18 =	245	140	232-235 [f]
⎱ Elaidate . .		280	120	—
Erucate . . .	22 =	—	—	—
Stearolate . .	18 ≡	decomp.	—	—
† α Brom-stearate .	—	,,	—	—
Linoleate . .	—	—	—	—
Ricinoleate . .	—	215	175	—

TABLE VI.—CEROTATES.

		T_1.	T_2.
† Sodium . .		361	155
† Potassium . .		362	195
† Rubidium . .		360	185
† Cæsium . .		293	133

TABLE VII.—OTHER SOAPS.

	T_1.	T_2.	Previous.
† Cobalt Caprylate . . .	—	— 13	—
Aluminium myristate [w] . .	—	—	—
Nickel laurate	—	—	—
Mercury laurate . . .	m.p.	137	—
† Beryllium acetate . . .	,,	—	183,[m] 285-286 [n]
,, propionate . .	,,	—	119,[o] 133-135 [n]
,, butyrate . . .	,,	—	liquid [o]
,, propionate-butyrate .	,,	—	127,[p] 140 [n]
† ,, caproate . . .	,,	glass at — 80	—
† ,, laurate . . .	,,	10	—
† ,, stearate . . .	,,	35	—

[a] Vorlander, *Ber.*, 1910, **43**, 3122.
[b] Jacobsen and Holmes, *J. Biol. Chem.*, 1916, **25**, 29.
[c] A. E. Koenig, *J.A.C.S.*, 1914, **36**, 951.
[d] Heintz, *Ann. Physique*, **87**, 564 ; *J. Pr. Chem.*, **1**, 66, 29.
[e] Wagner, Muesman and Lampart, *Chem. Zentr.*, 1914, 1458.
[f] Krafft, *Ber.*, 1899, **32**, 1599.
[g] Tichborne, *J. Chem. Soc.*, 1885, 1443.
[h] Gottlieb, *Ann.*, **57**, 45.
[i] Reih, *Monatsch.*, **23**, 1041.
[j] Escales and Koepke, *J. Pr. Chem.*, **87**, 264.
[k] Pelouze and Gelis, *Ann.*, **47**, 249.
[l] Green, *Chem. Zentr.*, 1909, 837.
[m] Steinmetz, *Z. Ch.*, **54**, 218.
[n] Sir W. Bragg and G. T. Morgan, *P.R.S.*, 1923, 437.
[o] Lacombe, *Comptes Rendus*, 1902, **134**, 772.
[p] Tanatar and Kurawski, *Ber.*, 1910, **43**, 1230 ; *J. Russ. Phys. Chem. G.*, **39**, 939.
[q] Klemgard, *Lubricating Greases*, 1927, 176.
[r] Whitmore and Lauro, *J. Ind. Eng. Chem.*, 1930, 646.
[s] Kahlenberg, *Chem. Zentr.*, 1902, 1040.
[t] G. Martin, *Modern Soap and Detergent Industry*, 1924.
[u] A. S. C. Lawrence, *Trans. Faraday Soc.*, 1933, 1010.
[v] K. Hermann, *ibid.*, 1933, 973.
[w] W. Ostwald and R. Riedel, *Koll Z.*, 1935, **70**, 67.

Preparation and Purification of Soaps.

The soaps of the alkali metals and of thallium are readily prepared from the fatty acids and the hydroxides in alcoholic solution. They crystallise well provided the amount of water present is small. In anhydrous alcohol, their solubility is small : the cerotate is almost insoluble in boiling ethyl alcohol. Higher alcohols, such as amyl, can be used with advantage. When water is added, the solubility is increased considerably but the soap retains much of the water on crystallising and tends to form ropy masses. It is advisable to have a small excess of alkali present since the wet soaps are readily decomposed by CO_2. The free fatty acid formed lowers their melting and transition points considerably.

The presence of water in the gelating Nujol solutions of sodium soaps was suspected. The effect of water on gelation in turpentine solution has already been reported.[19] The authors prepared their " anhydrous " soap by drying at 103°. They then found that addition of water to the sol. increased the volume of turpentine held as gel.[19] When the curve connecting volume of liquid held in gel against water added is drawn as a straight line through their points, the origin of zero gelation for zero

[19] H. N. Holmes and R. N. Maxson, *5th Colloid Symposium*, Monographs, 1927, 287.

water suggests that their " anhydrous " soap contained some 7 per cent. of water.   The monohydrate corresponds to 6 per cent.   The correctness of this view was proved by preparing anhydrous sodium stearate in turpentine from stearic acid and clean sodium.   No gelation then occurred on cooling ;   the soap crystallised out.

It appears that the last molecule of water cannot be removed from the alkali soaps without decomposition.   Analysis of the soap dried as far as possible is not a satisfactory method of determination of the residual water. Anhydrous soaps were therefore prepared in Nujol from stearic acid and clean sodium.   No gelation occurred (Fig. 3).   When water was added in small amounts, gelation followed.   The monohydrate seems to be sufficient to form gels.   With more water, gels are still formed but the excess of water encourages particle growth.   All the figures in Table V refer to the monohydrates.

FIG. 3.

The metals of the alkaline earth series behave in a similar manner except that the water can be removed by drying in vacuo at a high temperature or by solvents.   Their solubility is influenced markedly by small traces of water.[20]   This property is made use of in preparation of commercial lime base greases, sufficient water being added — about 3 per cent.—to reduce their dispersion temperatures in oil to practicable v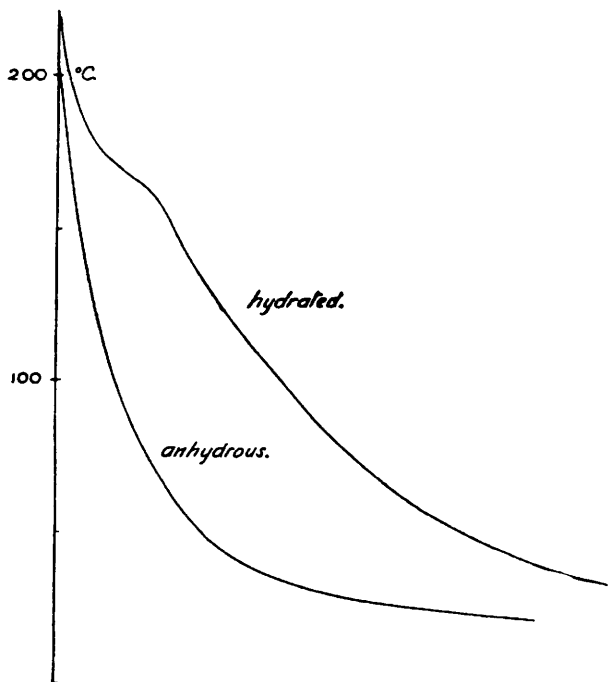alues.   In this case there is a well-defined saturation value for the amount of water taken up.   It may be noted that some of the lower salts of these metals crystallise with one molecule of water of crystallisation.[21]   Three per cent. of water in calcium stearate is the amount required for the monohydrate.   The metal soaps do not present difficulties by retention of water.[22]

The chief difficulty in preparing pure metallic soaps lies in the stickiness of the precipitates when they are prepared by metathesis.   This prevents proper filtration, adequate washing or recrystallisation.   In the presence of organic solvents, the stickiness is increased by swelling.   A few of the soaps can be prepared in hot solution so that they separate as a liquid, from which the impurities can be washed by hot alcohol.   If necessary, the soap is rendered fluid enough for complete separation in a separating

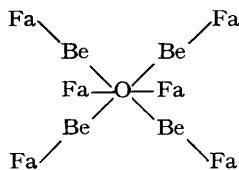[20] Lewkowitsch, *Chemical Technology of Oils, Fats and Waxes*, 1, 549.

[21] *E.g.*, caprylate (Zincke, *Lieb. Ann.*, **152**, 10) pelargonate, caprate (A. Fischer, *ibid.*, **118**, 314), and laurate (Caspari, *J.A.C.S.*, **27**, 308.   See [also J. W. McBain, H. I. Bull, and L. S. Staddon, *J. Physic. Chem.*, 1934, **38**, 1075.

[22] Boner, *loc. cit.*[8], p. 3.

funnel by addition of petroleum ether. In some cases, *e.g.*, aluminium oleate, this is not sufficient owing to the stickiness of the resulting solution but it is rendered fluid by a little pyridine. This solvent is the best found for the metallic soaps. It is the only solvent found for recrystallising calcium stearate and barium oleate (dry). Its smell is also especially useful as a check on the completion of the subsequent drying of the soap. Most workers have tried to overcome this difficulty of the stickiness of the soaps by working in cold aqueous solution. This procedure is open to serious objections. If the soap of the alkali used is colloidally dispersed, the chance of occlusion of undecomposed alkali soap [23] in the precipitate of metal soap is very much increased. Whitmore and Lauro suggested this method and followed filtration of the precipitate by washing with alcohol and ether.[r] This is most objectionable unless the soap is subsequently dried by heating in vacuo at 200° for at least an hour. The amount of solvent retained in their soaps, for which they record melting-points, is well illustrated by their description of nickel oleate as an oil which could be separated from the mother liquors in a separating funnel.[s] The dry substance has a consistency greater than that of commercial water glass.

The difficulties of the metathesis method can be evaded in the cases of mercury, lead, iron and the alkaline earths by dissolving the oxide in molten fatty acid, washing out free acid by hot alcohol and dissolving the residue in petrol ether, filtering and drying in vacuo. The plastic soaps with higher T_2 can be crystallised from amyl alcohol but the soap separating is in a messy state. Soaps of nickel, cobalt, copper, and chromium form complexes with pyridine which crystallise excellently.[ ] They break down in air but complete removal of the pyridine requires heating in vacuo to 200°. This method failed with cobalt oleate as the complex would not crystallise from pyridine, even when cooled to $-30°$. The oleates are generally troublesome owing to their soft sticky nature. They were therefore precipitated hot in 50 per cent. alcoholic water solution, washed with hot water, and then hot alcohol and dissolved in petroleum ether, filtered and dried as described.

The beryllium soaps form a special class. They were prepared by Jacobson and Holmes but described as basic substances of the formula $Be\overline{\overline{Fa}}OH$.[24] The lower members, however, had been prepared in 1902 by Lacombe[o] who showed that they were co-ordination compounds. The structure of the acetate and propionate in the solid state has been found to be:[25]

$$
\begin{array}{ccc}
\text{Fa} & & \text{Fa} \\
\diagdown & & \diagup \\
\text{Be} & & \text{Be} \\
& \diagdown \quad \diagup & \\
\text{Fa} & \text{O} & \text{Fa} \\
& \diagup \quad \diagdown & \\
\text{Be} & & \text{Be} \\
\diagup & & \diagdown \\
\text{Fa} & & \text{Fa}
\end{array}
$$

The four Beryllium atoms lie at the apices of a tetrahedron at the centre of which is the oxygen.

By metathesis, the co-ordination compound is formed predominantly but a better method of preparation is by heating the fatty acid with beryllium oxide and vacuum distilling unchanged acid. Up to the laurate, the soap may be vacuum distilled. Above that the boiling-point is too high but they become solid again by C_{12} and can be crystallised.

[23] Under these conditions the amount may easily reach 5 per cent. even in the presence of considerable excess of metal ions. When observations of gelating properties are made in 10 or 15 per cent. solution, this impurity becomes serious since it is enough to cause gelation alone.

[24] Jacobson and Holmes, *J. Biol. Chem.*, 1915, **25**, 29.
[25] Sir W. Bragg and G. T. Morgan, *P.R.S.*, 1923, 437.

The aluminium soaps are peculiar in that only one fatty acid radicle can be introduced, their general structure being :—[7]

$$Al(OH)_2\overline{Fa}.[4]$$
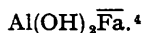
Soap-Nujol Gels.

The soap-nujol system may exist in three forms :

(1) True solution.
(2) True gel.
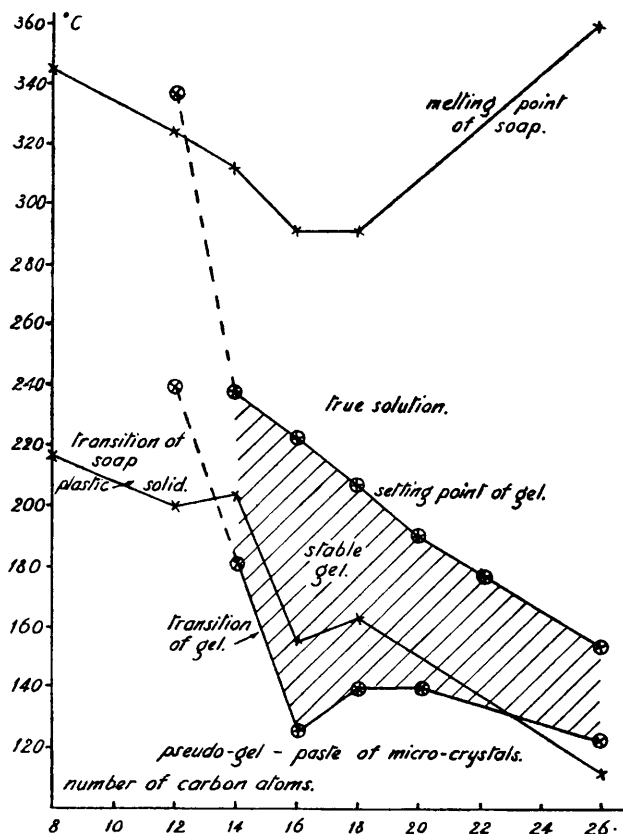(3) Pseudo-gel paste of micro-crystals suspended in oil. The transition from (1) to (2) is sharp only in solutions of those soaps which show a sharp transition at T_1 from liquid to soft crystalline. Those soaps whose transition is gradual also show a gradual transition from sol to gel. The transition from (2) to (3) has not been previously recognised since, except at low concentrations, the system retains the appearance of the gel to casual inspection. It develops a slight opacity only. Its heterogeneity, however, is shown by stirring as the pseudo-gel breaks into lumps, Fig. 4. Artefracts do not "heal." It has also been shown that in this type of system, particles of soaps can be detected microscopically by dark ground illumination. The "shortness" of the paste depends upon the shape of the crystal-lites.[26] In dilute solution—0·1 per cent. or less—the change from (2) to (3) is quite clear since the crystallites are not held in a plastic paste and segregation occurs. Sedimentation of the micro-crystalline soap occurs and the solid may be examined microscopically.

FIG. 5.—Sodium soaps of saturated fatty acids.

Table VIII gives the gelation and transition temperatures of the gels of the metal soaps in nujol. The relation between these values and T_1 and T_2 for the soaps is made clear by Figs. 5 and 6. Fig. 6 shows the results for the soaps of the saturated fatty acids. Fig. 7 for the alkali cerotates. These are chosen in preference to the stearates since the stearates of cæsium and rubidium do not have a well-defined T_2 in the nujol solution.

[26] B. W. Farrington and W. N. Davis, *J. Ind. Eng. Chem.*, 1936, 414.

FIG. 2.—Thallous stearate in smectic state showing flow in sheets.   Grandjean's terraces.   × 200.

[See page 664.

FIG. 4.—Micro-photograph of sodium stearate pseudo-gel rubbed between glass plates.   × 74.
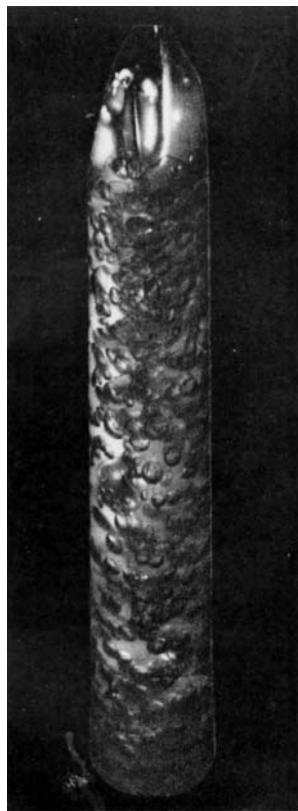

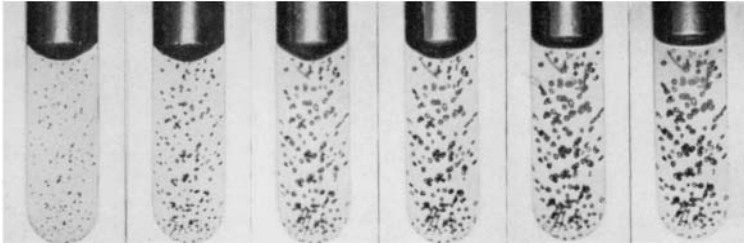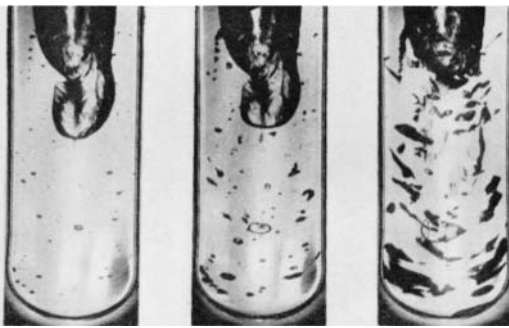FIG. 7.—Lenticular bubbles in Sodium Stearate nujol gel.

[To face page 670.

FIG. 8.—Growth of bubbles in silver stearate-nujol gel.

(1)   (2)   (3)

FIG. 9.—Expansion of bubbles in gel along cleavage planes.

[*See page* 672.

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TABLE VIII.

			Soap.		Gel.	
			s.p.	trs.	s.p.	trs.
Stearate of :						
Sodium	.	.	291	163	207	140
Potassium	.	.	270	138	224	130
Rubidium	.	.	360	185	258	82
Cæsium	.	.	340	105	235	—
Silver	.	.	180	130	127	45
Aluminium	.	.	280	90	—	50
Calcium	.	.	decomp.	—	270	< 0 *
Magnesium	.	.	240	109	—	40
Copper	.	.	111	80	no gelation	
Uranyl	.	.	82·5	70	,, ,,	
Cobalt	.	.	200	—	60	4
Nickel	.	.	240	—	insoluble-decomp. 190°	
Ferric	.	.	—	—	no gelation	
Chromium	.	.	75	—	,, ,,	
Manganese	.	.	200	80	,, ,,	

Thallous ⎫
Lead ⎪
Mercurous ⎬ . . No gelation.
Thorium ⎪
Beryllium ⎪
Zinc ⎭

Cerotates of :

			Soap s.p.	trs.	Gel s.p.	trs.
Sodium	.	.	351	—	155	110
Potassium	.	.	362	—	195	134
Rubidium	.	.	360	—	185	124
Cæsium	.	.	293	—	133	109

Sodium Salt of :

Acetic ⎫
Propionic ⎪
Butyric ⎪
Valeric ⎬ . . Insoluble in Nujol up to 340°.
Caproic ⎪
Caprylic ⎪
Capric ⎭

			Soap s.p.	trs.	Gel s.p.	trs.
Lauric	.	.	324	200	337 (as liquid)	240
Myristic	.	.	312	205	206	180
Palmitic	.	.	291	150	223	125
Stearic	.	.	291	163	207	139
Arachidic	.	.	—	—	175	140
Cerotic	.	.	360	108	153	122
Oleic	.	.	245	140	226	100
Elaidic	.	.	280	120	190	c. 100
Stearolic	.	.	—	—	—	—
Ricinoleic	.	.	—	—	—	—
Linoleic	.	.	—	—	—	—
α Brom stearic	.	.	decomp.	—	203	—
Cetyl sulphate	.	.	—	—	Separates at 210—no gelation	

* Gel segregates at 140.

Gelation is quite sharp where the phase of the solute is soft crystalline.† Where it is plastic, gelation temperature can be observed extending over 5 or so. This is the temperature at which it retains its form under gravity and at which small air bubbles cease to rise through it. In both cases there is separation from solution and syneresis occurs through the slow aggregation of the solute. It is at first distributed throughout the liquid but the particles cohere and slowly squeeze out nujol. At room temperature all the oil is eliminated if the fully crystalline phase has been reached. If it is still in the plastic state, the solute retains permanently a considerable volume of oil. 1 gm. of calcium stearate retained 4·7 c.c. of nujol. 1 gm. of barium oleate retained 3·0 c.c. of nujol after syneresis. A 5 per cent. solution of magnesium oleate had a viscosity of 10^8 c.g.s. units measured by the rate of fall of a $\frac{1}{4}$ inch steel ball. After two weeks, however, 30 per cent. of the nujol had been squeezed out from the system. The remainder was a clear liquid of still higher viscosity.

Hatschek has reported lenticular gas bubbles in gels.[27] In this work lenticular bubbles were observed frequently. They were seen best when the specimen of gel was exhausted at 200°, sealed off and left to cool slowly. They then form as in Fig. 7, progressive shrinkage increasing their angle of tilt. Finally syneresis occurs and the structure breaks away from the walls and a plug of swollen soap is left surrounded by oil. Fig. 8 shows the formation of such bubbles in a gel of silver stearate. The concentration was 0·2 per cent. The rigidity of this gel is small and the bubbles are nearly spherical as a result of surface tension. The exposures were made at half-hourly intervals. The more concentrated gels may require several days for formation of bubbles. Aqueous silicic acid gels also form lenticular artefracts on standing for several weeks. The necessary condition seems to be that the specimen should be a cylinder whose length is considerably greater than its diameter. Fig. 9 shows the effect of lowering the external pressure. Bubbles formed at atmospheric pressure expand in lenticular form.

FIG. 6.—Cerotates of alkali metals: setting and transition points for dry soaps and for solutions in nujol.

Meyer and Mark in their discussion of the swelling of polymers, point out that swelling without dispersion can take place only when the swollen mass is restrained from dispersion by a certain number of bonds holding the mass in a three-dimensional structure. In the soap-oil gels there is no evidence for swelling by solvent action. This is to be expected

† Values for the oleate gels are not tabulated owing to uncertainty about T_1. T_2 is always sharp, etc., Fig. 4.

[27] E. Hatschek, *J. Soc. Chem. Ind.*, 1929, 397; D. L. Talmud, *Phys. Zeit. Sowjitunion*, 1933, 861.

since the molecules of soap are held together in particles by adhesion of the —COO metal groups. This is unaffected by the oil. If the soap is heated, the lattice opens out and oil penetrates between the hydrocarbon chains. Complete dispersion obviously requires the temperature to be raised to a point approaching the melting-point of the soap at which thermal disruption of the —COO metal lattice occurs.[28] *Cf.* Fig. 12. The swelling of sodium laurate is easily observed directly since this substance separates from the nujol in the form of an oil-swollen liquid. Fig. 10 shows the contraction of sodium laurate in nujol. The density of the soap at 15° is 1·90. At the temperature at which it disperses, its density has fallen to about 0·5. The expansion of sodium stearate without oil was examined by heating slowly in a small inverted bulb attached to a U-tube filled with mercury. Air was removed by heating the soap until fluid in vacuo.

Fig. 11 shows the results for heating and cooling. No break in the curve was found at T_2, but at T_1 the behaviour was peculiar. The reason for this is not known. It is clear that melting is preceded by an opening-up of the lattice until the density is below 0·5. This supports the idea that entry of oil into the soap is due to thermal opening-up of the —COO metal lattice and

FIG. 10.—Volume change of sodium laurate in nujol on heating.

not to solvent action by the oil on the hydro-carbon chains of the soap. Fig. 11 also shows the greater expansion of soap nujol systems by expressing the difference between the expansion of nujol and sodium stearate solution in nujol as density change of the soap.
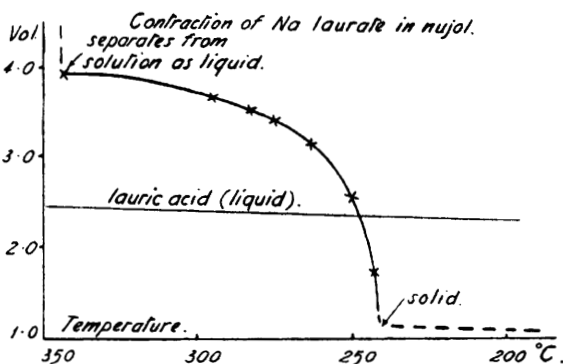
It is seen that up to T_2, the expansion of the soap system is that of the pure solvent. Above this point the lattice is opening up faster. This suggests that above T_2 we are dealing with increase of spacing of the —COOM groups between which nujol cannot penetrate and thereby offset their expansion.

The heat of gelation of sodium stearate in nujol was determined by comparison of rates of cooling of nujol, a 2 per cent. solution of soap in the nujol and a 10 per cent. solution. The difference between the last two rates was due to the heat of crystallisation of 8 gm. of soap. The value found was 30 Cals. per gm. : that is 9 Cals. per gm. mol. The values for palmitic and arachidic acids are 12·98 and 16·95 Cals./gm. mol.[29]

[28] It is remarkable how the soaps fall into groups which are the ordinary chemical ones of the kations. The alkali soaps form one distinct class with high melting-point and gelation points. The alkaline earths form another group. Their soaps cannot be melted without decomposition. Their gelation points are above 300° or else they are insoluble in boiling nujol. The trivalent ferric, chromium and mangan ese fall together and are distinguished by not forming gels although the dry soaps pass through a plastic state. They show intense super-saturation and separate from solution in very finely divided form. Zinc and mercury soaps are similar and magnesium is intermediate between them and those of the alkaline earths. The lead soaps resemble those of mercury. The divalent cobalt, nickel and copper form another class. Of the higher valency soaps only thorium stearate has been prepared. Here the influence of the kation is clearly submerged by the four stearate radicles and the substance more nearly resembles a hydrocarbon in its physical state.

[29] W. E. Garner and A. M. King, *J.C.S.*, 1931, 580 ; 1936, 1368.

Gelation.

The name " gel " is usually taken to mean a permanently stable, optically empty, elastic dispersion in which the concentration of solute is small—1 per cent. or less. A weak Faraday-Tyndall cone is usually visible but single particles cannot be detected ultra-microscopically. None of these criteria can be regarded as definitely established, although they are probably sound. It is now generally accepted that gels have a fibrillar structure. For the fibrils to hold the solvent it is obviously necessary that they should be numerous and therefore of very small cross-section. Gels are isotropic except where shrinkage has caused strain birefringence. They are isotropic because the fibrils have a random orientation. Maximum gel strength obviously requires this condition. The value of the rigidity of a gel will depend upon the number of points of adhesion of the fibrils and upon the nature of the bond.
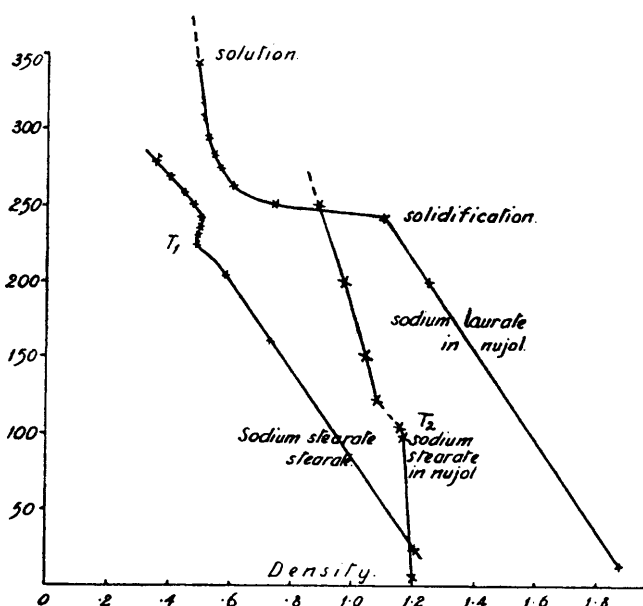

Fig. 11.—Volume changes with temperature in sodium stearate and laurate (monohydrate).

Gelation is always caused by reduction of solubility—by cooling a hot solution, by salting out or by removal of the stabilising ions of a hydrophobic sol. It is easy to see that any very large molecules whose shape is too irregular to form a regular crystal lattice and which contain a number of polar groups will form a three-dimensional meshwork linked together at the random points of adhesion. For a hydrophobic sol to gelate requires that the particles already present in the sol should have the necessary anisodimensional form, or, if spherical, that they should coagulate first to streptococcal chains. Silicic acid is a special case since its gelation is an irreversible polymerisation. Here the mechanical properties of the system will depend upon the number of nuclei at which the polymerisation start. It will consist of polyhedra whose planes of contact will be planes of weakness.

Gels can be divided into four classes by considering the bonds holding the fibrils and the means by which gelation is brought about :—

(1) Irreversible polymerisation, *e.g.*, silica gel.
(2) Joining up of large ampholyte molecules, *e.g.*, gelatin, by salt formation or by other chemical linkages.
(3) Hydrophobic sols in which coagulation is caused by disturbance of their stabilising charge, *e.g.*, vanadium pentoxide.
(4) Gels in which the particles separate from solution and are held by van der Waals' forces, *e.g.*, the soap-nujol gels and poly-mermolecule gels.

Any heteropolar molecules separating from a liquid system will first form micelles attached by their most polar groups in non-polar solvents or from a melt ; and by their least polar groups in a polar solvent. The size of the resulting micelle is fixed by packing considerations so that the size remains constant as temperature falls and their number increases. When the temperature has fallen to a point where the solution is saturated by the exterior lyophilic groups, adhesion of the micelles by their lyophilic groups occurs. A mechanism on these lines for the gelation of aqueous soap solutions has been proposed by the writer.[30] Where hydrophobic sols gelate, particle growth may occur by the operation of van der Waals' forces between surfaces unstable through having lost their stabilising ions.

The nujol gels of the soaps present one special peculiarity : at their gelation point, the hydrocarbon tails of the molecules are in a state of violent kinetic agitation owing to the high gelation temperature (see Fig. 12). The same phenomenon occurs in the soaps alone. This is perhaps the origin of their glassy state. Only when the temperature has fallen can the molecules fit into a regular lattice. It is noticeable that the solidifying temperatures of the oleates are lower than those of the stearates although the melting-points and dispersion temperatures in nujol are much the same for a given kation.

Arveson has found that the apparent viscosity of commercial calcium soap greases falls at very high rates of shear to a value approaching that of the solvent oil.[31] He suggests that the soap is present as flexible fibres. The analysis given above suggests rather that the particles must be rigid rods to account for the behaviour observed. Calcium soaps can be crystallised from liquid fatty acids, olive oil and pyridine. The stearate forms small elongated plates with a length/breadth ration of about 15 to 1. These usually grow in flat spherulite discs which can be broken by rubbing. Addition of water to the solutions markedly reduces the size of the crystallites and increases their length/breadth ratio.

It is clear that separation of soap at the gelation point is primarily an adhesion of the polar —COO metal groups. Micelle formation, therefore, occurs as the first stage. The micelle cannot be spherical since this would involve an empty space in the centre. At T_1 the kinetic activity of the hydrocarbon chains, especially at the free ends, is sufficient to increase their effective cross-section. The most probable form of the micelle is the serpentine one shown in Fig. 13. At T_1 the effective cross-section of the ends of the hydrocarbon chains is larger than that of the —COO metal groups but falls with temperature. There

[30] *Trans. Faraday Soc.*, 1935, 189.
[31] *J. Ind. Eng. Chem.*, 1932, 71, and 1934, 628.

need be no interlocking of the chains as appears in Fig. 13 where it is due to the two-dimensional drawing.   In three dimensions, all the tails are free. T_2 is the temperature at which the kinetic activity is reduced sufficiently for the soap molecules to pack into their normal lattice. It is not necessary that the micelle should be very long since gelation does not occur at the lowest concentrations of soap.   This picture of the aggregation of soaps is supported by the X-ray examination of the plastic form which showed side spacings only whereas below T_2 a long spacing appears as well.
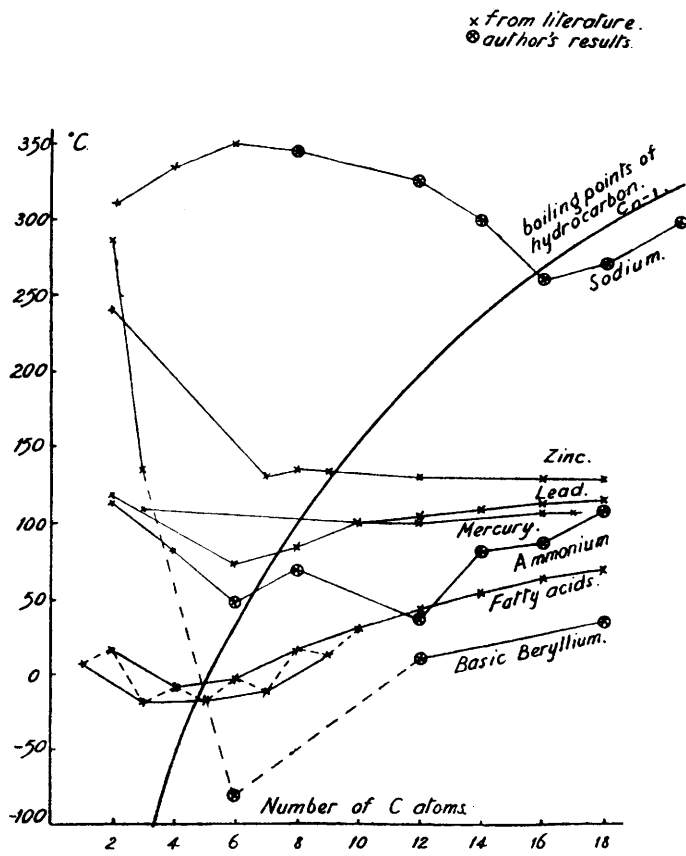

FIG. 12.—Melting-points of homologous series of soaps.

The stability of gels has not received the attention which it deserves. The solvation theory of gels does not, of course, raise this problem but this theory is not generally accepted now.   If gelation is a separation from solution, it is necessary to explain how it is that particle growth does not occur ; or, alternatively, to admit that gels are not stable systems.   Comparison is often made with the growth of large drops at the expense of small ones which have higher vapour pressure.   On this analogy, the rate of growth will depend upon the molecular solubility. If, however, the micelles are insoluble, as they are in the soap-nujol systems, growth cannot occur by this process of molecular distillation.

It can occur when the thread-shaped micelles approach one another as a result of their kinetic motion. This would seem to be the mechanism of syneresis of the soap-nujol gels. In those gels which have a honeycomb structure, such as gelatin, there may be at any moment a certain number of molecules free but this will not lead to instability of the gel unless there is preferential detachment of molecules from the smaller micelles and condensation on the larger ones. In cases such as dibenzoyl-cystine,[32] in which the particles in the gel seem to be crystalline fibrils, the energy differences at edges and corners of the crystals may provide a mechanism for growth. It seems to be a general rule that any gel will be unstable at temperatures at which the dry solute has a fully crystalline form. When it is not fully crystalline, syneresis proceeds at a rate which decreases as the separated gel becomes more concentrated and complete separation into solute and solvent is never reached.
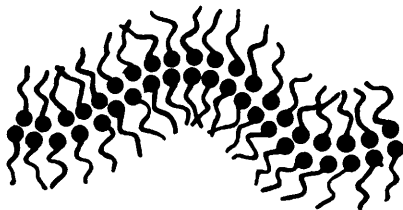

FIG. 13.—Soap micelle in plastic and gel state.

The work described above forms part of certain researches undertaken for the Fuel Research Division of the Department of Scientific and Industrial Research. I am grateful to Dr. Sinnatt, the Director, for his encouragement. The work was carried out in the Laboratory of Colloid Science by kind permission of Prof. E. K. Rideal to whom I am indebted for numerous useful discussions and for his interest throughout the work.

Summary.

A number of soaps form gels in paraffin and other organic solvents. The corresponding dry soaps pass through a plastic or soft crystalline form between solid crystalline and isotropic liquid. The temperature range of stable gel corresponds with this plastic range. Below the lower limit, the gel becomes an opaque paste of micro-crystals. At concentration above about 0·5 per cent., the paste is plastic and therefore behaves as a pseudo-gel. It is not homogeneous. In more dilute solution, sedimentation of the crystalline soap occurs. Solution in nujol and melting of the dry soap are thermal disruptions of the —COO metal groups. In the plastic and gel stages, the hydrocarbon tails are in kinetic agitation which prevents the soap's molecules forming into their regular lattice. The behaviour of a given soap depends on both kation and hydrocarbon tail. Gels of the oletes have much lower rigidity than those of the corresponding stearates. With some kations, moreover, the oleate forms gel and plastic form while the stearate does not. The gels of the alkali metals and of the alkaline earths are sensitive to small additions of certain polar substances with which they seem to form complexes. The theory of gels is discussed and the various possible types reviewed. It is emphasised that gelation requires more than a particular state of dispersion and particle size. Adhesion of the particles into a three-dimensional structure is necessary. The physical properties of the gel will depend upon the nature of the bonds holding them in this structure and upon the physical properties of the individual micelles.

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[32] Gortner and Hoffmann, *J.A.C.S.*, 1921, **43**, 2199 ; Wolf and Rideal, *Biochemical J.*, 1922, **16**, 548.