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Some Thermodynamic Properties of Potassium Soaps

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The thermal properties of five potassium soaps in the homologous series $C_nH_{2n-1}O_2K$ have been studied between room temperature and their melting points by the technique of Differential Scanning Calorimetry (D.S.C.). Heats and entropies of transitions and transition temperatures are reported. A detailed discussion of the thermodynamics of the A → C phase transition in potassium caprate, $C_{10}H_{19}O_2K$, is given in terms of the structural model of the C phase recently proposed by Glover.[1] It is concluded that the nature of the molecular disorder proposed in the model is not inconsistent with the measured entropy change.

INTRODUCTION

This paper reports the results of measurements of heats of transitions in a homologous series of potassium soaps of the general formula $C_nH_{2n-1}O_2K$, (abbreviated to KC_n in the following) with n ranging from 8 to 18. It is well established that these soaps exhibit complex polymorphism.[2,3] For each soap many mespohases exist between the crystalline form, stable at low temperatures, and the isotropic liquid that occurs above the melting point. Many authors have regarded the existence of the mesophases as evidence of a progressive melting of the crystal in the sense that, as the temperature is raised each successive mesophase has a higher degree of structural disorder than its predecessor. The transition temperatures between the various phases have been measured by a variety of techniques. Vold and his co-workers[4,5] used dilatometry, polarised light microscopy and heat of transition measurements while Grant and Dunell[6,7] observed a change in the proton magnetic resonance line width at temperatures corresponding to known transition points. In general the measurements of the transition temperatures using these

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techniques agree with those determined by the X-ray diffraction measurements of Lomer[2] and Gallot and Skoulios[3] although not all transitions have been detected by all techniques.

At room temperature all the soaps are crystalline. KC_8 and KC_{10} adopt the monoclinic A-phase structure and the others the triclinic B-phase structure. (These room temperature phases are called lamellaire crystalline, abbreviated to LC_1 by Gallot and Skoulios). All soaps in the series transform to the crystalline monoclinic C-phase (called LC_2 by Gallot and Skoulios) at temperatures between 50°C and 100°C.

Although the unit cell dimensions and space group of this C-phase were known no details of the crystal structure were reported until recently when Glover[1] suggested a detailed model in which the hydrocarbon chains in the crystal were partially disordered by rotational isomerism.

It is known[8] that in the A-phase of KC_{10} the hydrocarbon chains are in the fully extended all trans-conformation. The introduction of one gauche-bond, corresponding to rotation of one section of the chain through an angle of 120° relative to the other section, about a C—C bond, results in a new possible configuration for the molecule, known as a rotational isomer. Glover's suggestion is that the disorder in the C-phase is due to the presence of such rotational isomers. On the basis of molecular packing considerations and the interpretation of X-ray diffraction data, both Bragg peaks and diffuse scattering, he concludes that in the C-phase of KC_{10} rotational displacements are possible about three specified bonds in the chain. For each such bond there are three possible conformations, one trans and two gauche, resulting in twenty seven possible rotational isomers for each molecule. Although not all these conformations are equally probable, the associated configurational entropy should form a substantial fraction of the total entropy change at the $A \rightarrow C$ transition.

This paper reports measurements of heats and entropies of transitions in some potassium soaps in the temperature range from room temperature to the melting points. Special attention is given to the $A \rightarrow C$ phase change in KC_{10}.

EXPERIMENTAL

Samples of the soaps were prepared from commercially available fatty acids by the method described by Lewis and Lomer.[8] 5 mg samples of each soap in turn were sealed in small aluminium containers and investigated in a Perkin-Elmer D.S.C.-2 differential scanning calorimeter. D.S.C. traces were recorded from 50°C up to approximately 450°C with a heating rate of 10°C per minute. Two samples of each soap were studied in this way. Calibration of both the temperature and the integrated power signals from the instrument was effected by melting samples of pure indium, tin and lead.

The temperature and enthalpy change associated with the A → C phase transition in KC_{10} were also measured in the adiabatic calorimeter recently described by Smith and Rae.[9] These measurements are of higher accuracy than those obtained from the D.S.C. method.

RESULTS

D.S.C. traces obtained from samples of KC_8, KC_{10}, KC_{12}, KC_{14} and KC_{18} are reproduced in Figure 1. KC_{16} has not been studied. All the features of the traces presented were reproduced in the second run with each of the soaps. For ease of comparison the temperatures at which transitions have been observed in potassium soaps by other techniques (X-ray diffraction and N.M.R. spectroscopy) have been marked on the temperature axes of the traces given.

The molar enthalpy changes, ΔH, at the transitions were determined from the peak areas and are given, together with the corresponding entropy changes, ΔS, in Table I. The temperatures reported are those at which the trace first detectably departs from the base line. The agreement between these temperatures and those previously reported is not good but is sufficient for the majority of the peaks to be identified with known transitions. Some thermal anomalies which can not be associated with any previously reported transitions have been detected.

Use of the adiabatic calorimeter in the temperature range below room temperature revealed a hitherto unreported broad anomaly in the specific heat capacity of KC_{10} centred on $-3°C$.

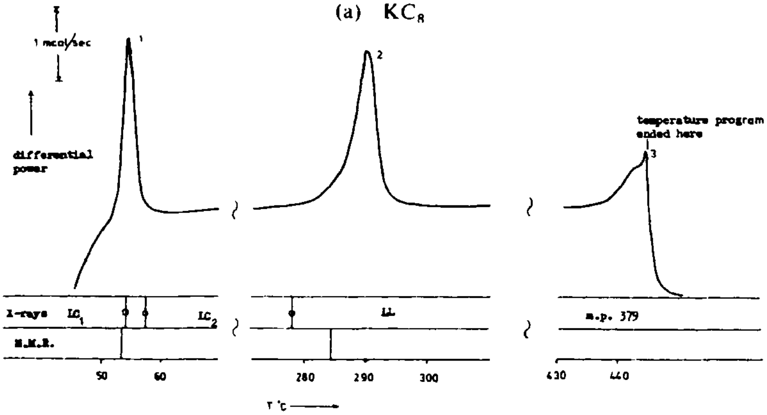
DISCUSSION

The measured entropy change ΔS at the A → C transition in KC_{10} can be compared with an estimate of the configurational entropy change, ΔS_c to be expected on the basis of Glover's model.

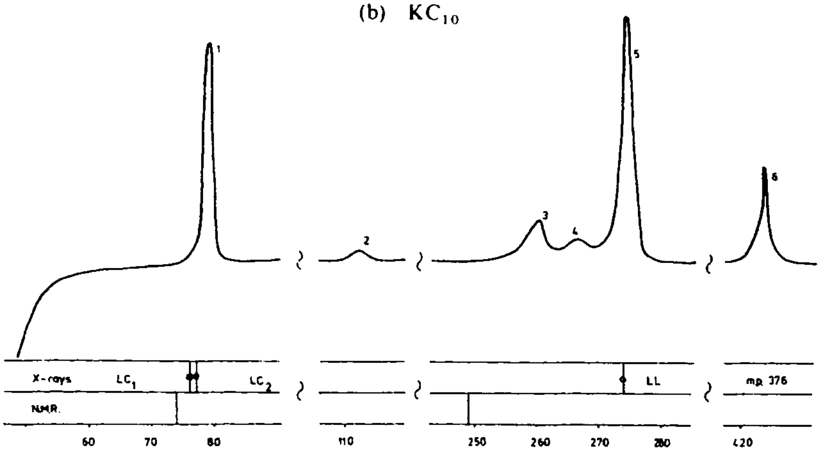
The crystal may, for simplicity, initially be assumed to be an assembly of localised, independent, (or very weakly interacting) molecules each of which may be in one of twenty seven possible configurations. One of these configurations has no gauche bonds, six have one gauche bond, twelve have two gauche bonds and eight have three. If the energy of a gauche bond is ϕ (per mole) we may therefore write a partition function as

$$Z = 1 + 6\exp(-\phi/RT) + 12\exp(-2\phi/RT) + 8\exp(-3\phi/RT) \quad (1)$$

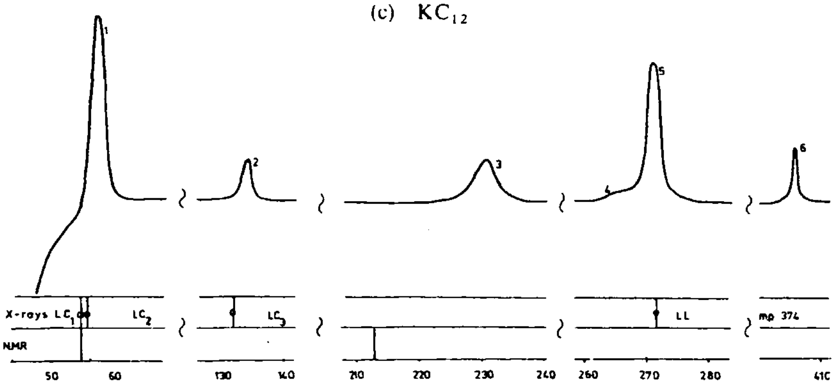
(a) KC_8



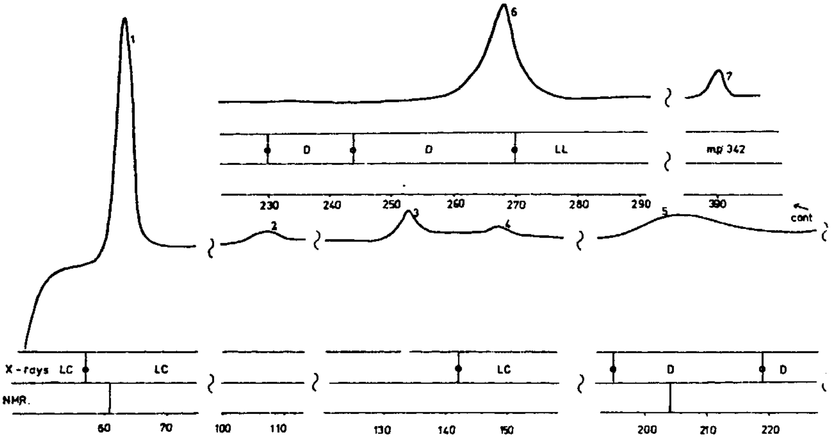
(b) KC_{10}



(c) KC_{12}



(d) KC_{14}



(e) KC_{18}

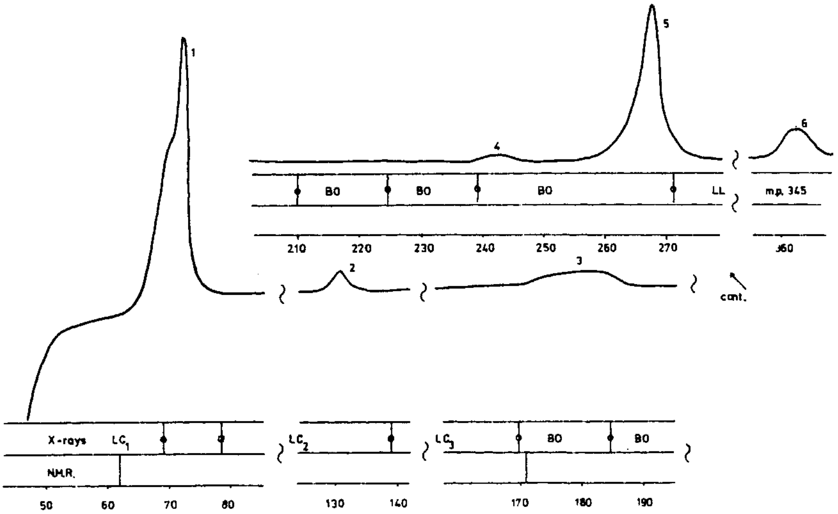


FIGURE 1 D.S.C. Traces. The vertical axis corresponds to differential power input and the horizontal axis to temperature (labelled in °C). The temperatures at which transitions have been observed by other physical techniques have been marked along the temperature axes. The phase designations given by Gallot and Skoulios[3] are also marked

$$\text{X-rays} = \begin{cases} \text{Gallot and Skoulios}^3 \sim \phi \\ \text{Lomer}^2 \sim \varphi \end{cases}$$

N.M.R. = Grant and Dunell[6,7] ~ |

TABLE I

Soap	Transition	T_c(°C)	Previously reported as the transition:	ΔH kJ mole^{-1}	ΔS JK^{-1} mole^{-1}
KC$_8$	1	52	L.C$_1$ → L.C$_2$	8.8 ± 0.6	27.0 ± 2
	2	282	L.C$_2$ → L.L.	15.1 ± 0.8	27.0 ± 1.5
	3	437	L.L. → F.	?	?
KC$_{10}$	1	72	L.C$_1$ → L.C$_2$	8.6 ± 0.6	25.1 ± 2
	2	109		0.7 ± 0.2	1.7 ± 0.6
	3	255	N.M.R.	3.9 ± 0.2	7.4 ± 0.4
	4	263	—	2.5 ± 0.4	4.7 ± 0.8
	5	269	L.C$_2$ → L.L.	12.6 ± 0.8	23.2 ± 2.5
	6	420	L.L. → F	3.3 ± 0.4	4.8 ± 0.6
	1*	75.6	L.C$_1$ → L.C$_2$	8.19 ± 0.2	23.5 ± 0.5
KC$_{12}$	1	53	L.C$_1$ → L.C$_2$	12.6 ± 0.5	38.5 ± 1.5
	2	132	L.C$_2$ → L.C$_3$	1.6 ± 0.2	3.9 ± 0.5
	3	225	N.M.R.	5.4 ± 0.5	10.9 ± 1.0
	4	262	—	0.6 ± 0.2	1.2 ± 0.4
	5	268	L.C$_3$ → L.L.	9.6 ± 0.5	17.8 ± 1.0
	6	402	L.L. → F.	1.3 ± 0.3	1.9 ± 0.5
KC$_{14}$	1	58	L.C$_1$ → L.C$_2$	13.2 ± 0.6	39.8 ± 1.9
	2	102	—	0.4 ± 0.1	1.1 ± 0.2
	3	127	—	1.2 ± 0.1	3.0 ± 0.3
	4	146	L.C$_2$ → L.C$_3$	0.4 ± 0.1	1.0 ± 0.2
	5	195	L.C$_3$ → D.;	5.0 ± 0.4	10.7 ± 0.9
	6	258	D. → L.L.	10.0 ± 0.4	18.9 ± 0.8
	7	387	L.L. → F.	1.5 ± 0.2	2.3 ± 0.3
KC$_{18}$	1	65	L.C$_1$ → L.C$_2$	17.6 ± 0.8	52.0 ± 2.5
	2	127	L.C$_2$ → L.C$_3$	0.5 ± 0.1	1.2 ± 0.3
	3	170	L.C$_3$ → B.O.	2.4 ± 0.3	5.4 ± 0.7
	4	238	B.O. → B.O.	0.2 ± 0.1	0.4 ± 0.2
	5	264	B.O. → L.L.	12.6 ± 0.6	23.4 ± 1.2
	6	356	L.L. → F.	1.7 ± 0.4	2.7 ± 0.7

* Adiabatic calorimetry

And the internal energy

$$\Delta E = \phi[6\exp(-\phi/RT) + 24\exp(-2\phi/RT) + 24\exp(-3\phi/RT)] \quad (2)$$

Then

$$\Delta S_c = R\ln Z + \frac{E}{T_c} \quad (3)$$

In comparing this estimate of the configurational entropy with the measured change in total energy we may argue as follows.

Below T_c let the intermolecular internal energy and vibrational entropy be E_1 and S_1 and the corresponding quantities above T_c be E_2 and S_2 together with ΔS_c as the configurational entropy above T_c.

Thus the measured quantities are $\Delta H \simeq E_2 - E_1 + \Delta E$, the small term $P\,\delta V$ being neglected and

$$\Delta S = S_2 - S_1 + \Delta S_c$$

The calculated ΔS_c thus gives an approximate lower bound to the total entropy change and may also be a not unreasonable estimate of the total entropy change since $S_2 - S_1$ may be expected to be small compared to ΔS_c for the following reasons.

i) The change in the overall crystal structure is small and would be expected to make little change to the phonon spectrum.

ii) The specific heat capacity of the two phases is the same just above and below the transition temperature which again implies little change in phonon spectrum, certainly when averaged in the manner appropriate to a specific heat capacity calculation.

Similarly the calculated ΔE gives a lower bound for ΔH. The change in intermolecular energy $E_2 - E_1$ however may be at least comparable to, and even greater than ΔE, the intra-molecular contribution.

Results of Mizushima[10] and Person and Pimental[11] suggest that the energy required for the formation of one gauche bond is ~2.1 ± 0.4 kJ mole^{-1}. When this figure is used in equation 3 it is found that ΔS_c is 25.78 JK^{-1} mole^{-1} which is higher than the observed value of 23.5 ± 0.6. The calculated value would be reduced by the presence of short range order, or correlations between the conformation of neighbouring molecules, perhaps substantially so but it is at least plausible that the configurational entropy associated with the disorder in Glover's model is the dominant contribution to the total entropy change at the transition.

The calculated value for ΔE, using the same value for ϕ is 3.0 kJ mole^{-1} and is thus only about one third of the observed ΔH of 8.19 kJ mole^{-1}. This too is plausible because the whole of the crystal undergoes a volume expansion of some two percent, whereas only some six atoms per molecule partake in the changes to the intra-molecular energy.

The entropy changes associated with the B → C phase change in the longer chain soap increase progressively with chain length. This would be in accord with the idea that the ionic layer preserves order among the first few carbon atoms of the chain, leaving a progressive increasing number to become disordered at the transition. It is not possible however to set up simple calculations for these cases because it is not known just how many bonds are available to partake in the disorder.

The entropy change in KC_8 is larger than in KC_{10} which is surprising in view of the shorter chain length. Even with three disordered bonds per molecule the calculated entropy is 25.57 JK^{-1} $mole^{-1}$ to be compared with 27 ± 2 JK^{-1} $mole^{-1}$.

The structural or vibrational changes in KC_{10} associated with the broad specific heat anomaly centred at −3°C are not known. The total entropy change due to the anomaly is ~6.5 JK^{-1} $mole^{-1}$. Lewis and Lomer[8] interpreted their room temperature X-ray data in terms of an ordered structure in which the last four carbon atoms in the chain showed large mean square deviations from their mean positions. It may be that, whether these deviations are due to thermal vibration, or to static disorder they contribute to the total entropy of the crystal. Further X-ray studies below this transition temperature are called for.

CONCLUSION

While not an accurate method for the determining of transition temperatures, differential scanning calorimetry has detected thermal anomalies which have not previously been reported and does provide a rapid means for surveying the thermal properties of a compound.

The measured A → C transition entropy change is not inconsistant with Glover's[1] detailed model of the nature of the disorder in the C-phase of KC_{10}.

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