Melting Mechanisms of n-Alkanecarboxylates ($C_nH_{2n+1}CO_2^-$; $n \leq 6$)

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Chemically stable ionic melts can now be prepared from alkali salts of short-chain aliphatic acids. In view of the interest of these liquids, systematic data have been obtained on the first melting points T_f and on the transition points T_{cl} (if any), from ' liquid crystal ' to optically isotropic melts, of n-alkanecarboxylates ($n \leqslant 6$) with the monovalent cations Li, Na, K, Rb, and Cs.

No evidence could be obtained for the existence of mesophases of ' liquid crystal ' type, for salts of lithium. Temperature ranges for mesophase melts of salts containing all the other cations extend well over 100 °C in many cases, before their isotropic melts are reached.

DESPITE their interest as a distinctive class of ionic liquids, melts from the salts of organic acids have until recently received little attention. This appears to be due mainly to the fact that such melts decompose more or less rapidly to numerous breakdown products, unless appropriate precautions are taken to exclude certain impurities. However, by removing molecular oxygen, transition-metal ions, and hydroxy-ions incorporated in place of carboxylate anions during their isolation, melts of many of these salts are stable for long periods, up to temperatures where spontaneous thermal cracking of the anions probably occurs, even in the absence of any impurities.[1] For alkali-metal salts of alkanoic acids this cracking limit appears to be somewhat above 300 °C.

The course of chemical reactions in stable melts of salts of organic acids can differ notably from that in more familiar solvents.[2] Also, many organic salts show more than one mechanism of melting, with melting transition points often separated by a considerable interval of temperature. At their first melting point many organic salts melt to ' liquid crystals.'[3] This makes them of special interest in relation to general theories of melting.[4]

Physico-chemical properties of this class of liquids are most distinctive when the ratio of ionic charge to the total number of atoms in the molecule is fairly high. In such liquids, strong primary electrostatic forces between the ions are not highly screened by the organic part of the molecule. Electrostriction effects in these fluids are prominent.

The present paper gives information about melting transitions of the n-alkanoate salts with anions containing up to 7 carbon atoms, with the cations Li, Na, K, Rb, and Cs.

EXPERIMENTAL

Experimental work was carried out with the help of Mr. Gordon Phillips.

Salts were prepared from AnalaR reagents (Hopkin and Williams) or materials of comparable quality. An excess (*ca.* 1% by mass) of redistilled acid was added to a stoicheiometric quantity of sodium carbonate in deionised distilled water (200 g l^{-1}). Water was evaporated on a steam-bath until only a crumbly paste remained. The rest of the solvent (which was mainly the excess of acid) was removed under vacuum ($<1{\cdot}3$ Pa) for at least 24 h, with temperature gradually raised to 180 °C. Dried salts were stored under oxygen-free nitrogen (O_2 <10 p.p.m.; H_2O <1 p.p.m.) until required for use. For normal handling, a glovebox was used.

Melting transitions can in principle be observed in a number of different ways. It was considered desirable to adopt a systematic procedure. This is all the more important since at their first melting point (T_f), many of these salts transform to mesophases of a ' liquid-crystal ' type, and do not change to isotropic melts until a second melting transition at a considerably higher temperature (T_{cl}). There are indications that if observations are made on very small specimens, *e.g.* as confined in conventional m.p. tubes, or on a heated microscope stage, the findings depend

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[1] A. R. Ubbelohde, *Chem. and Ind.*, 1968, **311**, 313; J. J. Duruz, H. J. Michels, and A. R. Ubbelohde, *ibid.*, 1969, 1318.

[2] J. J. Duruz, H. J. Michels, and A. R. Ubbelohde, *J. Chem. Soc.* (*B*), 1971, 1505.

[3] (*a*) D. Vorländer, *Ber.*, 1910, 3120; (*b*) A. R. Ubbelohde, H. J. Michels, and J. J. Duruz, *Nature*, 1970, **228**, 50.

[4] A. R. Ubbelohde, ' Melting and Crystal structure,' Oxford University Press, 1965; A. R. Ubbelohde, *J. Chim. phys.*, *numéro spécial*, 19*th Meeting of the Society*, Montpellier, 1968, **59**; J. J. Duruz, H. J. Michels, and A. R. Ubbelohde, *Proc. Roy. Soc.*, 1971, *A*322, 281.

somewhat on the nature of the confining walls. In the present work, transition points were determined systematically to ±1° with a Perkin-Elmer differential scanning calorimeter (D.S.C.), in which samples of salt in small aluminium dishes (6 mm diam.) are subjected to a definite programme of temperature change (usually ±8 deg min^{-1}). With lids crimped on, sample thicknesses were often <1 mm.

Some melting transition peaks determined from calorimetric observations were checked independently, from peaks obtained with a DuPont 900 differential thermal analysis apparatus, with samples (*ca.* 20 mg) in glass container tubes. This method gave peak temperatures for the melting transition, within 2 °C of the calorimetric data regarded as norms. Although the change of containers had no major effect on melting transition peaks T_f and T_{cl} for alkanoates, significant differences were observed in some cases (not illustrated) with regard to delayed appearance of solid–solid transitions on a cooling cycle. These were probably due to nucleation effects originating from the walls of the container (*cf.* ref. 5). Figure 1 illustrates results for sodium n-butyrate, obtained with scanning calorimetry and with differential thermal analysis, at comparable rates of temperature change. For better resolution, a more expanded temperature scale was generally used with D.S.C.

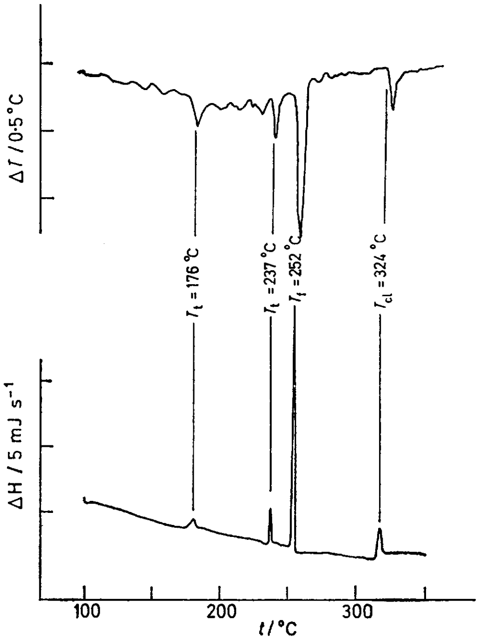

FIGURE 1 Comparable records for the determination of transition points of sodium n-butyrate by differential thermal analysis (20 mg; 10 deg min^{-1}) and by differential scanning calorimetry (1 mg; 8 deg min^{-1})

Precise melting and clearing points observed with D.S.C. are recorded in the Table (T_{cl} is expressed in the form $T_{cl} = T_f + \Delta T_{meso}$).

DISCUSSION

The Table records the best data based on thermal observations. General relationships between melting mechanisms are more clearly seen from Figure 2. These

M.p.s (T_f/°C ±1) and mesomorphic temperature ranges ΔT_{meso} of metal n-alkanoates, $C_nH_{2n+1}CO_2M$

Cation	*n*	T_f/°C	ΔT_{meso}/°C
Li	1	70	0
	2	327	0
	3	310	0
	4	300	0
	5	282	0
	6	274	0
Na	1	324	0
	2	287	0
	3	251	73
	4	229	124
	5	232	126
	6	238	123
K	1	292	0
	2	358	0
	3	347	50
	4	312	102 [a]
	5	307	111 [a]
	6	296	122 [a]
Rb	1	*b*	*b*
	2	345	0
	3	370	0
	4	362	44
	5	338	82 [a]
	6	324	111 [a]
Cs	1	*b*	*b*
	2	295	0
	3	343	0
	4	367	0
	5	351	44
	6	340	69

[a] Salt decomposes on clearing, probably because the temperature for spontaneous thermal cracking of the anion was exceeded. [b] Not available.

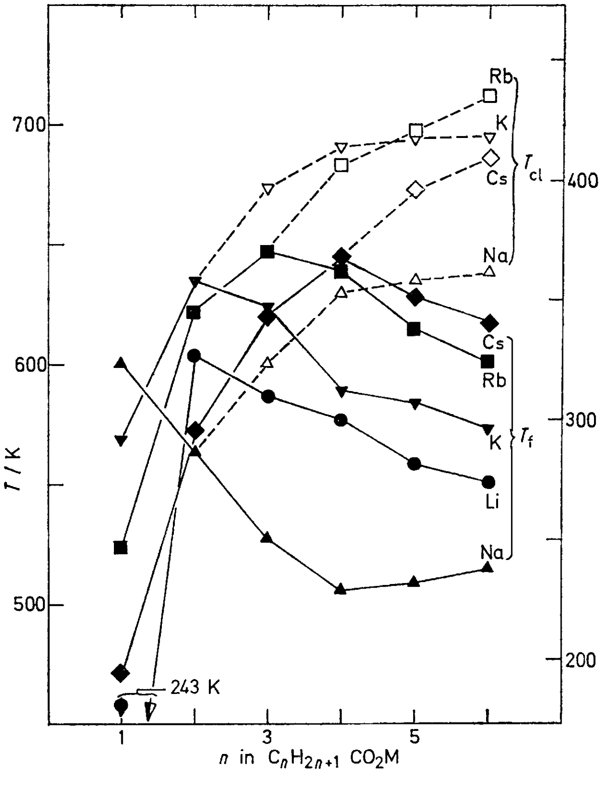

FIGURE 2 Melting T_f and clearing T_{cl} points for alkali salts of n-alkanoic acids

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[5] A. Cimino, G. S. Parry, and A. R. Ubbelohde, *Proc. Roy. Soc.*, 1959, *A*252, 445.

data cannot be very closely compared with more approximate and much earlier results,[3a] which were obtained in small tubes by microscopic observations (Vorländer did not provide means for stabilising his melts). We now know that in sealed tubes, any oxygen would have been rapidly used up by his melts, but foreign cations or an excess of OH^- anion, if present, could have led to serious decomposition.

Recently,[6] further microscope-slide observations have been listed for various sodium and potassium salts. Differences from values given in the Table are erratic, and are considerably larger than errors estimated for the thermal data. It is not yet possible to state whether these microscope observations differ because of wall effects, or for other experimental reasons.

Figure 2 and the Table both show that for all alkali metals except lithium, mesophases exist over considerable ranges of temperatures when the n-alkane chain contains three (or in the case of Cs, four) carbon atoms. However, in any family with the same anion, the actual first melting points (T_f) and the clearing points (T_{cl}) depend markedly upon the cation. There is no very smooth relationship between trends in T_f or T_{cl} in relation to the nominal ion contact radius of the cation, as measured for salts of simple structure, such as the inert gas type ionic halides.[7]

Erratic trends actually found from the present work point to more than one factor influencing melting temperatures of these alkali carboxylates. Although detailed crystal structures of any of these salts are practically unknown, general considerations about molecular forces suggest that in the crystal packings a prominent role must be played by layers of charged carboxy-groups, in contact with adjoining cations, and separated from adjacent layers by the alkane ' tails ' of the anions. Structural studies[8a,c] illustrate the kind of ' electrostatic sandwich ' of carboxy-groups and cations determined for crystalline soaps. Similar crystal structures are to be expected in salts with the shorter organic tails of the group of organic salts under discussion here (see Figure 3, which is based on actual crystal structure determinations of sodium caproate[8b]). Optical studies[6] together with *X*-ray studies[9] of mesophases of the present series of salts clearly indicate similar electrostatic sandwich structures. Compared with soaps, the main difference is that forces between adjacent ' electrostatic sandwiches ' in the present series are not so well screened by the shorter alkane tails, so that electrostriction in the present series of melts should be considerably stronger than in the soaps.

It might be expected that, for any given carboxylate anion, the size of the univalent cation should, by comparison, have only a subsidiary influence, *e.g.* on the thermal properties of the salt. Smooth sequences in the series Li, Na, K, Rb, and Cs should be more obvious only for a particular anion. In fact, however, contact packings of oxygen atoms of the carboxy-group around an alkali cation seem to depend in a rather sensitive way not only on the cation repulsion radius, but also on the cation polarisability; accordingly, conflicting trends are found. As is well known, other properties of salts of Group I cations likewise show out-of-sequence trends in relation to ion contact radii.[4] It is particularly noteworthy that whilst deliquescence is a general property of alkali carboxylates, the potassium salts often show this property in more marked degree than the sodium salts, while rubidium and caesium salts are only sometimes even more deliquescent.

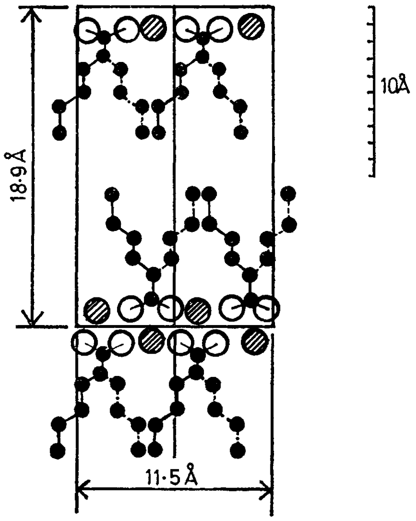

FIGURE 3 Alternative configurations of n-alkane chains between ' electrostatic sandwiches '[8b] for solid potassium caproate (ions and atoms not to scale)

Thanks are due to Dr. J. J. Duruz for useful discussions and to the S.R.C. for support.

[2/539 *Received, 7th March,* 1972]

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[6] E. Baum, D. Demus, and H. Sackman, *Wiss. Z. Univ. Halle*, 1970, **19**, 5, 37—46.

[7] Handbook of Physics and Chemistry, Chemical Rubber Co., Ohio, U.S.A., 1970—1971.

[8] (*a*) V. Vand, T. R. Lomer, and A. Lang, *Acta Cryst.*, 1949, **2**, 214; (*b*) T. R. Lomer, *ibid.*, 1952, **5**, 14; (*c*) J. H. Dumbleton and T. R. Lomer, *ibid.*, 1965, **19**, 301.

[9] J. J. Duruz and A. R. Ubbelohde, in the press.