354. *The Solubility of Zinc Soaps in Organic Solvents.*

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The solubility of zinc soaps in organic solvents has been found to increase abruptly at a critical temperature. This increase is not due to an alteration in the degree of aggregation of the soap in solution but is a result of mesomorphic changes which occur in the solid soaps. Solution occurs at the critical temperature when solvent molecules penetrate between the hydrocarbon chains of the soap lattice. In discussing these results attention is drawn to the similarity between the structure of the metal soaps and materials of the high-polymer class.

FOR the present experimental study the zinc soaps were chosen for two main reasons. In the first place, some of the zinc soaps had been reported as differing from the majority of metal soaps in not exhibiting a plastic phase on heating (Lawrence, *Trans. Faraday Soc.*, 1938, **34**, 660), which suggested that their solutions might show points of interest. Secondly, the fact that the zinc soaps were known to have sharp melting points suitable for characterisation favoured accurate measurements. Much previous work in this field had for practical reasons been carried out with commercial grades of metal soaps which are well known to vary widely in composition, depending on the exact method of manufacture (cf. Elliott, "The Alkaline Earth and Heavy-metal Soaps", *Amer. Chem. Soc. Monograph*, 1946, 54).

Lawrence (*loc. cit.*) prepared a wide variety of metal soaps, a number in a pure state for the first recorded time, and showed that they dissolved at sufficiently high temperatures in Nujol to give clear solutions which, in the majority of cases, set to gels on cooling. The zinc soaps were again found to be anomalous, no gelation occurring on cooling their solutions. Lawrence concluded that dispersion of the soaps in Nujol in the form of micelles resulted when the thermal agitation of the paraffin chains was sufficient to overcome the adhesion of the polar groups which were mainly instrumental in maintaining the crystal lattice. Gallay and Puddington (*Canadian J. Res.*, 1944, *B*, **22**, 161) noted a partial melting phenomenon with calcium stearate in various mineral oils at about 100°, the soap dissolving rapidly above this temperature, and Mardles and Clark (General Discussion on Swelling and Shrinking, Faraday Society, 1946) have shown that the swelling of sodium stearate powder in a mineral oil increases very markedly at about 70°, which corresponds with the temperature at which a mesomorphic change occurs in the solid soap.

Definite investigations on the existence of micelles in metal soap solutions in organic solvents have only been reported on a few occasions. Soyenkoff (*J. Physical Chem.*, 1930, **34**, 2519) carried out a careful study of nickel and iron soaps in benzene, from which it was concluded that particles of colloidal dimensions were present. It was difficult to explain the stability of the dispersions; ions were shown to be absent by measurement of the conductivity of the solutions. Bhatnagar, Kapur, and Hussain (*Proc. Indian Acad. Sci.*, 1939, **9**, *A*, 143) found that zinc oleate gave a negligible depression of the freezing point of benzene, although from some measurements by the Rast method they concluded that the soap in camphor solution was unimolecular. [Elliott (*op. cit.*, p. 176) appears to misquote these authors as authority for the statement that zinc oleate is unimolecular in *benzene* solutions.]

Palit and McBain (*J. Soc. Chem. Ind.*, 1947, **66**, 3; cf. Gonick, *J. Colloid Sci.*, 1946, **1**, 393) have investigated hexanolamine oleate solutions in benzene and concluded that the micelles in the absence of water had an average size of 3—4 molecules, increasing to a very large size when water was added to the system.

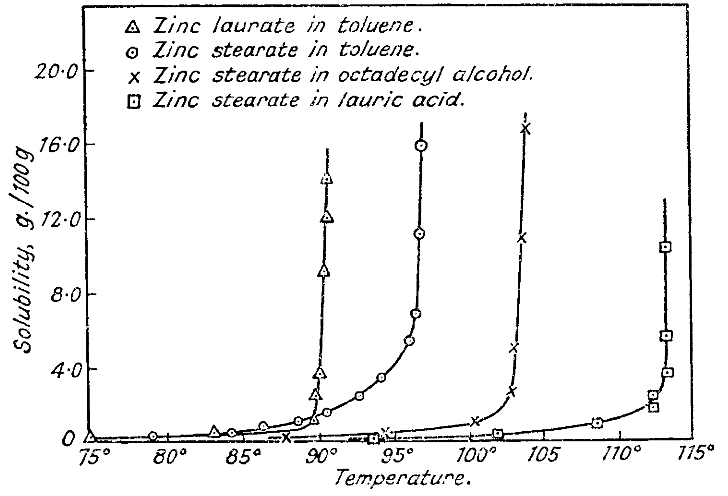
EXPERIMENTAL.

Preparation and Purification of Materials.—The acids used were decoic, lauric, myristic, and stearic. Pure samples of the first three acids were available (lauric and myristic acids were pre-war samples of Kahlbaum's "purissimus" grade) which were recrystallised from alcohol before use. Stearic acid was obtained from the B.D.H. purified grade *via* the methyl ester and subsequent fractional crystallization of the acid from alcohol until the m. p. rose to 69·2°. From these acids the soaps were prepared by the simple method already described (Pink, *J.*, 1938, 1252) and were dried in a vacuum-oven at 105°. The m. p.s of the acids and soaps are shown below :

Decoic acid ...	31·0°	Myristic acid ...	53·5°	Zinc decoate...	130·0°	Zinc myristate...	128·0°
Lauric acid ...	44·4	Stearic acid......	69·2	Zinc laurate ...	130·5	Zinc stearate ...	129·0

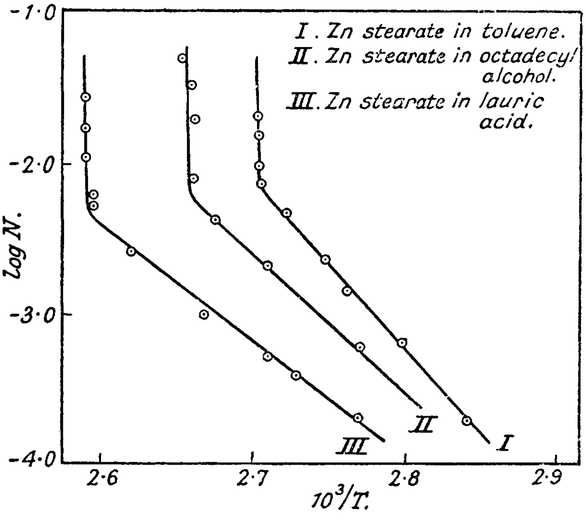
Towards the end of this investigation an attempt was made to distil the zinc soaps in a molecular still, since the comparatively low and sharp m. p.s suggested that the metal–carboxyl link in the soaps might be largely covalent rather than ionic in character. Nine hours' distillation of zinc stearate (distillation path 5 mm.; still temperature 133°; condenser temperature — 70°; vacuum 10^{-4} mm.) gave about 100 mg. of a product which melted at 126° (as against 129° for the original soap) and, since it contained zinc, was neither the ketone (m. p. 88°) nor the acid (m. p. 69·2°). Although the m. p. indicated that some decomposition (probably to the ketone) had occurred and that therefore the process, apart from the low yield, was not immediately available for purification, yet the fact that some zinc soap distilled provides further evidence for the covalent character of the metal–carboxyl link in these soaps. It may be noted that Bhatnagar, Kapur, and Hussain (*loc. cit.*) found zinc oleate solutions in benzene to be non-conducting, whereas magnesium oleate solutions in the same solvent were conductors, which may be regarded as additional evidence for the covalency of this link in the zinc soaps. Investigation of the possibility of using molecular distillation for purification of the soaps is continuing.

FIG. 1.



Solubility of zinc soaps in organic solvents.

FIG. 2.



Solubility Measurements.—The organic solvents employed were: toluene, b. p. 110·0—110·1°; xylene (mixture of isomers), b. p. 137—138°; *n*-octadecyl alcohol, m. p. 58·0°; lauric acid, m. p. 44·4°; nitrobenzene, b. p. 208—209°.

Measurements of solubility were made by a method similar to that described by Adam and Pankhurst (*Trans. Faraday Soc.*, 1946, **42**, 523) for measurements with aqueous solutions of paraffin-chain salts. The results with zinc laurate and stearate in toluene and zinc stearate in *n*-octadecyl alcohol and lauric acid are shown in Fig. 1, and the corresponding Hildebrand plots for the stearate are shown in Fig. 2.

In each case it will be seen that, after a slow rise in solubility, there is a sudden increase over a very small temperature range. The temperatures at which this occurs (the critical solution temperature or C.S.T.) for these cases and for the other solutions examined are shown in Table I. In this table the C.S.T. is taken arbitrarily to be the temperature at which a solubility of 10 g./100 g. of solvent is reached,

TABLE I.

Critical solution temperatures of zinc soaps in organic solvents.

	Toluene.	Xylene.	Octadecyl alcohol.	Lauric acid.	Nitrobenzene.
Zinc decoate	86·0°	89·0°	—	—	—
Zinc laurate.....................	90·8	93·7	—	—	111·0°
Zinc myristate	93·0	96·0	108·0°	114·0°	113·0
Zinc stearate	97·0	98·5	104·0	113·0	112·0

but owing to the steep rise in solubility little difference would be made by taking another arbitrary basis provided the concentration chosen was sufficiently high. In all the solvents, dispersion of the soap occurs very rapidly at the C.S.T., and particularly at the high concentrations, no difficulty is experienced in determining this point. Separation of the soap in a very finely divided form occurs below the C.S.T. In no case was gelation of the soap solutions observed. The behaviour of solutions in nitrobenzene was unusual. When solutions in this solvent were heated above the m. p. of the soap, it separated, not as a solid, but as a finely divided emulsion which settled out on standing as a gelatinous mass obviously containing much nitrobenzene. The reasons for this behaviour will be discussed later. No similar phenomenon was observed with the other solvents.

Molecular-weight Measurements.—By analogy with the Krafft phenomenon in aqueous soap solutions, it seemed possible that this steep rise in solubility over a small temperature range might be due to a change in the degree of dispersion of the soap from molecular to micellar at the C.S.T. In order to settle this point, molecular-weight measurements of some of the soaps in toluene were made. A twin Cottrell apparatus (cf. Pearce and Hicks, *J. Physical Chem.*, 1926, **30**, 1678) was employed in which the difference in b. p. between the solutions and the pure solvent could be measured with an accuracy of $\pm$ 0·001° by means of a multi-junction copper–constantan thermocouple. The results of these measurements are shown in Table II. Some values for copper stearate are included for comparison. In agreement with previous work on organic solvents, micelles were found to be present at all concentrations examined. The apparent increase in micellar weight observed in the more concentrated solutions may be due to non-ideality of the solutions rather than to an increase in micellar size, although the fact that very concentrated solutions ($>$ 10%) show faint opalescence indicates that at any rate in these concentrated solutions some micelles of a larger size are present. The micellar weights measured are probably mean values and do not necessarily indicate the absence of single molecules or of aggregates of smaller or larger size. Measurements could not be made above the concentrations shown in Table II because of the incidence of foaming, which prevented the attainment of steady boiling temperatures in the solutions. Although the full concentration range in which the solubility of zinc stearate rapidly increases was for this reason not covered in the b. p. measurements, yet it is clear that with both the laurate and the stearate the increase in solubility observed at the critical temperature is not due to a change in aggregation of the soap from molecular to micellar.

TABLE II.

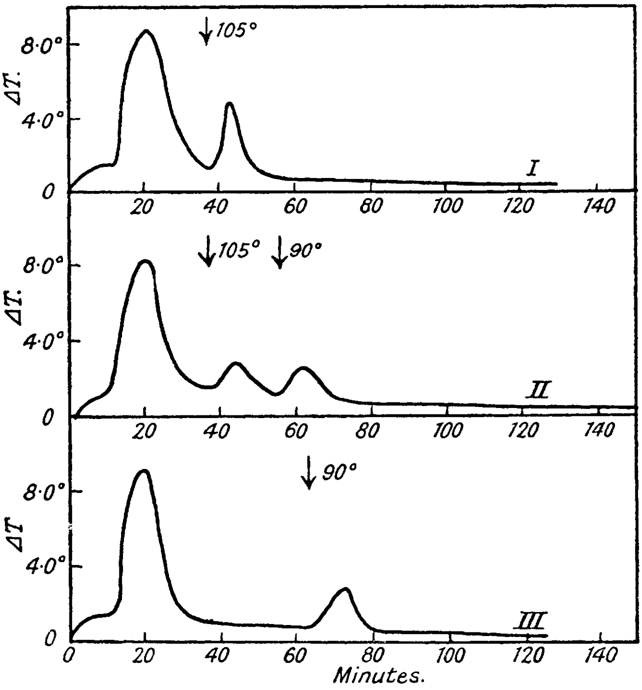
Micellar weights of soaps in toluene.

C = concn. in g./100 g.; M = micellar weight; N = number of molecules per micelle.)

Zinc laurate.			Zinc stearate.			Copper stearate.		
C.	*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

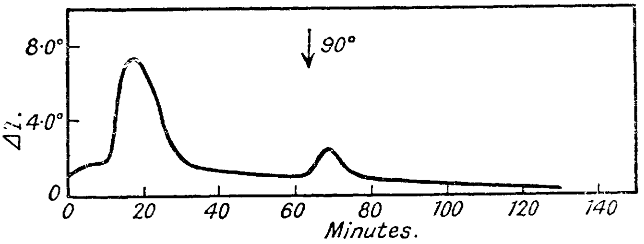
Phase Changes in the Solid Soaps.—Although zinc stearate and oleate had been reported by Lawrence (*loc. cit.*) as normal-melting substances, an investigation of the solid soaps by a cooling technique was undertaken in order to find out whether the steep rise in solubility could be attributed to a change in crystal structure at the critical temperature. It was found that, although zinc stearate showed no breaks in its cooling curve, the laurate and decoate had well-marked arrests in the temperature region in which the increase in solubility occurred (Figs. 3 and 4). In the case of zinc myristate a transition involving a very small heat change was observed at 73° (Fig. 5). Differential cooling curves were obtained in the following way. A sample of the soap contained in a Pyrex tube immersed in a mechanically stirred glycerol-bath was heated just above its fusion point and the difference in temperature between the cooling soap and the bath was measured by means of a ten-junction copper-constantan thermocouple, the junctions of which were dispersed as uniformly as possible throughout the sample. A difference in temperature between the soap and the bath of 0·002° could readily be observed by this arrangement, the large number of junctions ensuring that the maximum heat effect was measured : this is important because the thermal conductivity of the soaps is very low. The rate of cooling was not exactly the same in all the experiments but was usually about 0·7° per minute in the region in which the arrests were observed. The transition temperature in the case of zinc laurate and decoate was found to be affected by the presence of moisture. A freshly precipitated sample of zinc laurate which contained about 18% by weight of water before melting in the bath showed a well-marked transition at 105° (Curve I, Fig. 3). After partial drying over calcium chloride two transition points were observed (Curve II) while a dry sample of the soap showed only the transition at 90·0° (Curve III). Samples dried either by heating in the vacuum-oven or by keeping them for some time just above their m. p. in the glycerol-bath always showed the transition at 90·0° even on repeated fusion and cooling, while freshly precipitated samples containing water showed the transition at 105°. Estimates of the heat changes of the various transitions

FIG. 3.



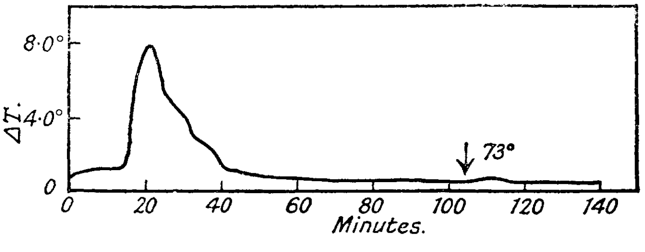
Cooling curves : zinc laurate.

FIG. 4.



Cooling curve : zinc decoate.

FIG. 5.



Cooling curve : zinc myristate.

were made by comparing the magnitude of the arrests with those obtained in the same apparatus with naphthalene and benzoic acid. The values obtained, with the corresponding entropy changes, are shown in Table III. The accuracy of the estimates relative to one another is about ± 5% but the absolute error may be greater than this.

TABLE III.

	ΔH_f.	ΔS_f.	ΔH_{105°.	ΔS_{105°.	ΔH_{90°.	ΔS_{90°.	$\Delta S_{(105^\circ+90^\circ)}$.	ΔS_{Total}.
Zinc laurate :								
Hydrated	15,000	37·2	3030	8·0	—	—	8·0	45·2
Partially dried	13,600	33·7	1870	4·9	1420	3·9	8·8	42·5
Anhydrous	12,900	32·0	—	—	2730	7·5	7·5	39·5
Lauric acid *	8,750	37·6	—	—	—	—	—	37·6
Stearic acid *	13,500	39·5	—	—	—	—	—	39·5

* Data from Int. Crit. Tables, First Ed., Vol. V, p. 134.

It will be noted that the total entropy of fusion of the anhydrous soap is approximately the same as the entropy of fusion of lauric and stearic acids, while the total entropy change for the transitions is approximately the same (*i.e.*, ~ 8 cals. deg.$^{-1}$ mole^{-1}) in all the samples, indicating a strong similarity between the processes involved in each case. The results indicate a different crystal arrangement in the presence and absence of water, and since the transition temperature is higher in the former case, it may be concluded that the low-temperature form is more stable in the presence of water. This is an unexpected result in view of the well-known effect of water in lowering the dispersion temperature of some other metal soaps in oils (Lawrence, *loc. cit.*). The explanation may be that the character of the metal–carboxyl bond in the dry soaps is predominantly covalent, and that the increased stability in the presence of water is due to the ionic nature of the lattice when water is present. There is no doubt that in some dry metal soaps this linkage is largely covalent as shown by their m. p.s lead oleate, for example, melts at 40° (Lawrence, *loc. cit.*). In all the curves, the first large arrest is that which occurs at the solidification point of the sample. It will be seen that the arrest observed with zinc myristate at the solidification point is of a complex type, containing at least two subsidiary arrests, indicating marked pre-melting a few degrees below the actual fusion point. It is possible that this pre-melting phenomenon involves the attainment of the same degree of freedom as that responsible for the arrests at 90° in the case of the decoate and laurate.

All the dry specimens of zinc laurate showed a further very small but reproducible arrest at about 98°, not shown in the curves. It was not clear whether this effect was due to a change in the zinc laurate crystals or to the presence of a small amount of impurity in the soap. The magnitude and position of the arrest were not affected by repeated crystallisation of the soap from toluene.

DISCUSSION.

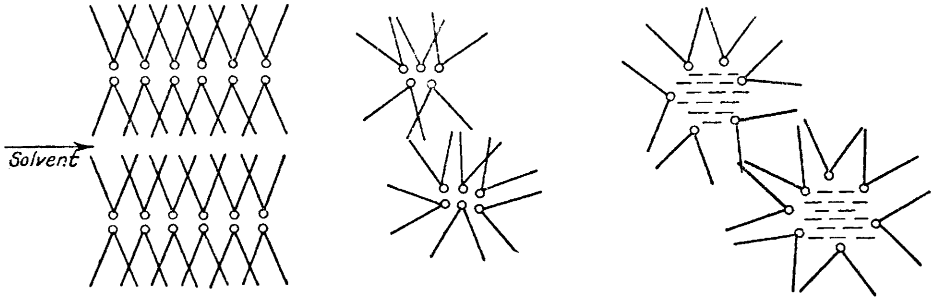
The behaviour of the zinc soaps and their solutions, described above, is caused by the amphipathic nature of the soap molecules. Lawrence (*loc. cit.*) has pointed out that, at a temperature at which the hydrocarbon chains are in violent kinetic motion, the polar groups still adhere sufficiently strongly to maintain a rigid crystal lattice. *X*-Ray investigations have shown that the arrangement in the soap lattice is of layers of double molecules with the carboxyl groups contiguous (Harkins, Mattoon, and Corrin, *J. Amer. Chem. Soc.*, 1946, **68**, 220, who give references to earlier work of Hess, Gunderman, Philippoff, Kiessig, and Stauff).

When the solid soap is heated, the thermal agitation of the hydrocarbon chains may be sufficient to bring about a change in the arrangement of the molecules in the lattice, resulting in a mesomorphic change of state. This is what occurs with the decoate, laurate, and myristate. With increasing chain length the effect becomes reduced, as shown by the smaller arrest observed with the myristate (C_{14}) as compared with the laurate (C_{12}) and decoate (C_{10}), while in the stearate, with eighteen carbon atoms in the chain, the attainment of the particular degree of freedom concerned is apparently postponed to the melting point. Zinc stearate is therefore a normal-melting substance. Polymorphism in the zinc soaps probably arises from variations in the angle of inclination of the hydrocarbon chains in the crystal lattice.

Solution in Non-polar Solvents.—When the soap is heated in presence of a solvent, the opening of the lattice, resulting from the thermal agitation of the chains, permits entry, between the chains, of solvent molecules provided the latter are of a sufficiently non-polar character, so that the heat of mixing with the hydrocarbon chains is small. The increased disorder in the lattice resulting from this penetration causes a breakdown of the rigid structure and dispersion of the soap in the form of micelles results. The reported insolubility of zinc stearate (Pink, *Trans. Faraday Soc.*, 1941, **37**, 181) in benzene is due presumably to the simple fact that its C.S.T. is above the b. p. of this solvent at atmospheric pressure. The process of solution is represented diagrammatically in Fig. 6, (*a*) and (*b*). In view of the size of the micelle in the solutions described in this paper, there is no *a priori* reason why its shape should not be spherical rather than the serpentine one suggested by Lawrence (*loc. cit.*). It should be noted that in the direction of the short spacing the hydrocarbon chains, above the C.S.T., have the structure of a liquid and not the regular arrangement shown in Fig. 6 (*a*).

Solution in Polar Solvents.—With relatively polar solvents such as lauric acid and *n*-octadecyl alcohol, the increased heat of mixing of the solvent with the hydrocarbon chains results in higher values for the C.S.T. as found experimentally (Table I). If the solvent is sufficiently polar, as is the case with nitrobenzene, it can also penetrate between the polar end groups of the soap molecules when the lattice approaches its maximum degree of disorder near the fusion point. This results in swelling of the micelles [Fig. 6 (*c*)], and the soap separates, on cooling, as a swollen mass containing much nitrobenzene. A similar phenomenon has been reported recently by Schulman and McRoberts in oil–water–soap systems containing aliphatic alcohols or phenols (Faraday Soc. Discussion on Swelling and Shrinking, 1946). The slight solubility of the zinc soaps in both classes of solvent below the C.S.T. probably occurs by solution of single molecules which tend to aggregate into micelles simply because the micelle, having a more predominantly non-polar exterior than the molecule, is thereby a more soluble unit. In the micelle the molecules are held together by the strong attractive forces around their polar end groups. The existence of these forces is demonstrated by the tenacity with which the metal soaps hold on to water, and their presence explains the paradox of their simultaneous insolubility in water and ease of taking up water of hydration (cf. Pink, *J.*, 1938, 1252; Lawrence, *loc. cit.*). Mark (*Trans. Faraday Soc.*, 1947, **43**, 447) has recently discussed in detail the mechanical properties of high polymers in relation to structure, pointing out the extreme anisotropy of the lattice of, *e.g.*, rubber, which has strong chemical bonds along the parallel chains of isoprene units, but only weak van der Waals forces perpendicular to the chains. On rise of temperature the weak intermolecular bonds are severed while the strong chemical linkages along the chains remain unaffected. The parallel between this picture as drawn by Mark and the structure of the metal soaps is very striking, the chemical linkages of the isoprene units being replaced in the soaps by the strong dipole forces around the metal–carboxyl links. These links appear to be less strong in the zinc soaps than in, *e.g.*, the magnesium soaps, which in the solid anhydrous state have a brittle glassy character (Pink, *J.*, 1938, 1252) having a very strong outward resemblance to that of materials of the high-polymer class. When the temperature of the magnesium soaps is raised, no sharp melting point is observed; instead, a highly viscous liquid capable of being drawn into threads is obtained. As Mark has pointed out, the mutual attraction of van der Waals forces alone is insufficient to prevent slip of whole chains along one another, and so in the case of metal soaps such as magnesium oleate a viscous liquid rather than a rubbery solid is produced on melting. It would seem possible that by suitably altering the hydrocarbon end of the metal-soap chain, this slip might be minimised and materials with interesting mechanical properties might become available.

FIG. 6.



(*a*) Crystal lattice before penetration of solvent.
(*b*) Micelles in non-polar solvent.
(*c*) Swollen micelles in polar solvent.

The authors wish to express their thanks to Professor A. R. Ubbelohde for many useful discussions and for his interest and advice throughout the work.

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[*Received, December 19th, 1947.*]