Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Solution behaviour in alcohols and phase transitions of cadmium(II), mercury(II) and lead(II) carboxylates

M. S. Akanni[a]; N. A. Abass[a]
[a] Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria

To cite this Article Akanni, M. S. and Abass, N. A.(1989) 'Solution behaviour in alcohols and phase transitions of cadmium(II), mercury(II) and lead(II) carboxylates', Liquid Crystals, 6: 5, 597 — 608

To link to this Article: DOI: 10.1080/02678298908034179

URL: http://dx.doi.org/10.1080/02678298908034179

LIQUID CRYSTALS, 1989, VOL. 6, NO. 5, 597–608

Solution behaviour in alcohols and phase transitions of cadmium(II), mercury(II) and lead(II) carboxylates

by M. S. AKANNI and N. A. ABASS (in part)
Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria

(*Received 22 August 1986; accepted 25 May 1989*)

Data were obtained for the solution behaviour of cadmium(II) and mercury(II) carboxylates in alcohols. A brief survey of the arguments about the existence of micelles and the current models of surfactant aggregation in non-aqueous media is presented. The plots of solubility against the carboxylate or alcohol chain length are linear for both cadmium and mercury soaps with the solubility having values higher in secondary than primary alcohols. The solution behaviour of metal 9,10-dihydroxyoctadecanoates shows the effect on solubility, of substitution of dihydroxyl groups at the middle of the carbon chain. Recrystallisation temperatures of the dihydroxyoctadecanoates suggest the loss of stereochemical configuration in solution and indicate similarity in the mode of aggregation. The solution temperatures of cadmium soaps are very close to the temperatures of their phase transitions while those of mercury and lead soaps are lower than their fusion or phase transition temperatures. This behaviour is interpreted to be due to differences in the energy required for the disruption of the crystal structure which dominates the solubility mechanism.

1. Introduction

The solution properties of metal carboxylates have been the subject of intense investigation for many years [1–8]. Some of the important uses of solutions of metal carboxylates which make them worthy systems for research were discussed in our recent article [9]. This presented data on the solution behaviour of some metal carboxylates (soaps) in organic solvents and particular emphasis was placed on the solubility of lead(II) soaps. While in decalin and pentan-3-one the behaviour of the lead soaps was interpreted in terms of solubilization of the mesophase, in alcohols Krafft type behaviour was followed, where the solubility was low up to a certain critical temperature and then increased dramatically. This behaviour showed that whether mesophases or micelles would dissolve depends on the type of solvent used. Thus, in continuation of the authors' interest in the solution and thermal [10–12] behaviour of metal soaps, we report here a detailed study of the solution behaviour of cadmium(II) and mercury(II) soaps in alcohols with references to some lead(II) carboxylate solutions. The effect of substitution on solubility of some other soaps is also examined.

2. Experimental

Preparation, purification and characterisation of cadmium(II) [12], mercury(II) [13] and lead(II) [14] carboxylates as well as the substituted soaps [15] have been described elsewhere.

The method used for solubility measurement in the present work has also been reported [9]. However, a liquid paraffin bath was substituted for the previous water bath to enable measurement above the boiling point of water to be made. The error of duplicate measurements in this work is not more than 2 per cent. Similarly, values of solubility points obtained presently and those from previous work for the same soap in the same solvent do not differ by more than 2 per cent.

3. Results

The solubility of a certain concentration of material in a suitable solvent occurs over a small temperature range rather than at an exact temperature. Two methods have been used to obtain such solubility temperatures. The first method obtained the Krafft point, T_k, from the plots of the logarithm of solubility against the inverse temperature [16, 17]. The second method determined the temperature at which a certain solubility was observed [3]. The two methods have been compared and were found to give acceptable results within the limit of experimental error [9]. The second method was used to obtain the present solubility data.

The solubility of some binary mixtures of lead(II) tetradecanoate-octadecanol was studied in order to gain an insight into the mechanism of dissolution. The values

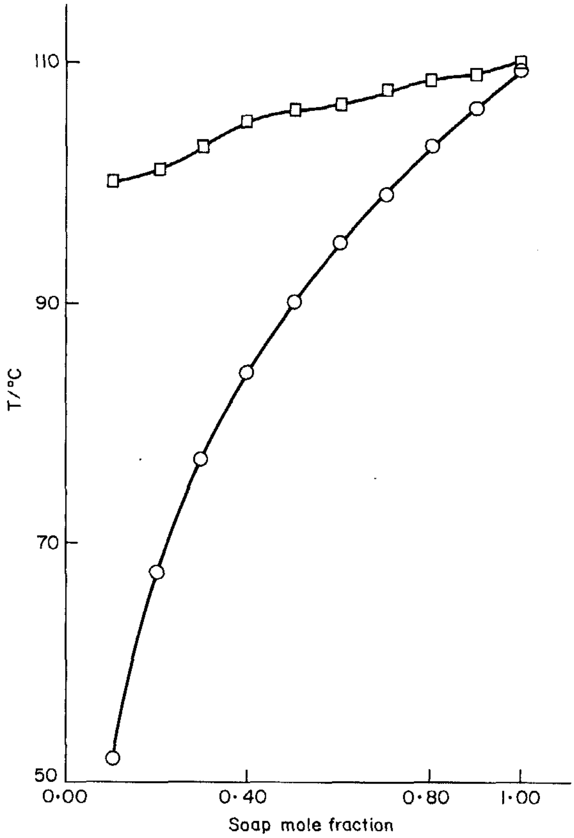

Figure 1. Plot of solubility temperature against soap mol fraction for □ binary mixtures of lead(II) tetradecanoate-octadecanol and ○ ideal mesophase → liquid in lead tetradecanoate.

Table 1. Solution behaviour of cadmium(II) carboxylates in hexan-1-ol and octadecan-1-ol.

			Hexan-1-ol		Octadecan-1-ol
Carbon chain length	Concentration (wt %)	Solution temperature °C	Temperature of recrystallization on cooling °C	Solution temperature °C	Temperature of recrystallization on cooling °C
10	1	100·0	97	108·5	102
	2	101·0	100	109·0	107
	3	102·0	100	113·0	109
	4	104·0	102	112·0	106
	5	105·0	103	115·5	111
14	1	102·0	88	11·0	81
	2	100·5	89	111·5	83
	3	101·5	91	112·0	87
	4	103·0	92	115·0	91
	5	105·0	89	117·5	102
16	1	103·0	84	112·5	75
	2	103·0	85	113·0	74
	3	104·0	84	116·0	76
	4	106·0	86	118·5	77
	5	108·5	87	120·0	77
18	1	105·0	74	114·0	58
	2	106·0	77	116·0	59
	3	106·5	86	118·0	62
	4	106·5	86	118·0	61
	5	108·0	87	121·5	62

obtained are compared with those calculated for mesophase → liquid transition temperatures, in different mole fractions of lead tetradecanoate, using an expression derived from the Clausius–Clapeyron equation [18]

$$\ln \chi = -\frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right),$$

where χ is the mol fraction, ΔH is the enthalpy of mesophase → liquid transition and T_0 is the transition temperature of the mesophase → liquid transition for pure lead tetradecanoate. Values [19] for ΔH of $41{\cdot}6\,\mathrm{kJ\,mol^{-1}}$ and for T_0 of $382{\cdot}7\,\mathrm{K}$ were used for the calculation. Both the experimental and the calculated data are presented in figure 1.

For cadmium(II) and mercury(II) soaps, temperatures of 1–5 per cent solubility by weight were measured by dissolving a known weight of solute (soap) in 5 g of alcohol and the values in hexan-1-ol and octadecan-1-ol are presented in tables 1 and 2. The recrystallization temperatures for some of the soaps are also recorded in the tables.

The recrystallization mechanism is such that the nuclei were first formed upon slow cooling. The process of stirring of the solution helped the nuclei to grow. Consequently, the supersaturation pressure above the solution caused the moving nuclei to develop to a critical dimension with the result that a fog of liquid was observed initially followed by a precipitate. The details of such a nucleation process is well documented in the literature [20–22]. The crystals redissolved at the same temperature on reheating. The temperature of 1 per cent (0·05 g of soap in 5 g of

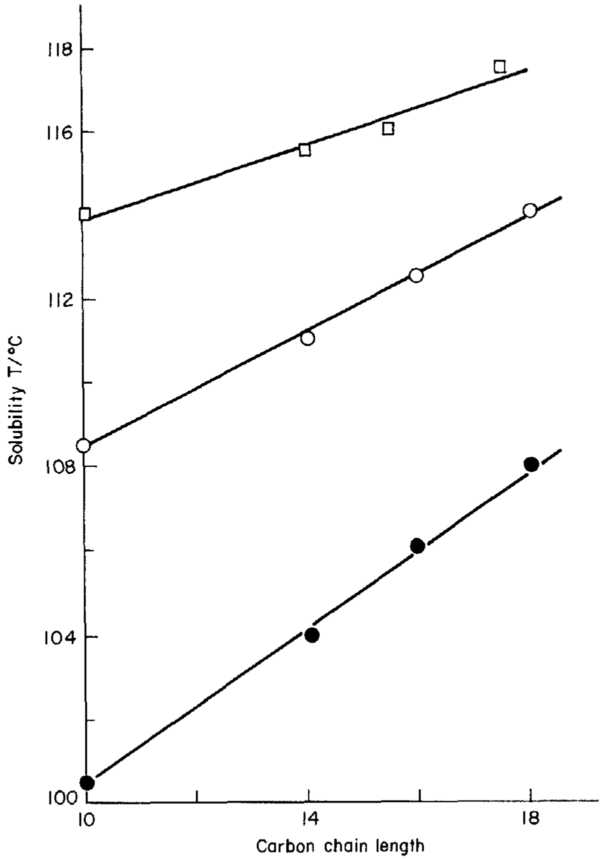

Figure 2. Plot of solubility temperature against carbon chain length for cadmium(II) carboxylates in ● decan-1-ol, ○ octadecan-1-ol and □ octan-2-ol.

Table 2. Solution behaviour of mercury(II) carboxylates in hexan-1-ol and octadecan-1-ol.

			Hexan-1-ol		Octadecan-1-ol
Carbon chain length	Concentration (wt %)	Solution temperature °C	Temperature of recrystallization on cooling °C	Solution temperature °C	Temperature of recrystallization on cooling °C
14	1	80·0	No crystal	90·5	68
	2	83·5	–	91·0	70
	3	85·0	–	89·5	69
	4	86·5	–	92·0	71
	5	86·5	–	91·5	70
16	1	82·0	–	91·5	71
	2	82·0	–	92·0	71
	3	84·0	–	93·0	71
	4	85·5	–	93·0	70
	5	86·5	–	92·5	72
18	1	82·5	56	92·5	73
	2	82·5	57	93·0	72
	3	84·5	58	91·0	70
	4	85·0	58	93·5	71
	5	86·0	61	92·5	73

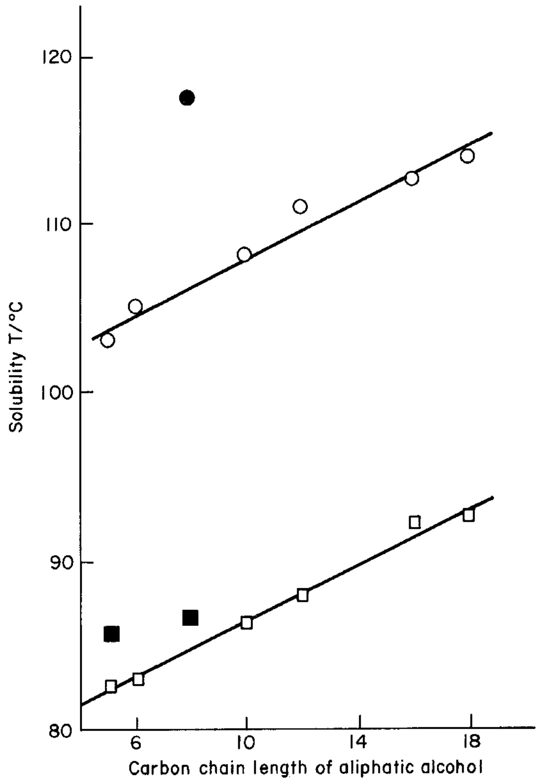

Figure 3. Plot of solubility temperature against carbon chain length of aliphatic alcohols for □ mercury(II) and ○ cadmium(II) octadecanoates. ■ and ● represent secondary alcohols.

Table 3. Solubility temperatures (1 per cent) of even chain length cadmium(II) carboxylates in alcohols

	Solubility temperatures °C			
	Carbon chain length of soap			
Solvent	10	14	16	18
Pentan-1-ol	99·5	102·0	102·5	103·0
Pentan-2-ol	–	–	–	–
Hexan-1-ol	100·0	102·0	103·0	105·0
Octan-2-ol	114·0	115·3	116·0	117·5
Decan-1-ol	100·5	104·0	106·0	108·0
Dedecan-1-ol	107·0	108·5	110·5	111·0
Hexadecan-1-ol	107·0	109·0	110·0	112·5
Octadecan-1-ol	108·5	111·0	112·5	114·0

solvent) solubility is presented in tables 3 and 4 for cadmium and mercury carboxylates in various alcohols. Plots of the 1 per cent solubility against the carbon chain length for cadmium soaps in some selected alcohols are shown in figure 2. Similar plots for mercury(II) soaps were found to be linear. The solute-solvent interaction effect are examined by plotting the 1 per cent solubility values against the alcohol carbon chain length. Figure 3 shows the linearity of such plots for both cadmium and mercury octadecanoates with the soaps having higher solubility values in secondary alcohols,

Table 4. Solubility temperatures (1 per cent) of even chain length mercury(II) carboxylates in alcohols

Solvent	Solubility temperatures °C Carbon chain length 14	16	18
Pentan-1-ol	80·0	81·5	82·5
Pentan-2-ol	83·0	84·5	85·5
Hexan-1-ol	80·0	82·0	82·5
Octan-2-ol	84·0	85·0	86·5
Decan-1-ol	82·0	85·0	86·5
Hexadecan-1-ol	90·0	90·5	92·5
Octadecan-1-ol	90·5	91·5	92·5

Table 5. Solubility temperature (1 per cent) and recrystallization temperatures of divalent metal 9,10-dihydroxyoctadecanoates in dodecan-1-ol.

Metal 9,10-dihydroxyoctadecanoate	Solubility temperature °C	Temperature of recrystallisation on cooling °C
Lead (*R*)	127	96
Lead (*M*)	148	98
Zinc (*R*)	132	94
Cadmium (*R*)	136	81
Mercury (*R*)	114	–

R is racemic mixture and *M* is meso-product.

pentan-2-ol and octan-2-ol (in the case of mercury soaps) and octan-2-ol (in the case of cadmium soaps), than the corresponding primary alcohols.

Table 5 shows the effect on solubility, of substitution of dihydroxyl groups at the middle of the carbon chain of soaps. The data in the table also show the solution behaviour of stereochemical isomers of lead(II) 9,10-dihydroxyoctadecanoate.

4. Discussion

4.1. *The nature and mechanism of aggregation of metal soaps in organic solvents*

In spite of the large number of studies of metal soap solubility in organic solvents [1–9] and the evidence for the existence of aggregates in a number of cases, no clear pictures exist on the structures of these systems. In his extensive review [6] Pipel suggested the presence of micelles (presumably of inverted structure), and the possibility of a definite, though low, critical micelle concentration. Such a model requires the existence of monomers at low concentrations and aggregates at high concentrations. Evidence of this has been obtained with certain long chain copper carboxylates [4, 9, 23]. With this model for the aggregates, the narrow temperature range over which a dramatic increase in solubility is observed can be viewed as a Krafft point [9, 16] analogous to that observed in aqueous solutions.

However, it may be argued that the problem of applying a reversed micellar structure to these systems is that such an aggregate should possess a large number of surfactant molecules associated *via* their polar head groups. Ebulliscopic measurements on zinc and copper carboxylates suggests 5–7 molecules (i.e. 10–14 carboxylate chains) per aggregate, [3, 24] whereas spherical reversed micelles may be expected to be considerably larger. An alternative model is that dissolution of the soap involves swelling of the soap lattice in a similar fashion to that observed in polymer solubility [25]. In this case it is expected that mixed soap–solvent aggregates may be observed. Some support for this model comes from the relationship between the solution temperature and solvent solubility parameter. In their study of metal soap solutions, Nelson and Pink [24] suggested that though aggregates exist in toluene solutions, in isobutyl alcohol and pyridine only monomers or dimers are present. Further, vapour pressure osmometry failed to detect aggregates in a lead dodecanoate-solvent system although other techniques suggested their presence [17]. In these cases it is reasonable to consider some kind of specific soap–solvent interaction helping to break up the reversed micelles, such that the aggregation phenomena are very solvent dependent.

It is noteworthy that viscosity and thermal studies on lead and zinc carboxylates [19, 26] indicate the presence of aggregates of a similar size to those observed in solutions in non-polar solvents like toluene. Crude geometric arguments provide an estimate of the minimum number of monomers needed to form a micelle. If we take a disc as the smallest possible structure and take a circle composed of n monomer chains of length l and maximum cross section d, the area of each unit is approximately $\frac{1}{2}ld$ whilst the area of the circle is πl^2; thus $(n/2)ld = \pi l^2$. For lead(II) decanoate, values of 23 Å for the length of two chains and 29 Å^2 for the maximum area have been reported [27]. If we take these as appropriate magnitudes to give $l = 11{\cdot}5$ Å, $d = 6{\cdot}1$ Å, from which we calculate $n = 12$, i.e. 6 divalent metal soap molecules are needed to form the simplest possible micelle. While drastic assumptions are made in this calculation, in particular the use of the values of l and d for a lamellar phase which shows no curvature, it may be more than coincidence that this value is close to that observed with the aggregates in these systems in non-polar media.

To appreciate what is happening in the various solvent systems, it is informative to consider briefly the current models of surfactant aggregation in non-aqueous media. Three mechanisms [28] are commonly considered;

(1) Mass action model

$$n \text{ monomers} \rightleftharpoons \text{micelles.}$$

(2) Stepwise association model

$$\text{monomer} \rightleftharpoons \text{dimer} \rightleftharpoons \text{trimer} \rightleftharpoons n\text{-mer.}$$

(3) E model

$$\text{monomer} \rightleftharpoons \text{linear aggregates} \rightleftharpoons \text{micelles.}$$

While the model operating is likely to depend on the specific solvent-amphiphile system [29] evidence for the E model has been presented for various ionic surfactants in cyclohexane [28]. If such a mechanism occurs for metal soap solutions, we have a ready explanation for the differences in behaviour between non-polar solvents, where aggregation acts to minimize contact between the solvent and $M^{2+}(^{-}O_2C)_2$ grouping, and the aggregates are probably very similar to those in the molten soaps, and polar solvents such as alcohols and pyridine, where solvent coordination to the metal ion and interaction with the carboxylate group are possible to give metal soap-solvent species. We discuss the present results, and those in a previous article [9] on the basis of this model.

4.2. *The present study*

It can be seen from figure 1 that the experimental solubility temperatures are consistently higher than the values calculated from the ideal freezing equation. Further the curve of the experimental data shows a shoulder at around 0·5 mol fraction. This probably suggests that the mechanism of dissolution is not just a matter of the increased alcohol composition lowering the transition temperature. In our earlier viscosity and thermal studies, mixtures of dodecanoic acid [30] or lead(II) oxide [31] and pure lead(II) dodecanoate were found to give aggregates of soap-additive in the molten state. The number of aggregation in either mixture was different from that obtained for the pure soaps. The acid or the oxide was also found to modify the number of phases and the phase transition temperatures [10, 32] of the pure soap. Similarly the behaviour in alcohol solutions is such that the increased concentration of alcohol serves to modify the solid → liquid transition temperatures *via* the formation of soap-solvent aggregates. This view is examined further by plotting log (mol fraction) against $1/T$. The enthalpy of fusion calculated from the least squares slope of this graph (correlation coefficient = 0·98) is 251·1 kJ mol^{-1}. This value is more than double that obtained (DTA result) for the fusion of lead(II) tetradecanoate (crystal → liquid) and about six times that of mesophase → liquid [19]. The high value probably corresponds to the process for some aggregate.

The solutions of cadmium soaps in hexan-1-ol and octadecan-1-ol are observed to be colourless with higher concentrations of the soaps going into solution at higher temperatures (see table 1). This is just a consequence of increased saturation. The solution temperatures are found to increase generally with increasing chain length of carboxylate. This is expected because the longer carbon chain length carboxylates are generally less soluble. The recrystallization temperatures on cooling in most cases are much lower than the solution temperature. This is quite significant as the behaviour tends to support the presence of aggregates of the soap molecules in solution. In solution the properties of monomers and aggregates are likely to be different such that the temperatures at which the monomers go into solution will be different from those at which aggregates revert to solids. It is noteworthy that the solution and the recrystallization temperatures are reproducible on reheating and recooling a sample, respectively. This may suggest the physical nature of these aggregates.

All of the mercury soaps dissolve to give clear solutions in octadecan-1-ol (see table 2). In these cases the recrystallization temperatures are lower than the solution temperatures, and similar to the behaviour of cadmium soaps in the same solvents. This would suggest, as in cadmium soap solutions, the process of some aggregate even though the number and the structure of such aggregates may be different in both cases. However, in all other alcohols (pentanol to hexadecanol), all of the mercury soaps, except mercury octadecanoate, dissolve to give yellow solutions. The colour became intense with increase in the weight of the soaps. Thus the recrystallisation temperatures of these solutions could not be determined. The yellow colour in systems containing mercury is often associated with the formation of a trimercury ion (Hg_3^{2+}) which could be obtained through oxidation reactions [33]. Such oxidation processes frequently occur in acidic solutions where liquid mercury is present. Data on pyrolytic decomposition have shown that mercury(II) carboxylates decompose to give mercury, acids and other products [34]. It is not unlikely that mercury hexadecanoate and the lower chain length mercury soaps have decomposed slightly in short chain alcohols to give mercury and the corresponding acids. The mercury may subsequently undergo an oxidation reaction to give the observed yellow colour. The reason why such oxidation leading to the formation of yellow colour does not occur for mercury octadecanoate in all of the alcohols and all the mercury soaps in octadecan-1-ol is not immediately clear. Probably the soap-solvent aggregates of longer carbon chain length mercury octadecanoate and those of shorter carbon chain length alcohol are more stable with respect to decomposition–oxidation reactions.

The solubility values of 1 per cent solution for cadmium and mercury carboxylates in various alcohols in tables 3 and 4 show a linear dependence on the aliphatic alcohol chain length. This trend is indicative of the important role of solvent–solute interactions in solubility phenomena. Cadmium(II) soaps, like their lead counterparts [9], are not appreciably soluble in propan-2-ol even at its boiling point whereas mercury(II) soaps dissolve readily in this alcohol on warming. Plots of solubility values against the carbon chain length of cadmium soaps in selected alcohols are linear (see figure 2). These plots are also linear for mercury soaps and the behaviour is similar to the case of lead soaps earlier reported [9]. However, solubility values in a secondary alcohol, octa-2-ol are considerably higher than those in primary aliphatic alcohols (see figure 3). Such linear correlations between solubility parameters and carbon chain length have been interpreted as clear evidence of hydrophobic interactions [35].

The result in table 5 shows the effect on solubility, of substitution of dihydroxyl groups at the middle of carboxylate chain. The values in the table are considerably higher than those observed for the corresponding unsubstituted metal octadecanoates. This is in conformity with our earlier observation that found lead 2-ethylhexanoate to be only sparingly soluble in various warm alcohols [36] whereas straight chain lead carboxylates dissolve readily in them. The solubility of the lead soap (meso product) is higher than its racemic mixture counterpart. The behaviour is indicative of differences in the packing arrangement of the soaps in the solid phase. In fact, recent DSC studies confirmed this assertion as the total entropy of transition (solid → liquid) of the meso isomer was found to be much higher than that of its racemic counterpart [37]. It is noteworthy that the recrystallization temperatures on cooling of these stereoisomers are about the same, and this may illustrate the loss of stereochemical configuration effect in solution and also suggest the formation of aggregates of similar kind for the isomers as the recrystallization temperatures are lower than the solution temperatures.

On heating the long chain carboxylates of cadmium(II) and mercury(II), using a quantitative differential thermal analysis, one or more mesophases have been observed between the solid and liquid phases [12–13, 38]. The results of such a study are summarized in tables 6. It should be mentioned that in a recent study carried out

Table 6. Phase transitions and temperatures reported for even chain length cadmium(II) and mercury(II) carboxylates ([12, [13] and [38]).

	Temperature °C				
	Carbon chain length				
Phase transition	10	12	14	16	18
	Cadmium soaps				
Crystal → mesophase 1	–	94·7	101·7	107·4	107·0
Mesophase 1 → mesophase 2	–	–	–	114·1	113·2
Mesophase 2 → liquid	–	97·5	107·4	125·0	–
	Mercury soaps				
Solid → Phase 1	107·8	–	104·4	110·4	–
Phase 1 → liquid	116·3	–	114·0	114·0	120·0

by Ellis [38], no evidence was found for the presence of mesophases in mercury soaps. Instead, crystals phases were identified for some of the soaps. However, his fusion temperatures are in agreement with those in table 6.

Comparison of solution temperatures (see tables 1 and 2) with the phase transition or fusion temperatures in table 6 indicates that while the solution temperatures are close to the phase transition temperatures for cadmium soaps, they are much lower than the fusion temperatures for mercury soaps. Two factors (lattice and solvation–coordination energies) may combine to produce this behaviour. A previous X-ray diffraction study of pure cadmium soaps between 100 and 200°C showed their structures to correspond to the packing of cylindrical structural elements in a two dimensional hexagonal array [39] while a bilayer structure was reported for some mercury soaps [38]. These structural differences should affect the flexibility of the hydrocarbon chains in the soap solid phases differently such that the differences in solubility behaviour is a consequence of this in part. The effect of the solvation energy on solubility can be attributed to differences in the orbitals of cadmium and mercury ions that are engaged in coordination with the solvent molecules to form the soap-solvent aggregates.

The solubility behaviour of the mercury carboxylates is similar to that of lead soaps for which previous thermal [19] and the present solubility data are put in the same diagram (see figure 4). The figure shows clearly that the solubility temperatures are much lower than the premelting or melting temperatures. It may be reasonable to

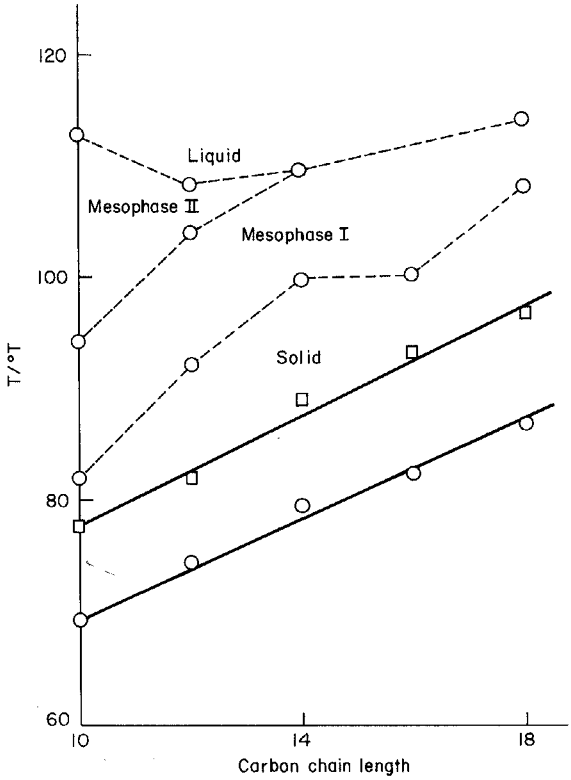

Figure 4. Phase transitions (– – –) and solubility temperature of lead(II) soaps against carboxylate chain length. Soaps in ○ hexan-1-ol □ octadecan-1-ol.

assume that the energy required for the rupture of the crystal structure in solution plays a dominant role in the mechanism of solubility. This fact is made attractive by the different values obtained for the meso and racemic isomers of lead(II) 9,10-dihydroxyoctadecanoate in table 5. Thus it may be inferred that the similarity in the solubility behaviour of mercury and lead carboxylates stems in large part from the closeness in the structural packing of the soaps in the solid phase.

The contribution to the review of this article by Professor H. D. Burrows of the University of Coimbra, Portugal is appreciated with thanks. We are also grateful to Miss Bosede Akinsanya for helping to take some solution temperature readings which were used to monitor reproducibility.

References

[1] KOENING, A. C., 1974, *J. Am. chem. Soc.*, **36**, 951.
[2] LAWRENCE, A. S. C., 1938, *J. chem. Soc. Faraday Trans.*, **34**, 660.
[3] MARTIN, E. P., and PINK, R. C., 1948, *J. chem. Soc.*, 1750.
[4] MARTIN, R. L., and WHITLEY, A., 1958, *J. chem. Soc.*, 1394.
[5] NOBEL, W. R., SCALAN, J. T., and EISNER, A., 1962, *J. Am. Oil chem. Soc.*, **39**, 31.
[6] PIPEL, N., 1963, *Chem. Rev.*, **63**, 211.
[7] VARMA, R. P., and KUMI, N., 1977, *J. Am. Oil chem. Soc.*, **54**, 156.
[8] JAIN, A. K., SIDDIQUI, J., and SINGH, R. P. B., 1979, *J. chem. Tech. Biotechnol.*, **29**, 499.
[9] AKANNI, M. S., BURROWS, H. D., ELLIS, H. A., ASONGWED, D. N., BABALOLA, H. B., and OJO, P. O., 1984, *J. chem. Tech. Biotechnol.* A, **34**, 127.
[10] ADEOSUN, S. O., and AKANNI, M. S., 1978, *Thermochim. Acta*, **27**, 133.
[11] BURROWS, H. D., ELLIS, H. A., and AKANNI, M. S., 1981, *Proceedings of the Second European Symposium on Thermal Analyses*, edited by D. Dollimore (Heyden), p. 302.
[12] KONKOLY-THEGE, I., RUFF, I., ADEOSUN, S. O., and SIME, S. J., 1978, *Thermochim. Acta*, **24**, 89.
[13] ADEOSUN, S. O., 1927, *J. therm. Analy.*, **27**, 133.
[14] EKWUNIFE, M. E., NWACHUKWU, M. U., RINEHART, F. P., and SIME, S. J., 1975, *J. chem. Soc. Faraday Transac. I*, **71**, 1432.
[15] AKANNI, M. S., and MBANEME, P. C., 1986, *J. chem. Soc. Faraday Transac. I*, **82**, 3357.
[16] EVERETT, D. H. (editor), 1972, *Definitions, Terminology and Symbols in Colloid and Surface Chemistry* (*Pure appl. Chem.* **31**, 613).
[17] WOOD, J. A., 1986, *Memorial Symposium on Dispersions*, SCI Headquarters, London, 15 May.
[18] GLASSTONE, S., 1960, *Textbook of Physical Chemistry* (Macmillan), p. 644.
[19] ADEOSUN, S. O., and SIME, S. J., 1976, *Thermochim. Acta*, **17**, 351.
[20] DUNNING, W. J., 1969, *Nucleation*, edited by A. C. Zettlemoyer (Marcel Dekker).
[21] BRADLEY, R. S., 1951, *Q. Rev. chem. Soc.*, **5**, 673.
[22] BERKER, R., and DORING, W., 1935, *Ann. Phys.*, **24**, 719.
[23] BURROWS, H. D., and ELLIS, H. A., 1982, *Thermochim. Acta*, **52**, 121.
[24] NELSON, S. M., and PINK, R. C., 1952, *J. chem. Soc.*, 1744.
[25] LITTLE, R. C., 1966, *J. colloid Inter. Sci.*, **21**, 266.
[26] EKPE, U. J., and SIME, S. J., 1976, *J. chem. Soc., Faraday Trans. I*, 1, **72**, 1144.
[27] AMORIM DA COSTA, A. M., BURROWS, H. D., GERALDES, C. F. G. C., TEIXEIRA-DIAS, J. J. C., BAZUIN, C. G., GÚILLON, D., SKOULIOS, A., BLACKMORE, E., TIDDY G. J. T., and TURNER, D. L., 1986, *Liq. Crystals.*, **1**, 215.
[28] VERBEECK, A., GELADE, E., and DESCHRYVER, F. C., 1986, *Langmuir*, **2**, 448.
[29] MAGID, L., 1982, *Solution Chemistry of Surfactants*, Vol. 1, edited by K. Mittal (Plenum), 1980, pp. 427–453.
[30] ADEOSUN, S. O., and AKANNI, M. S., 1980, *Thermochim. Acta*, **39**, 35.
[31] ADEOSUN, S. O., AKANNI, M. S., and BURROWS, H. D., 1980, *Thermochim. Acta*, **42**, 233.
[32] ADEOSUN, S. O., SIME, W. J., and SIME, S. J., 1977, *Thermochim. Acta*, **19**, 275.
[33] COTTON, F. A., and WILKINSON, C., *Advanced Inorganic Chemistry*, third edition (Wiley), p. 510.

[34] Akanni, M. S., Burrows, H. D., and Begun, P. B., 1984, *Thermochim. Acta*, **81**, 45.
[35] Tanford, C., 1980, *The Hydrophobic Effect*, second edition (Wiley), Chaps. 2 and 3.
[36] Akanni, M. S., 1980, Ph.D. Thesis, University of Ife.
[37] Akanni, M. S., 1987, *Thermochim. Acta*, **122**, 355.
[38] Ellis, H. A., 1986, *Molec. Crystals liq. Crystals*, **138**, 321.
[39] Spegt, P. A., and Skoulios, A. E., 1963, *Acta crystallogr.*, **16**, 301.