394. *Solutions of Metal Soaps in Organic Solvents. Part II.* Peptisation and Micelle Size in Solutions of Some Zinc Soaps in Toluene.*

By V. D. Tughan and R. C. Pink.

The peptisation of zinc soaps in toluene by a variety of organic compounds has been investigated. The most effective peptising agents are compounds with powerful co-ordinating groups which are capable of forming complexes with the soap in solution. Although water is a moderately efficient agent the fatty acids corresponding to the soaps are ineffective. The action of water is therefore not due to the liberation of free fatty acid by hydrolysis. Boiling-point measurements indicate that peptisation is accompanied by a marked decrease in micelle size.

Part I (*J.*, 1948, 1750) reported a rapid increase in solubility of zinc soaps in non-aqueous solvents observed over a small temperature range. This critical increase was shown to be associated with a phase change in the solid soaps. The present report describes the effect on the critical solution temperature of a number of additives. Further evidence on micelle formation and peptisation in organic solvents has also been obtained. In addition to solubility measurements, experiments have been made to determine the effect of peptising agents on the micelle size.

Peptisation in organic solvents differs in at least one respect from the apparently similar phenomenon in aqueous solutions since ionic dissociation cannot readily be invoked to explain the observed phenomena. According to Lawrence (*Trans. Faraday Soc.*, 1939, **35**, 702; 1937, **33**, 325; *J. Phys. Colloid Chem.*, 1948, **52**, 1504) the peptiser acts by co-ordinating itself to the soap molecules in solution, thus breaking down the soap aggregates and assisting swelling and dispersion of the soap. Essentially similar views have been expressed by Gray and Alexander (*J. Phys. Colloid Chem.*, 1949, **53**, 37) in connection with the peptisation of aluminium soaps.

In metal-soap solutions in organic solvents, water usually acts as a moderately efficient peptiser. Since the metal soaps are liable to hydrolysis the view has been held (Lawrence, *loc. cit.*; Alexander and Johnson, " Colloid Science," Vol. II, p. 697, Clarendon Press, 1949) that water acts as a peptising agent by liberating free fatty acid. The experiments now described were designed to test this hypothesis in the case of the zinc soaps by comparing directly the peptising effect of water and equivalent quantities of the corresponding fatty acids. One of the main results of the investigation is to show that with the zinc soaps the corresponding fatty acids are practically ineffective as peptising agents.

Experimental.

Preparation and Purification of Materials.—The zinc soaps were prepared by the general method previously described (cf. Part I) and dried at 95° to constant weight. Samples of soap containing small quantities of water were obtained by controlled drying over calcium chloride; the exact amount of water in the sample was determined by electrometric titration, the Karl Fischer reagent (K. Fischer, *Angew. Chem.*, 1935, **48**, 394; Carter and Williamson, *Analyst*, 1945, **70**, 369) being used.

The m. p.s of the acids and soaps used are :

Decanoic acid ...	31·0°	Myristic acid ...	57·4°	Zinc decanoate...	132·0°	Zinc myristate	128·5°
Lauric acid	44·1	Stearic acid	68·9	Zinc laurate	128·0	Zinc stearate...	130·0

For analysis, the soaps were hydrolysed with 7N-sulphuric acid; the hydrolysate was then filtered to remove the free acid, and its zinc content determined with standard ferrocyanide. The results of the analyses shown below indicate that in all cases the materials obtained were predominantly the neutral soaps with a slight excess of fatty acid.

	Zinc decanoate.	Zinc laurate.	Zinc myristate.	Zinc stearate.
Found, %	16·00	13·95	12·17	9·97
Calc., %	16·03	14·03	12·57	10·34

Thiophen-free toluene, which was used as solvent throughout, was dried over potassium hydroxide and then over sodium wire from which it was finally distilled immediately before use in an all-glass still. It had b. p. 110·2°/760 mm. The peptising agents were dried by previously described methods (Weissberger and Proskauer, " Organic Solvents," Oxford Univ. Press, 1935).

Peptisation Experiments.—The critical solution temperature, or C.S.T., is defined as the temperature at which there is a sudden increase in solubility of the soap over a small temperature range (cf. Part I). The peptising action of the additives was studied by determining their effect on the C.S.T. An arbitrary

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* The paper, " Solubility of Zinc Soaps in Organic Solvents " (Martin and Pink, *J.*, 1948, 1750), is regarded as Part I of this series.

mixture of 10 g. of soap and 100 g. of solvent was chosen for all initial soap solutions; little difference would be made by taking another arbitrary basis, owing to the steep rise in solubility at the C.S.T. Determinations of the C.S.T. for the various solutions were made by sealing weighed quantities of soap, toluene, and additive in " Pyrex " tubes and heating them very slowly in a large bath until the contents of the tube dissolved to give a clear solution. The tube was attached at an angle to the vertical to a rotating spindle which served to agitate simultaneously the soap solution and the bath, the temperature of the latter being controlled to ±0·2° by a combination of an electrical heater and a cold finger. The reproducibility of the measurements was approximately 0·5°. To check that sufficient time had been allowed for equilibrium to be established the solution was maintained at a temperature just below the C.S.T. for a considerable period to verify that complete solution did not take place.

Results obtained with some of the peptising agents in zinc laurate solutions are shown in Fig. 1. After a rapid initial fall a limiting C.S.T. value is reached, after which additions of peptising agent have

FIG. 1.

Effect of peptising agents on the critical solution temperature of zinc laurate–toluene solutions.

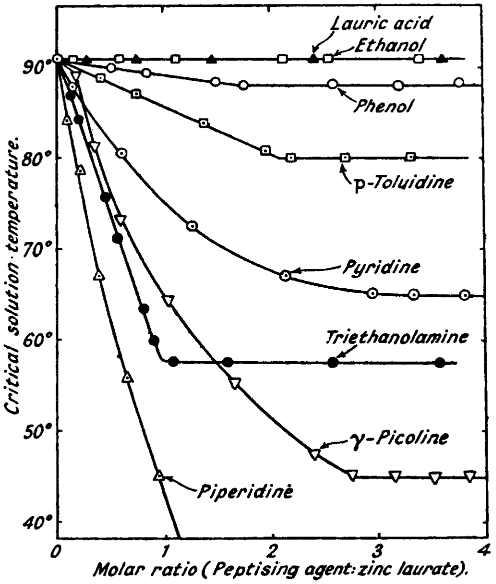


TABLE I.

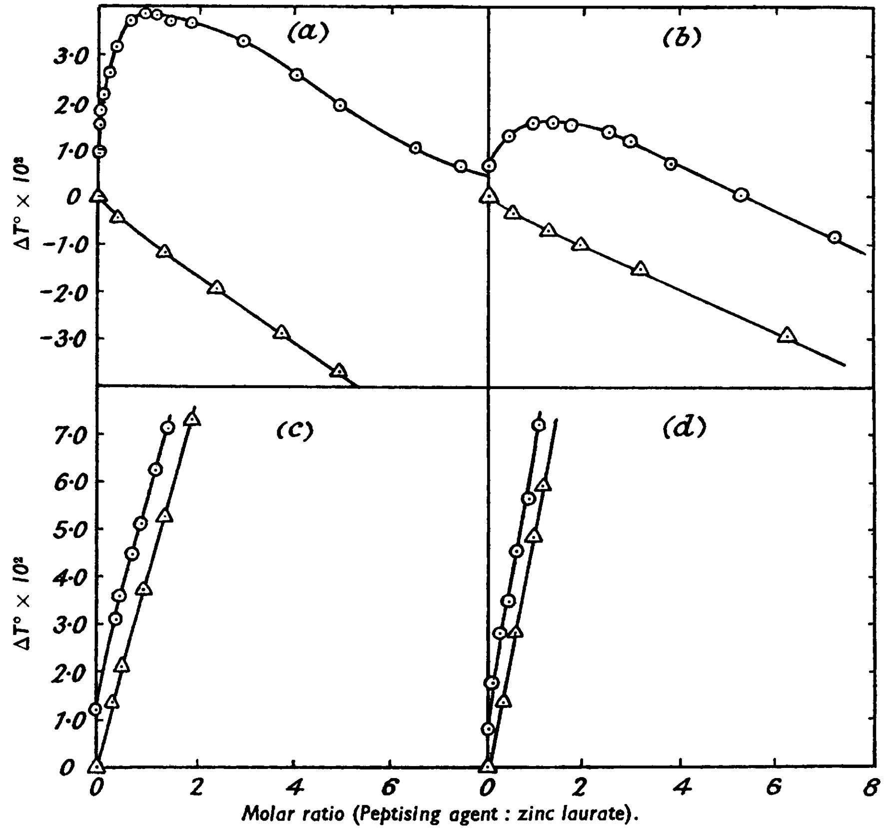
Effect of peptising agents on the critical solution temperature (C.S.T.) of zinc soaps in toluene.

Soap.	Peptising agent.	Limiting C.S.T.	Molar ratio, peptising agent : soap.
Zinc laurate	—	91·0°	—
	pyridine	65·0	3·0
	γ-picoline	45·0	2·8
	piperidine	<15·0	>1·6
	quinoline	79·0	3·3
	p-toluidine	80·0	2·1
	triethanolamine	57·5	1·0
	ethylenediamine	no peptisation	
	hexamethylenediamine	gelling agent	
	decamethylenedicarboxylic acid	no peptisation	
	sebacic acid	no peptisation	
	acetic acid	70·5	1·7
	lauric acid	no effect	
	stearic acid	83·5	0·1
	phenol	88·0	1·7
	ethanol	no effect	
	hexadecanol	no effect	
	water	77·5	0·7
Zinc decanoate	—	93·0°	—
	pyridine	63·0	1·8
	piperidine	48·0	1·9
	acetic acid	68·5	2·8
	decanoic acid	no effect	
	water	75·0	0·8
Zinc myristate	—	90·5	—
	pyridine	64·0	1·8
	piperidine	46·0	2·0
	myristic acid	no effect	
	water	82·0	0·8
Zinc stearate	—	89·0	—
	pyridine	62·0	1·6
	piperidine	50·0	2·1
	stearic acid	no effect	
	water	85·5	0·9

little further effect. The limiting C.S.T. and the molar ratio peptiser : soap at which this temperature is first attained are shown for all the additives and soaps studied in Table I. Piperidine proved to be the most efficient peptising agent for all the soaps; for example, zinc laurate solutions with a piperidine : soap mole ratio in excess of 1·6 gave clear solutions at room temperature, although the C.S.T. of the pure soap is 91°. That this was not due to supercooling was shown by the fact that even after being frozen out in liquid air the soap redissolved on being warmed to room temperature. In contrast to the effectiveness of the organic bases, alcohols, phenol, and the corresponding fatty acids were practically without effect. Unusual results were obtained with additives containing two functional groups. With sebacic acid, decamethylenedicarboxylic acid, and ethylenediamine, no peptising effect was observed, but instead an insoluble product was produced which appeared to contain both additive and soap. The exact nature of these products has not been investigated. Hexamethylenediamine on the other hand appeared to have definite gel-producing properties. When the solution containing this diamine was cooled, clear jellies were produced which slowly became opaque at room temperature. With all the effective peptisers the soap separated, when the solution was cooled, as a highly swollen pseudo-gel which could readily be broken into lumps. These pseudo-gels exuded solvent at room temperature and broke down completely after a few hours, the soap separating in the form of very fine crystallites.

FIG. 2.

Effect of peptising agents on the boiling points of toluene and zinc laurate–toluene solutions.



—△—△—△— *Solvent (toluene).* —⊙—⊙—⊙— *Soap solution.*

(*a*) *Piperidine :* 1·81% *soap solution.* (*c*) *Lauric acid :* 1·65% *soap solution.*
(*b*) *Pyridine :* 1·14% ,, (*d*) *Stearic acid :* 1·21% ,,

Micellar-weight Measurements.—Micellar weights were determined with an apparatus in which the difference in boiling point between the solution and solvent in two identical Cottrell tubes was determined to ±0·001° with a multijunction copper–constantan thermocouple. The precision obtained with this apparatus with a non-associated solute of high molecular weight is indicated by the results obtained in a series of measurements with phenanthrene (M = 178·1) for which the following results were obtained, 180·8, 180·0, 179·0, 178·2, 180·9, and 179·6, leading to a mean value of 179·7. Micellar weights of zinc laurate in toluene so obtained were in good agreement with previously reported values (cf. Part I). The effect of additives on the apparent micellar weight of zinc laurate in toluene was examined in the following way. To one of the Cottrell tubes soap was added as in a normal micellar-weight measurement.

and the boiling-point elevation noted. Successive amounts of peptising agent were then added to the same tube, and the effect on the boiling point observed. The effect of the additive on the boiling point of the solvent alone was similarly determined by its addition to the other Cottrell tube. The results obtained in this way with a number of additives are shown in Fig. 2. With piperidine and pyridine, addition of a small amount of the peptising agent to the solvent alone causes a boiling-point depression. When the same amount of peptising agent is added to the *soap solution* an *elevation* of boiling point is observed. [Fig. 2 (*a*) and (*b*)]. Addition of excess of peptising agent produces the normal effect as on the pure solvent, *i.e.*, a boiling-point depression. The boiling point of the soap solution thus passes through a maximum at a concentration of peptising agent which for pyridine and piperidine corresponds approximately to an equimolecular ratio of peptising agent to soap. With the additives which were relatively ineffective as peptisers, *e.g.*, lauric acid, no abnormal rise in the boiling point of the soap solution was observed [see Fig. 2 (*c*) and (*d*)]. Acetic acid produced an effect similar to that of pyridine and piperidine. The results obtained with water were inconclusive, since steady ebullition could not be obtained when water was added to the soap solutions.

Formation of Soap–Peptising Agent Complexes.—Since it seemed likely that the effective peptising agents acted by co-ordination to the soap, unsuccessful attempts were made to isolate crystalline soap–peptising agent complexes from the toluene solutions. Zinc stearate, however, on crystallisation from cold pyridine gave a crystalline monopyridine addition compound which decomposed when warmed, regenerating the soap and pyridine [Found : loss of weight on a sample heated to 110°, 11·0, 11·05. Calc. for $(C_{18}H_{35}O_2)_2Zn,C_5H_5N$: 11·12%. M. p. of recovered soap 129·5°]. This addition compound is analogous to the crystalline compounds obtained by Koenig (*J. Amer. Chem. Soc.*, 1914, **36**, 956), with the palmitates and stearates of copper, nickel, and cobalt and pyridine. With zinc stearate and pyridine Koenig obtained only a " sticky amorphous mass with adherent pyridine."

DISCUSSION.

The fact that the most efficient peptising agents for all the soaps are the organic bases with their characteristically powerful co-ordinating groups supports the view that these compounds act as peptising agents by forming co-ordinate linkages with the soap molecules. Also supporting this view is the observation that the maximum effect on the boiling point of the soap solution occurs when these peptising agents and the soap are present in approximately equimolecular proportion. The formation of the monopyridine–zinc stearate complex and the analogous compounds isolated by Koenig indicates that the formation of complexes in solution is not improbable.

While water was a moderately effective peptising agent for all the soaps the corresponding fatty acids were found in every case to be ineffective. The experimental evidence is, therefore, strongly against the view that in these systems the effect of water is to cause hydrolysis of the metal soaps with liberation of free fatty acid. It seems much more probable that, as with the organic bases, water acts by forming complexes with the soaps. While stable hydrates of the zinc soaps of simple stoicheiometric composition have not, so far as is known, been reported, analogous metal soaps have been shown to form such hydrates (Vold and Vold, *J. Phys. Colloid Chem.*, 1948, **52**, 1424; Vold and Hattiangdi, *Ind. Eng. Chem.*, 1949, **41**, 2311; Caspari, *J. Amer. Chem. Soc.*, 1905, **27**, 308; Pink, *J.*, 1938, 1252; Gardiner, Buerger, and Smith, *J. Phys. Chem.*, 1945, **49**, 417).

Micellar Weights.—The ebullioscopic data obtained with piperidine and pyridine can be accounted for in a qualitative way by assuming that the addition of the peptising agent causes a break-up of the original micelles with a resultant increase in the number of osmotically active particles. Quantitative evaluation of the data in terms of micellar weights meets with two main difficulties, the obviously non-ideal character of the solutions and a lack of knowledge of the exact distribution of the peptising agent between solvent and micelle. A semi-quantitative interpretation is obtained by assuming that with less than the critical concentration of peptising agent all of it is taken up to form a co-ordination complex and that the ebullioscopic constant of the solvent is unaffected by the presence of the small concentrations of peptising agent employed. Justification for the first assumption lies in the fact that the maximum effect on the boiling point is found when the peptising agent and soap are present in approximately equi-

TABLE II.

Effect of peptising agents on the micellar weight of zinc laurate in toluene.

Pyridine–1·14% soap solution.

Molar ratio, $Zn(C_{12}H_{23}O_2)_2 : C_5H_5N$	0	0·431	0·724	1·015
Micellar weight	2620	1740	1410	1470

Piperidine–1·81% soap solution.

Molar ratio, $Zn(C_{12}H_{23}O_2)_2 : C_5H_{11}N$	0	0·090	0·272	0·452	0·912
Micellar weight	3070	2530	1860	1490	1250

molecular proportions; the second assumption was shown to be approximately true by molecular-weight measurements on naphthalene in dilute solutions of the peptising agent. Micellar weights calculated on the basis of these simplifying assumptions are shown in Table II. The micellar weight falls rapidly with either pyridine or piperidine to a value approximately half that in the pure solvent. Since the non-ideal character of these solutions makes the results only approximate, speculation on the exact composition of the micelle in the presence of peptiser is unwarranted. To a first approximation the data in Table II would be accounted for by assuming that the micelle in the presence of excess of peptising agent is one in which half of the soap molecules have been replaced by molecules of peptising agent. In any event, it is quite clear that in these solutions peptisation is accompanied by a considerable decrease in micelle weight.

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