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THE PROPERTIES OF MOLTEN CARBOXYLATES: PART 7. ODD–EVEN VARIATIONS IN MELTING AND MESOPHASE FORMATION IN THE LEAD(II) CARBOXYLATES

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ABSTRACT

Measurements have been made of the temperatures and heats of transition of the phase changes in the lead *n*-alkanoates of odd carbon chain length from heptanoate to nonadecanoate inclusive. These salts form mesophases, those with 11 carbon atoms or fewer in the chain showing 2 phases, those with 13 or more, only one. The temperatures of the crystal to *G* phase transitions show no odd–even variations; however, the heats of transition do. All other properties except the specific heats of the V_2 phases do show such variations. The results are discussed in terms of the degree of ordering of the carbon chains in the various phases.

INTRODUCTION

In a previous paper in this series[1] we have reported the existence of mesophases between the crystal and isotropic liquid in the even chain length lead alkanoates. In this paper we report similar data for the odd chain length alkanoates. Odd–even variations in melting points and transition enthalpies have been observed in many homologous series, for example in the melting points and heats of fusion of the alkanes themselves[2] and of the alkanoic acids[3]. Odd–even variations have been observed in the temperatures and transition enthalpies of isotropic–nematic transitions in homologous series of non-amphiphylic mesogens. Marčelja[4] has derived a theory of the isotropic–nematic transition which predicts such variations, for example in the *p*, *p*'-di-*n*-alkoxy-azoxybenzenes. The physical interpretation he gives of this effect is that, in the case of these compounds, the addition of a carbon atom to the chain in an even position in the preferred *trans* configuration is along the major molecular axis, allowing more ordered packing in the nematic phase, whereas addition of a carbon atom in an odd position in the *trans* configuration is away from the molecular axis and acts as a steric interference to inter-molecular order. In the light

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TABLE 1

CARBON–HYDROGEN ANALYSIS DATA

Carbon chain length	*% C*		*% H*	
	Found	*Theory*	*Found*	*Theory*
19	57.29	56.91	9.29	9.24
17	54.81	54.75	8.59	8.56
15	52.34	52.23	8.47	8.42
13	49.45	49.27	7.92	7.90
11	46.07	45.74	7.59	7.28
9	41.77	41.44	6.24	6.52
7	36.66	36.11	5.47	5.59

of this interpretation, the presence of odd–even effects in liquid crystal transitions should indicate differences in the degree of ordering of the end region of the alkanoic chain between the two phases in question. There are no studies, known to the authors, of odd–even effects in mesophase formation in pure amphiphylic mesophases. Such studies may cast some light upon the degree of ordering of the alkanoic chain in the various phases. Having already reported thermodynamic data for phase transitions in the even chain length alkanoates of lead we have therefore prepared and studied phase transitions in their odd homologues with this aim in view.

EXPERIMENTAL

Materials were prepared and purified as has been previously described for the even chain length compounds[5]. Carbon and hydrogen analyses were performed as a test of purity, and the data are shown in Table 1. All quantitative DTA measurements were made as described previously; in particular the specific heats of the mesophases were measured by the same method of temperature jump. Attempts to purify the pentanoate failed, the DTA curves for this compound being broad and ill-defined; thus data are reported for chain length from nonadecanoate to heptanoate.

RESULTS

Phase changes found were consistent with those observed for the even chain length compounds, two phases being found for chain lengths 11 and shorter, one for 13 and longer. The lower temperature phase has been labelled a *G* phase and the other a V_2 phase in line with the nomenclature used for the phases of the even chain length compounds. Temperatures, enthalpy and entropy changes are shown in Table 2. Errors are included only if they were larger than the ± 2% expected for quantitative DTA. For the heptanoate an extra low temperature phase was observed. Specific heats were measured for all convenient phases. The specific heats of the solids were

TABLE 2

THERMODYNAMIC DATA FOR PHASE CHANGES

Carbon chain length	Crystal → G			G → V_2			V_2 → liquid		
	T (K)	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	T (K)	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	T (K)	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
7	336.6	17.1 ± 0.6	51 ± 2	356.8[a]	8.5 ± 0.3	24 ± 1	374.7	1.4	3.7
9	348.9	32.2	92	367.4	16.4	45	384.8	1.3	3.4
11	360.9	50.7	141	377.0	27.5	73	383.7	1.1	3.0
13	368.7	58.4	158	381.5	38.8	102			
15	374.7	64.1	171	384.6	48.1	125			
17	378.7	68.0	180	387.4	55.1	142			
19	383.8	75.9	198	389.1	64.3	165			

[a] An extra phase change was observed at 361.3 K, $\Delta H = 9.7 \pm 0.5$ kJ mol^{-1}, $\Delta S = 27 \pm 1$ J K^{-1} mol^{-1}.

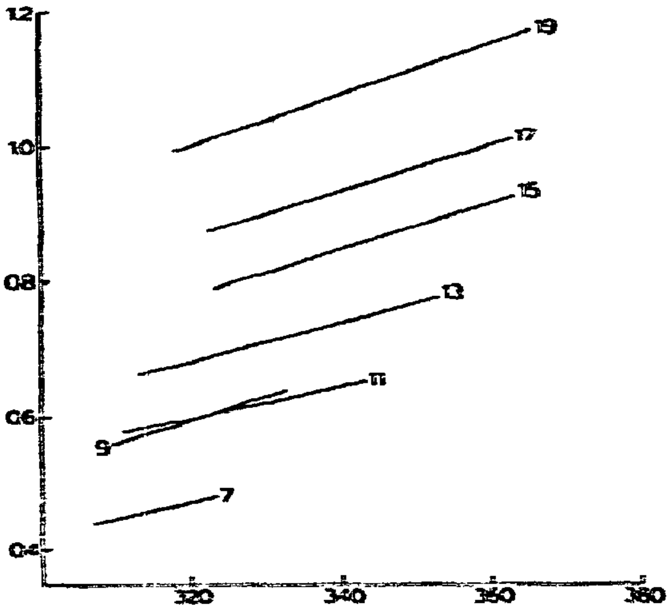

Fig. 1. Specific heats of the solid phases. Ordinate, C_p (kJ mol^{-1} K^{-1}); abscissa, T (K).

TABLE 3

SPECIFIC HEATS OF LIQUIDS AND MESOPHASES

Carbon chain length	*Phase*	*Mesophase*		*Liquid*	
		C_p (J mol^{-1} K^{-1})	*Temp. range (K)*	*C_p (J mol^{-1} K^{-1})*	*Temp. range (K)*
7	*G*	770	341–351	598	413–453
	V_2	664	363–371		
9	*G*	926	353–363	732	413–463
	V_2	830	370–378		
11	*G*	894	363–371	870	413–463
	V_2	952	379–381		
13	*G*	1230	371–377	950	413–463
15	*G*	1430	376–380		403–473
17		No reliable value			413–473
19		No reliable value			413–473

strongly temperature dependent and the data are presented graphically in Fig. 1. Liquid specific heats were temperature independent within the limits of accuracy of quantitative DTA and are presented in Table 3. Also included in this Table are average values for the specific heats of the mesophases. An attempt was made to determine whether the mesophase specific heats were temperature dependent, and jumps of 2 K were made over the range of stability of the phases. Unfortunately, jumps close to the temperatures of the phase transitions may include an enthalpy contribution due to possible slight lowering and spreading of the transition temperatures by impurities below the level of detection by carbon-hydrogen analysis and IR

TABLE 4

TEMPERATURE DEPENDENCE OF MESOPHASE SPECIFIC HEATS

G phase		*V_2 phase*	
Temp. jump (K)	*C_p (J K^{-1} mol^{-1})*	*Temp. jump (K)*	*C_p (J K^{-1} mol^{-1})*
(a) Heptanoate			
341–343	678 ± 50	363–365	669 ± 17
343–345	707 ± 38	365–367	648 ± 17
345–347	736 ± 25	367–369	657 ± 25
347–349	849 ± 79	369–371	678 ± 21
349–351	887 ± 46		
(b) Nonanoate			
353–355	788 ± 23	370–372	840 ± 35
355–357	836 ± 66	372–374	821 ± 31
357–359	883 ± 44	374–376	847 ± 19
359–361	980 ± 33	376–378	810 ± 41
361–363	1150 ± 50		

spectroscopy. It is thus often difficult to decide whether changes in the measured specific heats with temperature are significant. However, for the heptanoate and nonanoate the relatively wide range of stability of the phases enabled a series of measurements to be made well away from the phase transitions. Data for these two compounds, shown in Table 4, indicate significant temperature dependence of the specific heat of the *G* phase, but temperature independence for the V_2 phase.

DISCUSSION

Figure 2 shows a plot of transition temperatures against chain length for all the lead alkanoates studied. A qualitative interpretation of the trends may be given. Increasing carbon chain length increases the value of the Van der Waals' interactions between the carbon chains, thus helping to maintain an ordered laminar structure in both the crystal and *G* phases. In terms of the *R* theory of amphiphylic mesophases[6], this will break down when the inter-ionic head group interactions become stronger than the Van der Waals' interactions of the carbon chain causing the ionic/non-polar interface to become convex to the non-polar region. Thus the temperature of a transition from a laminar to a V_2 or liquid phase will increase with increasing chain length, as is observed. The range of stability of the V_2 (cubic isotropic) phase shows a maximum for a carbon chain length of 9 or 10. Existence of the V_2 phase rather than a liquid phase requires that a small spherical aggregate be stable and that the inter-aggregate forces are sufficient to make a cubic lattice arrangement stable. It is not known whether these inter-aggregate forces are mainly non-polar, ionic or a delicate balance of both and it is difficult to speculate on the reason for the maximum

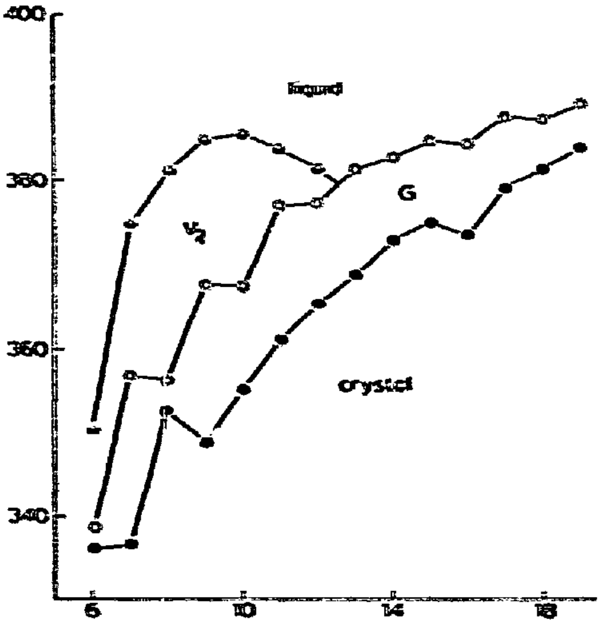

Fig. 2. Stability range of mesophases as a function of chain length. Ordinate, *T* (K); abscissa, chain length.

in stability. Evidence from the entropy of fusion of the V_2 phase[1] and from the variation of activation energy for viscous flow with chain length for the liquid[7] indicates that the aggregates consist of an average of 3 or 4 lead carboxylate molecules. A maximum stability at the nonanoate may indicate that this chain length allows an aggregate of 3 to 4 molecules to become effectively symmetric, with an inner ionic region surrounded by a non-polar hydrocarbon region. It is interesting to note that the viscosity data show an increase in the rate of change of activation energy with chain length for the tetradecanoate and longer, indicating a larger aggregate in the liquid phase for these compounds. Perhaps the aggregate of greater size is not able to form strong inter-aggregate interactions and thus the cubic arrangement of a V_2 phase becomes unstable.

Pronounced odd–even variations are observed in the temperatures of the *G* to liquid or V_2 transitions, but not in those for the crystal to *G* phase. This may indicate a much larger change in ordering of the rear end of the carbon chain in the *G* to liquid phase change. Following the interpretation of Marčelja, and with reference to Fig. 3, it is seen that the addition of a carbon atom to the chain in an even position

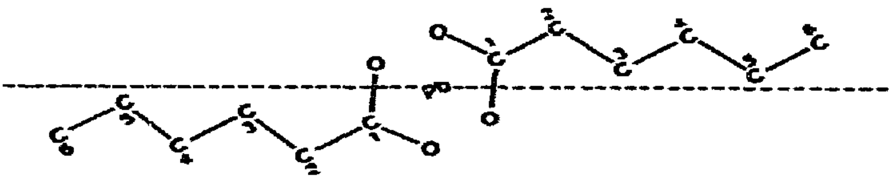

Fig. 3. The addition of an even number carbon atom in the *trans* configuration against the direction of the molecular axis.

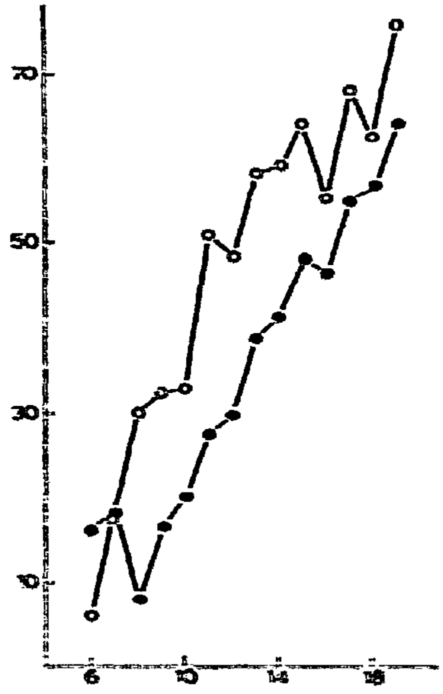

Fig. 4. Enthalpies of phase changes against chain length. ●, crystal to G; ○, G to liquid or V_2. Ordinate, ΔH (kJ mol^{-1}); abscissa, chain length.

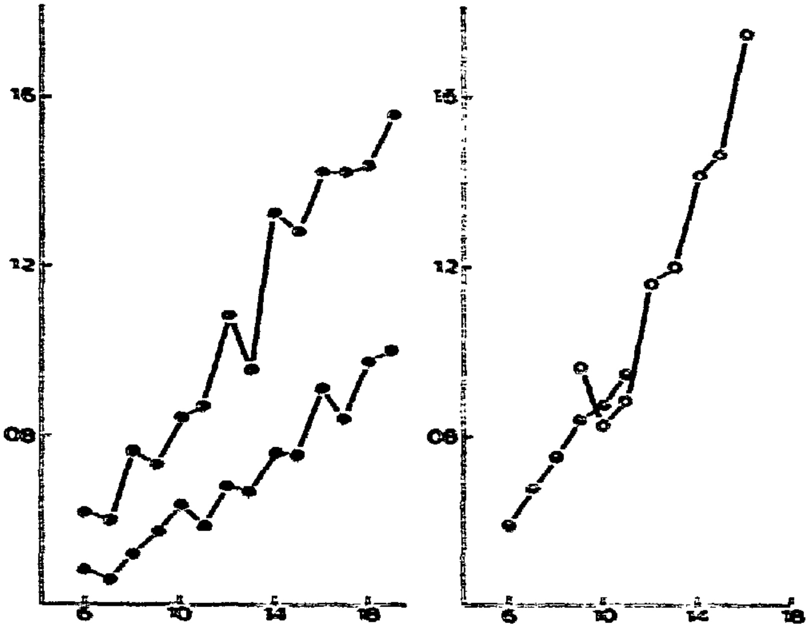

Fig. 5. Specific heats against chain length. ●, solid; ◑, liquid; ○, G; ⊖, V_2. Ordinate, C_p (kJ mol^{-1} K^{-1}); abscissa, chain length.

in the preferred *trans* configuration is away from the preferred molecular axis and hence, interferes with the packing of the chains in the non-polar part of the *lamellae* of both the *G* and crystal phases. Figure 4 shows a plot of the transition enthalpies against chain length. Odd–even variations are observed for both processes, particularly at longer chain lengths. The presence of variations in the enthalpy change for the *C* to *G* transition implies a greater increase in disorder between the phases for the odd chain length compounds. Thus there must be some disordering of the end of the carbon chain in the *G* phase. However, the presence of more consistent variations in both temperature and enthalpy change for the *G* to liquid transition must indicate an increase in disorder at the end of the chain for this transition; thus the original naive suggestion that in the *G* phase the residual ordering was in the region of the chain close to the head group must be abandoned. Disordering of the chain in both the crystal to *G* and *G* to liquid transitions must occur along the whole length of the chain.

Variations of the specific heats of the various phases are consistent with the interpretation suggested by Marčelja. Figure 5 shows plots of the specific heats against chain length. The values for both the solid and *G* phases are greater for the even chain length soaps, indicating the "loosening" of the crystal structure resultant upon the addition of an even carbon atom arranged away from the direction of the molecular axis. The specific heat of the V_2 phase shows no observable odd–even variations and it is tempting to suggest that there is complete disordering of the chain in this phase, or at least that any regularity in the packing of the chain is not laminar. This is consistent with the model presented for this phase. It is, however, difficult to account for the variations observed in the specific heats of the liquids. Bothorel[8] has pointed out that even in the liquid alkanes there is significant correlation of orientation between molecules but this effect does not give rise to odd–even effects in the specific heats of these liquids. The variation observed is inconsistent with the model of the liquid phase as a random arrangement of roughly spherical aggregates of 3 to 4 molecules with some ionic dissociation in which the chain is completely randomised. It is difficult to propse an adequate model to explain the odd–even variation in the liquid phase.

Thermodynamic studies, together with the concepts of *R* theory, have enabled the construction of a fairly complete model of the structure of the various phases formed by these compounds; however, this must be regarded as speculative until X-ray confirmation is obtained. The large range of stability of both the V_2 and *G* phases in the nonanoate (10 K in both cases) makes this the most promising compound for such an investigation.

REFERENCES

1 S. O. Adeosun and S. J. Sime, *Thermochim. Acta*, 17 (1976) 351.
2 J. Timmermans, *Physico-Chemical Constants of Pure Organic Compounds*, Vols. I and II, Elsevier, New York, 1960, 1965.
3 W. M. E. Garner and A. M. King, *J. Chem. Soc.*, (1929) 1849.
4 S. Marčelja, *J. Chem. Phys.*, 60 (1974) 3599.

5 M. E. Ekwunife, M. U. Nwachukwu, F. P. Rinehart and S. J. Sime, *J. Chem. Soc., Faraday Trans. I*, 71 (1975) 1432.

6 P. A. Winsor, in G. W. Gray and P. A. Winsor (Eds.), *Liquid Crystals and Plastic Crystals*, Vol. 1, Ellis Harwood, Chichester, 1974, Ch. 5.

7 U. J. Ekpe and S. J. Sime, *J. Chem. Soc., Faraday Trans. I*, 72 (1976) 1144.

8 P. Bothorel, *J. Chim. Phys., Phys.-Chim. Biol.*, (1974) 1133.