

A DIFFERENTIAL THERMAL ANALYSIS STUDY OF PHASE TRANSITIONS IN SOME MERCURY(II) CARBOXYLATES

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Data are presented on the heats of phase changes and heat capacities for the even chain number mercury(II) carboxylates from octanoate to octadecanoate. The octanoate and dodecanoate melt directly to the liquid, while the decanoate and octadecanoate pass through a solid \rightarrow solid transition before melting to the liquid. The tetradecanoate and hexadecanoate pass through a mesophase before finally melting. It is proposed that this mesophase is a *G* (smectic) phase. Addition of mercuric oxide to the tetradecanoate and hexadecanoate causes the appearance of an additional mesophase. The results are explained in terms of the *R* theory of fused micellar phases.

Mesophase formation in several metal carboxylates has been studied by a variety of techniques. However, there have been very few thermodynamic studies of these systems. One of the earliest thermodynamic studies of phase transitions in metal carboxylates was that of Vold [1]. Vold developed a differential calorimeter which he used to measure the heats of phase transitions in some long-chain sodium soaps. Similar results have been reported on the low chain-length sodium and potassium salts [2–4]. Meisel et al. have re-investigated the thermal behaviour of the sodium carboxylates [5], while thermodynamic data have been reported for some other metal carboxylates [6–9]. Recently, we reported heats of phase transitions and specific heats for some even chain number lead(II) carboxylates [10].

In the present paper we have extended the study to the mercury(II) carboxylates. Although the preparation and gelling properties of mercury octadecanoate have long been reported [11], there are no data in the literature on the thermodynamics of phase transitions in the mercury carboxylates. We now report heats of phase changes and heat capacities for the even chain number mercury(II) carboxylates from octanoate to octadecanoate inclusive. The effect of mercuric oxide on the thermal behaviour of some of the soaps is also discussed.

Experimental

Materials

All the fatty acids employed were “specially pure” grade, B. D. H. products and were stated to be of at least 99% purity by g.l.c. assay. They were used without further purification. Mercuric chloride and mercuric oxide were “Analar” grade B. D. H. products.

Preparation of soaps

The soaps were prepared by metathesis in alcohol solution [12]. The potassium salts of the acids were first prepared by dissolving the acids in hot ethanol and then adding the stoichiometric amount of solid potassiumhydroxide. A solution of the stoichiometric quantity of mercuric chloride was next added. The resulting precipitate was filtered and washed with water, followed by ethanol and finally acetone. The soaps were recrystallized from hot benzene.

Elemental analysis and IR spectra of the compounds showed that they were free of water and excess organic acids. The results of the elemental analyses of the compounds are shown in Table 1.

Table 1
C and H analyses of Hg(II) carboxylates

Carbon chain length	C, %		H, %	
	Theory	Found	Theory	Found
8	39.47	39.32	6.17	6.32
10	44.24	44.47	7.00	7.14
12	48.12	48.38	7.69	7.75
14	51.34	51.20	8.25	8.32
16	54.05	53.91	8.73	8.80
18	56.36	56.50	9.13	9.20

An attempt was made to prepare the hexanoate by a similar procedure, but without success. In another attempted preparation, potassium metal was used instead of KOH, but again no product was obtained. This latter procedure had been successfully used in the preparation of manganese hexanoate [13]. The failure to precipitate mercury hexanoate in this medium suggests that mercury hexanoate is extremely soluble in ethanol.

The mercury soap/mercuric oxide mixtures were made by weighing the appropriate amounts of the two compounds into a quick-fit conical flask. The flask was evacuated and the mixture melted. It was necessary to cool, grind and remelt the mixtures a few times before all the mercuric oxide would completely dissolve in the melt.

DTA measurements

About 20 mg samples were sealed in the standard aluminium crucibles of the Mettler TA 2000 Analyser and scanned at a heating rate of 0.5 K min^{-1} . Measurements were made in duplicate on at least three separate samples. Peak areas were measured by cutting and weighing.

Specific heats were obtained by the method of baseline displacement. Optical observation of the melts was made with a polarizing microscope to which a Kofler heating stage was attached.

Results and discussion

The DTA curves of the mercury(II) carboxylates are shown in Fig. 1. The octanoate and dodecanoate show a single peak corresponding to the transition solid \rightarrow liquid, while the others show an additional phase transition before melting to the isotropic liquid. We have called this additional phase, phase I in Table 2. Heat capacities for the solid phase are shown in Fig. 2, while the corresponding values for the liquid are listed in Table 3. All the values are accurate to within $\pm 2\%$. The heat capacities of the liquids are practically temperature-independent (over the temperature range studied), while those of the solid are temperature-dependent. They vary linearly with temperature over the temperature range studied. The temperature-dependence of specific heats in the solid probably

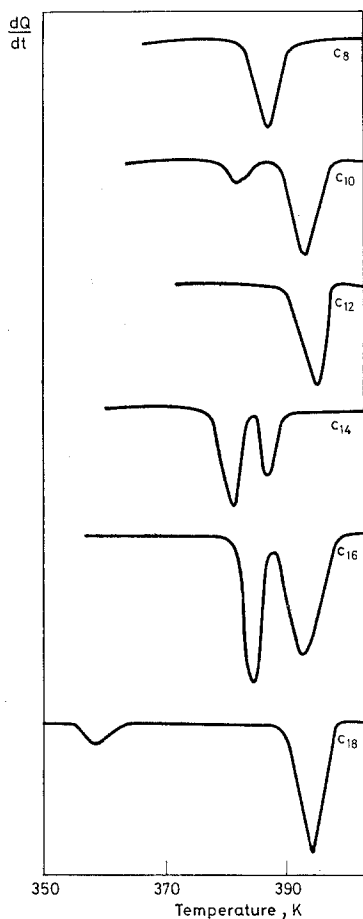


Fig. 1. DTA curves for the mercury carboxylates. Scan speed, 0.5Kmin^{-1}

demonstrates that subtle structural changes occur in the solid phase with changing temperature.

The temperature of phase transitions, as well as ΔH and ΔS values for each phase transition, are given in Table 2. Optical observation of the samples under a polarizing microscope suggests that the first phase (phase I) in mercury decanoate and mercury octadecanoate is probably a solid \rightarrow solid phase transition as it was not readily subject to mechanical deformation when pressed between coverslips on a hot stage microscope. This is supported by the relatively small heat change

Table 2
Thermodynamic data for phase changes

Carbon chain length	Solid \rightarrow phase I		
	T , K	ΔH , KJ.mol ⁻¹	ΔS , J.mol ⁻¹ K ⁻¹
8	380.8	5.3	14.0
10			
12			
14	382.4	57.9	151.4
16	383.4	49.5	129.1
18	355.2	4.4	12.3

Carbon chain length	Phase I \rightarrow liquid		
	T , K	ΔH , KJ.mol ⁻¹	ΔS , J.mol ⁻¹ K ⁻¹
8	389.3	70.2	180.3
10			
12			
14	387.0	40.0	103.2
16	390.3	59.5	152.4
18	393.2	116.5	296.3

Carbon chain length	Solid \rightarrow liquid		
	T , K	ΔH , KJ.mol ⁻¹	ΔS , J.mol ⁻¹ K ⁻¹
8	387.2	61.5	159.0
10	394.2	94.8	240.7
12			
14			
16			
18			

Error in T is ± 0.1 K and error in ΔH is within $\pm 2\%$.

Table 3
Molar heat capacities of liquids

Carbon chain length	C_p , $J \cdot mol^{-1} K^{-1}$	Temperature range, K
8	635.5	400–425
10	817.0	403–420
12	1089.2	413–430
14	1135.5	413–421
16	1217.3	396–421
18	1377.2	391–433

Error in C_p is within $\pm 2\%$.

that accompanies this transition. On the other hand, optical observation suggests that the first phase transition in mercury tetradecanoate and hexadecanoate is a solid \rightarrow mesophase transition, since these phases are readily deformable when pressed between coverslips on a hot stage microscope. Again, this is supported by the relatively large heat change (about 50% of the total heat change) which accompanies this phase change. Thus, there seems to be no correlation between the chain length and the number or type of phases exhibited by the mercury soaps.

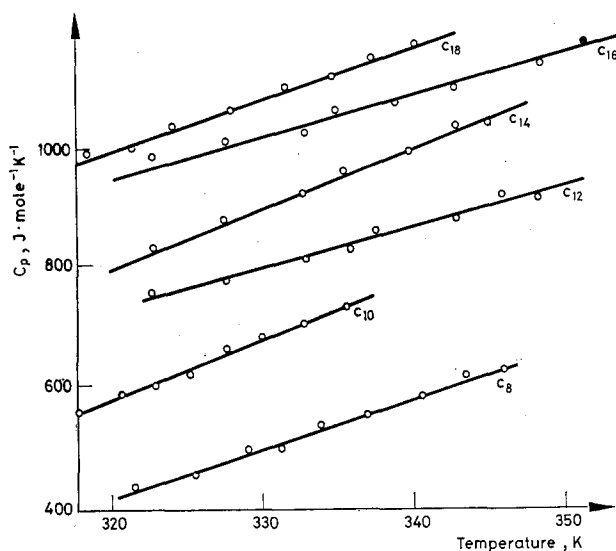


Fig. 2. Molar heat capacities of the solid mercury carboxylates

It was not possible from optical observation to classify the mesophases formed by mercury tetradecanoate and hexadecanoate. In an earlier DTA study of mesophase formation in lead(II) soaps [10], we suggested the phase sequence crystal \rightarrow G (smectic) $\rightarrow V_2$ (cubic isomorphous) \rightarrow liquid for the dodecanoate and lower chain length soaps, while for tetradecanoate and above the V_2 phase is absent and the G phase melts directly to the liquid. It is tempting to speculate that the mesophase formed by the mercury soaps is probably a G phase. This speculation is made more attractive by the fact that the heat change for the $G \rightarrow$ liquid phase transitions reported [10] for lead tetradecanoate and lead hexadecanoate (41.6

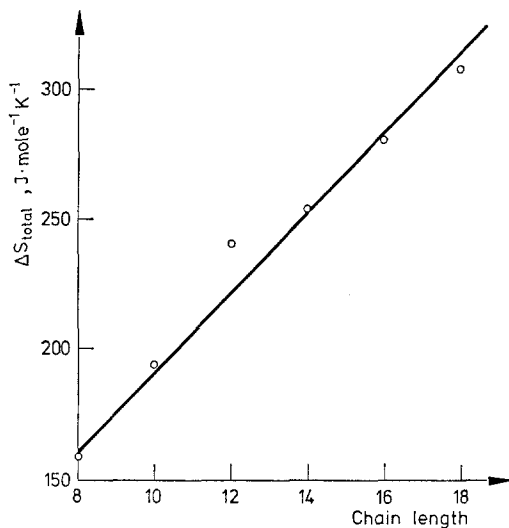


Fig. 3. Total entropy change for the process crystal \rightarrow isotropic liquid

and 46.4 KJ. mole⁻¹, respectively) are of the same order of magnitude as those of the corresponding mercury soaps (40.0 and 59.5 KJ.mole⁻¹ for the tetradecanoate and hexadecanoate, respectively). Furthermore, X-ray studies by Spegt [14, 15] and Luzzati [16, 17] on the mesophases of several divalent metal soaps show that they initially pass through a phase that has a lamellar structure (corresponding to the G phase) when slowly heated. Unfortunately, no X-ray studies on mercury soaps have so far been reported and further discussion should await an X-ray structural study of these soaps.

A plot of the total entropy change accompanying the phase change solid \rightarrow isotropic liquid against chain length is shown in Fig. 3. It is seen that ΔS_{total} is strongly chain length-dependent, increasing with increasing chain length. This is consistent with the idea that the major process during melting is the disordering of the hydrocarbon chains.

Figure 4 shows the DTA curves for mercury tetradecanoate and hexadecanoate to which small quantities of mercuric oxide have been added (mole fraction of $\text{HgO} = 0.1$). It can be seen that the addition of mercuric oxide to these soaps causes the appearance of a new phase on the low-temperature side of the DTA curves. Optical observation showed that this phase is an additional mesophase. However, optical observation did not help in characterizing this new mesophase.

It is well known that several amphiphilic systems are capable of incorporating into their polar regions a considerable amount of water, inorganic salts and water-soluble organic compounds [18], and in a recent paper [19] we reported thermodynamic data on mesophase formation in the lead dodecanoate/lead oxide system. We showed that the addition of a very small amount of lead oxide to lead dodecanoate causes the V_2 (cubic isomorphous) phase to disappear, and that the G phase breaks down into different G forms. These observations were rationalised in terms of the R theory of fused micellar phases [18].

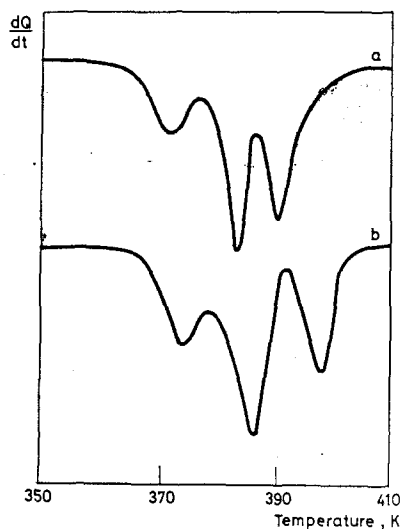


Fig. 4. DTA curves for mercuric oxide/mercury carboxylate systems. (a) Mercuric oxide/mercury tetradecanoate; (b) Mercuric oxide/mercury hexadecanoate. (Mole fraction of $\text{HgO} = 0.1$). Scan speed, 0.5Kmin^{-1}

The R theory interprets the structures of mesophases in terms of a balance between the intermolecular forces which tend to make the amphiphilic portion of the lamella become convex towards its lipophilic environment and those which tend to make it become convex towards its polar environment. Thus, the ratio $R = \text{tendency of amphiphilic layer to become convex towards its lipophilic environment} / \text{tendency of amphiphilic layer to become convex towards its polar environment}$, must be unity in all directions within the lamellae.

We can apply the concepts of the R theory to explain our results on the mercuric oxide/mercuric soap systems. Addition of mercuric oxide to the soap increases the strength of the ionic interactions inside the polar part of the lamellae of the G phase, tending to make them concave towards the polar region. Thermal disruption of the interaction of the hydrocarbon chains decreases the counterbalancing tendency, thus changing the value of R from unity, and the G phase breaks down at lower temperatures. The internal rearrangements to try and maintain a value of $R = 1$ result in the formation of a new distinct phase.

References

1. R. D. VOLD, *J. Am. Chem. Soc.*, 63 (1941) 2915.
2. J. J. DURUZ, H. J. MICHELS and A. R. UBBELOHDE, *Proc. Roy. Soc., Ser. A.*, 322 (1971) 281.
3. A. R. UBBELOHDE, H. J. MICHELS and J. J. DURNZ, *Nature*, 228 (1970) 50.
4. P. FERLONI and P. FRANZOSINI, *Gazz. Chim. Ital.*, 105 (1975) 391.
5. J. RÓTH, T. MEISEL, K. SEYBOLD and Z. HALMOS, *J. Thermal Anal.*, 10 (1976) 223.
6. T. MEISEL, K. SEYBOLD, Z. HALMOS, J. RÓTH and Cs. MÉLYKUTI, *J. Thermal Anal.*, 10 (1976) 419.
7. J. RÓTH, Z. HALMOS and T. MEISEL, *Thermal Analysis*, Vol. 2. (Proc. of the 4th ICTA) Budapest, 1974.
8. M. J. VOLD, H. FUNAKOSHI and R. D. VOLD, *J. Phys. Chem.*, 80 (1976) 1753.
9. S. SHIBA, *Bull. Chem. Soc. Japan*, 34 (1961) 804.
10. S. O. ADEOSUN and S. J. SIME, *Thermochim. Acta*, 17 (1976) 351.
11. A. S. C. LAWRENCE, *Trans. Faraday Soc.*, 34 (1938) 665.
12. S. M. NELSON and R. C. PINK, *J. Chem. Soc.*, (1954) 4412.
13. S. A. BIOBAKU, B. Sc. Thesis (Univ. of Ife, 1975).
14. P. A. SPEGT and A. E. SKOULIOS, *Acta Cryst.*, 21 (1966) 892.
15. V. LUZZATI and P. A. SPEGT, *Nature*, 215 (1967) 701.
16. V. LUZZATI, T. GULIK-KRZYWICKI and A. TARDIEU, *Nature*, 218 (1968) 1031.
17. V. LUZZATI, A. TARDIEU and T. GULIK-KRZYWICKI, *Nature*, 217 (1968) 1028.
18. P. A. WINSOR, *Liquid Crystals and Plastic Crystals*, Vol. 1, Ellis Harwood, Chichester, 1974, ch. 5.
19. S. O. ADEOSUN, W. J. SIME and S. J. SIME, *Thermochim. Acta*, 19 (1977) 275.

RÉSUMÉ — On présente des données sur les chaleurs des changements de phase et les chaleurs spécifiques des carboxylates de mercure(II), même à longue chaîne carbonée, de l'octylate à l'octadécanoate. L'octylate et le dodécanoate conduisent directement au liquide par fusion tandis que le décanoate et l'octadécanoate subissent une transition solide-solide avant de fondre. Le tétradécanoate et l'hexadécanoate passent par une mésophase avant la fusion finale. On propose pour cette mésophase une structure smectique (G). L'addition d'oxyde de mercure au tétradécanoate et à l'hexadécanoate donne une mésophase additionnelle. On explique les résultats en se référant à la théorie R des phases micellaires fondues.

ZUSAMMENFASSUNG — Daten der Phasenübergangswärmen und Wärmekapazitäten der Quecksilber(II)karboxylate mit geradzahligem Kohlenstoffatomen vom Oktanat bis Oktadékanat angegeben. Oktanat und Dodekanat schmelzen unmittelbar zur Flüssigkeit, während Dekanat und Oktadékanat durch einen Fest-Fest-Übergang in den flüssigen Zustand übergeführt werden. Tetradékanat und Hexadékanat werden über eine Mesophase endgültig ge-

schmolzen. Es wird für diese Mesophase die Struktur einer smektischen G-Phase vorgeschlagen. Der Zusatz von Quecksilberoxid zum Tetradekanat und Hexadekanat verursacht das Auftreten einer zusätzlichen Mesophase. Die Ergebnisse werden durch die R-Theorie geschmolzener Micellarphasen erklärt.

Резюме — Представлены данные теплот фазовых изменений и теплоемкостей для четнo-цепных карбоксилатов ртути(II) от октаноата до октадеканoата. Октаноат и додеканoат плавятся прямо до жидкого состояния, в то время как деканoат и октадеканoат перед плавлением проходят через переход типа твердое тело-твердое тело. Тетрадеканoат и гексадеканoат проходят через мезофазное состояние перед конечным плавлением. Предполагено, что эта мезофаза является Ж (смeстичeская) фазов. Добавка окиси ртути к тетрадеканoату и гексадеканoату вызывает появление дополнительной мезофазы. Результаты объяснены на основе *P* теории расплавленных мицеллярных фаз.