Thermodynamic properties of lithium n-alkanoates

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Abstract - In the framework of a systematic investigation on thermophysics of alkali metal alkanoates, the thermodynamic properties of lithium n-alkanoates from the formate to the eicosanoate have been determined. Phase transitions in all these salts were brought out mainly with differential scanning calorimetry, and heat capacities of the carboxylates from the formate to the n-heptanoate were measured by means of adiabatic calorimetry. The results thus obtained are discussed in comparison with literature data determined with different techniques. A qualitative discussion of the possible origins of the transformations displayed by lithium alkanoates is given, and the heat capacity data are analysed in terms of CH_2 contributions for members of the homologous series.

INTRODUCTION

Polymorphism and polytypism in long-chain aliphatic compounds are currently studied both from the standpoint of fundamental crystallographic research, and for the interest of various industrial applications (1).

Alkali metal alkanoates with saturated aliphatic chains, as well as other organic compounds with linear hydrocarbon chains, like fatty acids, alcohols, amines and paraffins, crystallize in lamellar structures usually undergoing a variety of polymorphic transitions (2). Their physical and chemical properties depend on the nature of the cation and on the geometry and length of the anion.

The polymorphism of alkali metal alkanoates can be very complicated. A further difficulty consists in the fact that no crystal structure data are available for most alkali metal carboxylates, and in particular for Li n-alkanoates. Other experimental difficulties are related to the techniques of preparation and handling of these products. A systematic investigation of their thermodynamical properties was undertaken in our laboratories with the purpose of clarifying the phase relationships in the five series of the mentioned salts. A review summarizing the thermal and transport data up to 1980 was previously published under IUPAC sponsorship (3). Moreover, phase diagrams of binary systems of alkali alkanoates were recently collected and critically evaluated (4).

The aim of the present work is to provide an overview of our current research on the thermophysics of one family of alkali metal alkanoates, namely those of lithium, with number of carbon atoms in the aliphatic chain, n_C, ranging between 1 and 20, hereafter shortly indicated as LiC_1, ..., LiC_{20}. In all these salts, phase transitions were investigated mainly with differential scanning calorimetry (dsc). In the LiC_1 - LiC_7 homologues, heat capacities were determined by means of adiabatic calorimetry. In order to draw a more complete and reliable picture of the detected transformations, the results obtained by thermal methods are compared with those published by other authors who made use of different experimental techniques, such as X-ray diffraction on powders, dilatometry, hot-stage polarizing microscopy.

PHASE TRANSITIONS

It is well known that several crystalline forms of an organic substance can be obtained by crystallization either from different solvents or from the same solvent in different experimental conditions (1). Other polymorphs are produced as a result of temperature changes. In compounds with aliphatic chains, like the alkali carboxylates, various crystal structures can occur, due to the possible combinations of different molecular interactions, such as: i) side-packing interactions between adjacent hydrocarbons inside a lamella; ii) interactions of methyl-terminal groups, or end-group packing interactions, between lamellae close to each other; iii) interactions of the polar -COO⁻ groups.

In the crystal forms existing at room temperature, i.e. in the lamellar structures, the aliphatic hydrocarbon chains are packed parallel to each other in a *tail-to-tail* arrangement, filling the intermediate space between the ionic layers formed by the polar groups of the anions and the corresponding cations, as shown in Fig. 1.
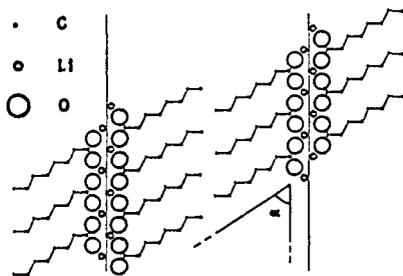
Fig. 1. Schematic arrangement of alkali metal alkanoate molecules in a crystalline lamellar structure.

On heating, the transformation of the lamellar crystal structures into different, but still lamellar, polymorphs can be associated with a change in the angle of tilt between the axes of the hydrocarbon chains and the ionic double layers (α angle in Fig. 1). On further heating, the paraffinic chains "melt", but in this disordered environment the polar groups still keep an ordered structure, being arranged in plastic crystals, or aggregates taking the shape of ribbons or disks. At higher temperatures, liquid crystals can form, which finally can give isotropic melts.

As for the lithium carboxylates with straight chains, two lamellar crystal polymorphs were observed by means of X-ray diffraction in all the even homologues with $10 \leqslant n_C \leqslant 18$ (2, d), with transition temperatures increasing as a function of n_C. Moreover, according to ref. (2,d), all the salts with $n_C \geqslant 12$ in their hydrocarbon chain form plastic crystals before melting, with ribbon-like structures of defined and small width and unlimited length, assembled in rectangular centered meshes.

A dilatometric investigation of the LiC_{14} - LiC_{18} soaps (6, and references 1-6 therein) confirmed that all these straight chain compounds undergo a stepwise fusion mechanism which can be described by the following sequence:

Lamellar crystal II ⇌ Lamellar crystal I ⇌ Plastic crystal ⇌ Melt,
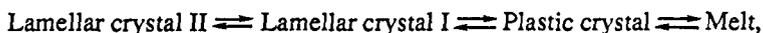
where the plastic crystal phase consists of networks of ribbon-like structures surrounded by disordered hydrocarbon chains. According to ref. 6, the ΔV changes for intercrystalline transitions in the LiC_{14} - LiC_{18} alkanoates are of the same order of magnitude and display an alternation effect in the homologues with even and odd number of carbon atoms in their chain.

Visual observation at the hot-stage polarizing microscope on the LiC_{14}, LiC_{16}, LiC_{18} soaps (7) practically confirmed the cited results.

The thermal behaviour of the lithium n.alkanoates as determined by dsc analysis from 100 K to the melting temperature (5) agrees with the above findings. A general view of the transition temperatures as a function of n_C in the considered Li carboxylates is illustrated in Fig. 2. Besides the presence of metastable phases (not detected upon heating and not shown in the figure, to be discussed below), the stepwise melting mechanism of the Li series summarized in this figure proved to be the simplest one, in comparison with those of the linear organic salts formed with different monovalent cations (3), which usually undergo a more complex sequence of transitions in the solid and mesomorphic states before melting.
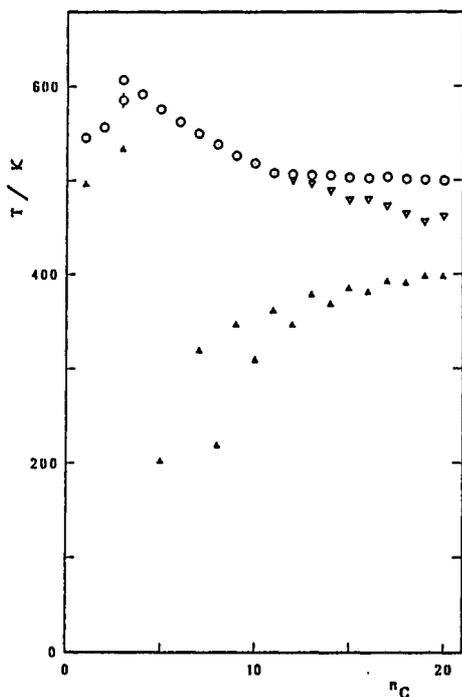
Fig. 2. Phase transition temperatures in Li alkanoates as determined by dsc.

▲ : *solid-to-solid;* ▽ : *solid-to-mesophase;*

○ :*solid-to-liquid and mesophase-to-liquid;*

◊̇ : *melting point of the metastable phase of LiC₃.*
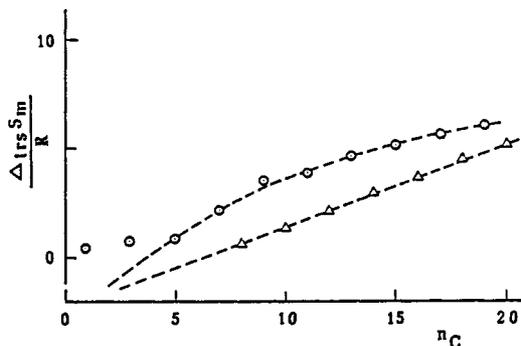
Fig. 3. Solid-to-solid transition entropies for Li n-alkanoates.
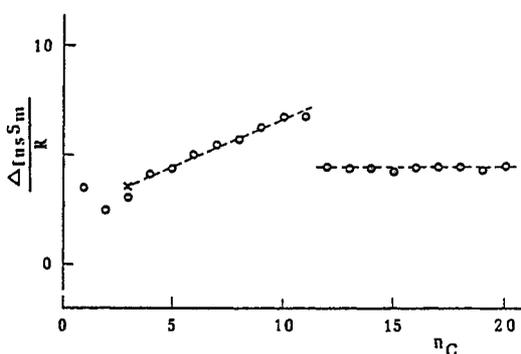
Fig. 4. Fusion entropies for Li n-alkanoates. x: fusion entropy of the metastable phase of LiC₃.

The most significant features of the lithium alkanoate series are:

- i) the odd-even alternation in the temperatures of the lamellar crystal II⇌lamellar crystal I transition for $n_C \geqslant 7$, with a definite tendency to approach a limiting value for $n_C = 20$;

- ii) the field of existence of the plastic crystal phase starting with LiC_{12};

- iii) the constant melting temperatures of the soaps with $n_C \geqslant 12$, in contrast with the decreasing trend for n_C increasing between LiC_3 and LiC_{11}. In the latter group of substances, as the hydrocarbon chain shortens, the cohesion forces between polar groups can hinder fusion more effectively, thus giving higher fusion temperatures.

Similar trends are observed in the corresponding heat effects and related entropies. In the plot of $\Delta_{trs}S_m/R$ vs. n_C, the entropies associated to the intercrystalline transitions occurring between 100 and 400 K in odd and even homologues, for $n_C \geqslant 8$ and 5, respectively, seem to be correlated (Fig. 3, curves 1 and 2). The dependence of $\Delta_{trs}S_m/R$ on n_C could be parabolic for the odd carboxylates, starting with the low T transition of LiC_5, and is linear for the even ones, as outlined by the dashed curves. On the basis of curve 2 in Fig. 3, negative values would be calculated for LiC_4 and LiC_6. Moreover, by extrapolating curve 1, one would obtain negative values for LiC_1 and LiC_3. This means that no sharp solid-solid transitions should be expected at lower temperatures in these short-chain carboxylates. As a matter of fact, the hydrocarbon chains in the first three Li alkanoates are too short to be compared with those of higher homologues. Therefore, it seems reasonable that the solid-to-solid transitions occurring in LiC_1 and LiC_3 should not be included in the mentioned correlation.

As for melting, the plot of $\Delta_{fus}S_m/R$ values vs. n_C presented in Fig. 4 shows a linear dependence of the fusion entropies on n_C for the LiC_4 - LiC_{11} carboxylates (curve 1, with the fusion entropy of the metastable phase of LiC_3 also lying on the interpolation line) suggesting that these homologues undergo similar fusion

processes. The practically constant trend for the fusion entropies of the LiC_{12} - LiC_{20} alkanoates (Fig. 4, curve 2) in turn suggests that fusion phenomena in these soaps occur by breaking the same kind of order in their plastic mesophases. Obviously, the fusion mechanism in this case is different from that of the short-chain Li carboxylates, since for $n_C \geq 12$ ribbon-like plastic crystalline phases melt.

Along with the above mentioned existence of a metastable melting point in Li propanoate (5, a), the spontaneous formation of a glass upon cooling in both the molten Li formate and acetate is worthy of mention. In Fig. 5, dsc traces showing the reproducible cycles of glass formation, crystallization and melting are illustrated for both salts. This tendency to glass formation has been previously reported as typical of a group of acetates of mono- and divalent metals (8).

The fact that metastable behaviour is not limited to short-chain homologues deserves a brief comment. Actually, it was observed by dsc that in all the Li soaps with $n_C \geq 12$ a remarkable hysteresis occurs on cooling in the transition from plastic crystal to lamellar crystal I (5, d). Moreover, the apparently single fusion peak was split on cooling into two peaks: this means that, on heating, the molten state is reached through a pair of transitions occurring very close to each other, whereas, on cooling, the different supercooling effect associated to the two phases allows recording of both their transition peaks. These phenomena are more clearly observed (5, d) in homologues with longer chains because, on cooling, the rearrangement of the hydrocarbon chains is more difficult the longer the chain.
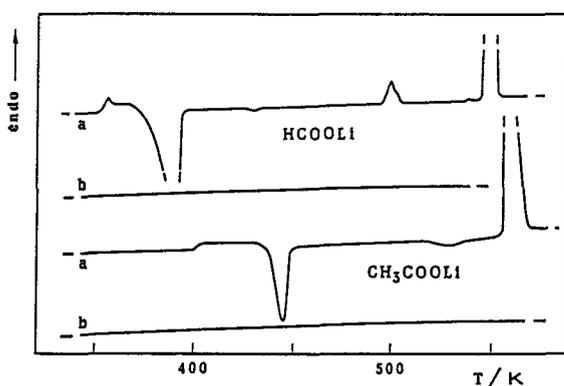
Fig. 5. Heating (a) and cooling (b) cycle of
Li formate and acetate.

HEAT CAPACITIES

Quantitative heat capacity measurements were performed by means of adiabatic equilibrium calorimetry over the temperature range between 5 and 350 K on the salts from LiC_1 to LiC_7 (9).

A comprehensive picture of the measured heat capacities is illustrated in Fig. 6, where the solid-to-solid phase transitions occurring in the considered T range are also shown.

The shortest chain carboxylates do not show any sharp phase transition in the examined T range (9, a, b). This is also the case of LiC_6, as it was expected from the above considerations on the alternating character of the entropy changes associated to the transitions in the solid state. The sharp transitions found at 209 K in LiC_5 and at 317 K in LiC_7 confirm the dsc data. Another smooth and broad transition in LiC_5, occurring slowly over a temperature range of about 110 K, from 220 to 330 K, was brought out by adiabatic calorimetry measurements (9, d), and subsequently detected also by dsc. The main reason why this phenomenon had not been seen in previous dsc scans was the fact that it occurs in a T range just half-way between the two usual limits of the operational modes of the calorimeter, i.e., the upper limit of the low T range and the lower limit of the high T range.

Gradual, and not discontinuous, transformations occur in LiC_3 at T > 280 K, in LiC_4 at T > 160 K, and twice in LiC_6, at T > 130 and T > 260, possibly corresponding to the progressive activation of either vibrational degrees of freedom or the rotation of the methyl end group. Phenomena of this kind, as a consequence of intramolecular orientational changes, could cause gradual changes in crystal packing, and therefore in heat capacity.
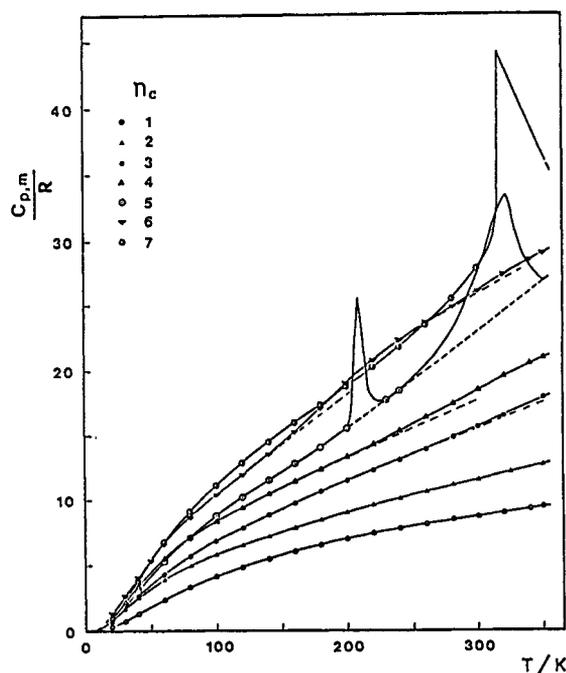
Fig. 6. Heat capacities of LiC_1 - LiC_7 n-alkanoates.

Additional contributions equal to multiples of R could be empirically estimated (9, c) for the processes occurring in LiC_4 and LiC_6. These transformations start in LiC_3 and in LiC_4 at temperatures higher than in LiC_6, because shorter hydrocarbon tails should be held more rigidly by the electrostatic field.

In the present series of Li carboxylates, an attempt can be made to use an approach interpreting the energetics and dynamics of long hydrocarbon chains in similar compounds (10) in terms of the number of CH_2 increments in the chain $m(CH_2) = n_C - 2$. In a first approximation, the fact that odd and even values of $m(CH_2)$ in alkanes, and in alkanoates, behave differently when n_C is small can be neglected, in particular for temperatures far enough from zero. The present approach, based, with modifications, on Pitzer's hydrocarbon model (11), gave a calculated heat capacity curve for the CH_2 group (9, c) fairly similar to that of ref. 10.

On the basis of the CH_2 contribution thus obtained, the "lattice" heat capacities for the linear lithium carboxylates with $3 \geqslant n_C \geqslant 7$ have been calculated and are compared in Fig. 7 with the corresponding experimental values. The agreement seems excellent between 80 and 350 K for the propanoate and butanoate, and between 80 and 280 K for the heptanoate. For the pentanoate and hexanoate, a good coincidence can be observed up to the temperature of the first transition or rearrangement, i.e. up to 209 and 120 K, respectively.
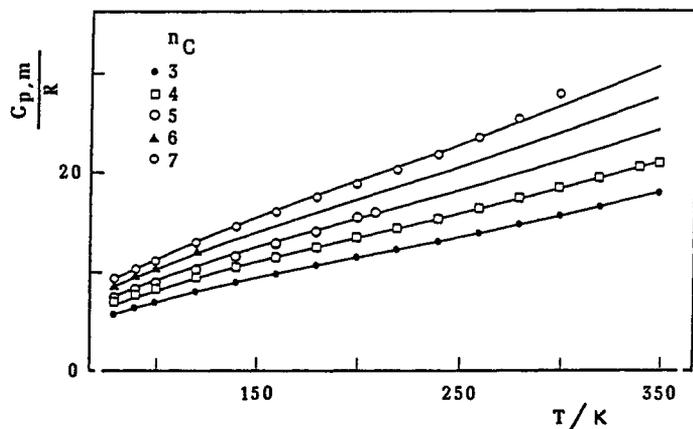
Fig. 7. Calculated (lines) and experimental smoothed heat capacities for LiC_3 - LiC_7.

CONCLUSIONS

A general and comprehensive picture of phase transitions in Li normal alkanoates from the formate to the eicosanoate has been drawn mainly on the basis of thermal data collected by means of differential scanning calorimetry and adiabatic calorimetry.

Among the alkali metal alkanoates, the Li series shows the simplest stepwise mechanism of fusion. Only the long chain homologues, from dodecanoate to eicosanoate, undergo the transition sequence:
lamellar crystal II ⇌ lamellar crystal I ⇌ plastic crystal ⇌ melt.

Various kinds of metastable behaviour are found in this series of compounds. Glass formation is a characteristic feature of the formate and acetate. A metastable melting point is shown in the propanoate. Metastable phases are also apparent in the region of existence of the plastic crystals, for the long chain soaps from dodecanoate to eicosanoate.

Heat-capacity data for the Li alkanoates from formate to heptanoate have been measured. Besides the phase transitions previously detected by dsc, gradual and continuous transformations have been brought out, in particular, in the butanoate and hexanoate, whereas a smooth and broad phase transition has been observed in the pentanoate. An analysis of the predicted "lattice" heat capacities for members of the homologous series in terms of CH_2 contributions has been performed.

Further adiabatic calorimetry will involve the Li n-octanoate and higher homologues. Moreover, for a deeper understanding of the phase relationships in these compounds, studies of molecular dynamics and determination of crystal structures would be of great interest.

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