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ORGANIC IONIC MELTS  
A NOVEL CLASS OF LIQUIDS

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## ORGANIC IONIC MELTS A NOVEL CLASS OF LIQUIDS

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SUMMARY — Crystalline ionic liquids consist of organic-ionic mixtures, which may be stable, and exhibit peculiar properties. The author has determined the structures of these crystals.

In a systematic classification of types of liquids, these must be referred to the types of crystal compounds from which they are formed on melting. In order to arrive at a realistic model for the liquid it is furthermore necessary to establish which of various mechanisms of melting operate.

This general approach leads to the conclusion that if one wants to explore new types of liquids, appropriate selection must be made amongst classes of crystal compounds of promising interest. My own researches had already included many molten inorganic salts, particularly amongst those with low melting points, say below 300°C (Ref. 1).

Although the field of inorganic chemistry no doubt offers

many other classes of low melting salts, I had been for some time looking longingly at the enormous number of salts of organic acids referred to in the literature. These have the attractive feature, for a chemical physicist, that salts of homologous series of acids, or of acids with only small differences of molecular structure can be studied, thus permitting comparison with respect to a variety of physical properties.

*Stability problems:*

Setting out with the hopeful plan of studying the class of organic ionic liquids, with all the modern refinements available, soon revealed an unsuspected general difficulty. Many salts of organic acids, particularly of Group I cations are quite stable in crystalline form. However, on melting, even when the melting points are quite low, trial experiments revealed marked instability in many cases. (Intrinsic i.e. due to effect of disordering, as well as extrinsic due to the various catalytic and other impurities).

Various explanations are possible when striking differences are found in chemical stability, between the crystalline and the molten states of a chemical substance. What may be described as *intrinsic reasons* arise from the much greater constraints on molecular rearrangement that prevail in the ordered crystalline state, compared with the disordered molten state. For one thing, most molecular rearrangements pass through an activated transition state, whose volume is greater than that of the ground state. Whenever this is the case in the crystalline state, the lattice environment may demand a much higher activation energy term, to do work against the internal pressure, than in the fluid. Again, if thermal decomposition involved actual bond breakage, the fragments of a molecule cannot diffuse away so rapidly from a reacting molecule whilst they are held in a crystal lattice, as in the

melt. They may actually even recombine after incipient fragmentation. Finally, in an ionic crystal the very strong electrostatic fields emanating from cations and anions are often substantially compensated by the lattice symmetry. On melting this symmetry is no longer retained. If the mechanisms of thermal decomposition of the molecules are strongly influenced by primary electrostatic fields, as is often the case, the less compensated fields in the melt have much greater freedom to exert their influence than in the crystal lattice.

These possibilities for intrinsic instability on melting organic salts at first looked rather daunting. Because of its very low melting point (304°C) and the ease with which it can be prepared in a chemically very pure state, some of our earliest intensive researches had focussed on potassium acetate. This salt decomposes in a somewhat unpredictable but quite unmistakable way, on melting. Fortunately, qualitative observations suggested that some of the decomposition was caused by molecular oxygen.

Much experience in removing even traces of oxygen from condensed states of matter soon settled this source of trouble. We established that molecular oxygen reacts powerfully with potassium acetate, as also with many other organic ionic melts. (Ref. 2). Fortunately, this gas is quite easily purged with nitrogen or argon. Greatly enhanced chemical stability of the organic ionic liquids results. To cut a long story short, at least two other extraneous sources of chemical instability had to be tracked down and eliminated. One of these may be described as electron acceptor impurities. There was a suggestion that even oxygen acted in this way, as first step e.g. towards the decomposition of a carboxylate anion  $\text{RCOO}^- + \text{O}_2 \rightarrow \text{R} \cdot + \text{CO}_2 \uparrow \text{gas} + \text{O}_2^- \text{(melt)}$  since a primary formation of free radicals followed by polymerisation could explain the brown tars formed even from melts of a simple molecule such as potassium acetate, when exposed to the air. It was readily verified that direct addition of transitional metal

ions of variable valence, such as  $\text{Cu}^{++}$  or  $\text{Fe}^{++}$ , greatly accelerated decomposition of organic ionic melts. Transitional metal impurities can however be excluded by careful exclusion of town dusts, as well as rigorous purification of the salt in the course of its preparation.

A second general source of trouble arises from the fact that organic ionic crystals are mostly formed from acids and/or bases that are rather weak. This makes it important to prevent products of hydrolysis from becoming incorporated with the salts. With alkali carboxylates for example, small quantities of free hydroxide can easily become incorporated. On melting, the  $\text{OH}^-$  ion attacks the carboxyl ion, possibly according to the reaction  $\text{OH}^- + \text{RCOO}^- \rightarrow \text{RH} + \text{CO}_3^{--}$  though the actual chemistry may be more complex. Hydrolysis during preparation can often be prevented (Ref. 2) by adding a small excess of the weak acid/or base. After separation of the salt, and removal of the solvent, the slight excess e.g. of acid still retained can be removed by high vacuum treatment.

With these precautions crystalline salts can be obtained which give organic ionic melts that are stable indefinitely. I should stress that such liquids were simply not available either for precise studies or bulk uses until all extraneous sources of instability had been overcome.

In what follows, I want to discuss the liquids obtained by melting alkali alkane carboxylates. Salts to be discussed in the present lecture were mostly prepared from the cations Li, K, Rb, Cs. The acids, of general anion formula  $\text{C}_n\text{H}_{2n+1}\text{CO}_2^-$  were usually chosen with  $n \leq 6$ . In this particular group of ionic melts, our object was to concentrate attention on organic ionic melts in which the ratio of charge/total number of atoms is still quite large, leading to liquids in which the electrostriction is still high, i.e. which are characteristic *ionic* liquids. It is equally possible to study organic ionic melts in which the ratio of charge/total number of atoms is much

lower. One obvious example is the molten soaps, which are alkane carboxylates with  $n > 10$ , and particularly with  $n = 16$  or 18. Many other large organic ions can also be considered that would also give ionic liquids with low charge/atom ratio. Some of these may show highly distinctive liquid properties, but these cannot be discussed here.

When purified as explained, organic ionic melts  $M^+ \cdot \overline{\text{OOC}} \cdot C_n H_{2n+1}$  are mostly stable to above about  $350^\circ\text{C}$ . Around this temperature, a decomposition sets in which provisionally we attribute to intrinsic i.e. spontaneous thermal rearrangements of valence bonds in the molecule, such as



If as supposed these cracking reactions are truly intrinsic this sets an upper limit to the study and technological use of these liquids.

#### *Two stage melting of ionic organic melts:*

One of the first items of systematic information required was to determine the *stable liquid range* of this novel class of liquids. In brief, this can be represented by a melting point diagram (Ref. 3). For all five alkali cations the first three families, up to  $n = 3$ , give stable ionic melts with a very useful liquid range, seldom less than  $100^\circ\text{C}$ . For  $n > 3$  melting in most cases takes place in two stages, in the first instance to mesophase birefringent "liquids". These are similar to the familiar "liquid crystals" of organic chemistry, except of course (Ref. 3) for the much higher electrostatic forces between the molecules in organic ionic melts.

Measurements we are currently making on *organic ionic melt mesophases* are compelling us to revise many classical ideas about what is actually meant by a "liquid". If one defines a liquid mechanically, as a condensed state of matter incapable of withstanding applied shear stress, then our recent studies suggest that organic ionic melt mesophases may be better described as extremely plastic solids, with an exceptionally low elastic limit. In particular *a*) Temperatures of peak thermodynamic disordering may not coincide with critical changes in mechanical properties *b*) Once flow starts, mechanical properties may alter because of molecular orientation induced by flow. (Ref. 4). To verify this, we have designed and constructed a "relaxometer" in which the forces applied can be as low as 30nN with shear stresses as low as 0.1 nNm<sup>-2</sup>. Shears depend on the shape of the plunger used. This clearly reveals very low elastic threshold shears which give way to a lock-stop kind of flow when exceeded, though above about 55nNm<sup>-2</sup> continuous flow was observed. Above this critical shear stress one can quite readily induce flow in organic ionic melt mesophases. As might be expected, such flow is not strictly Newtonian. To indicate the order of magnitude of the viscosities observed, these are about 100 poise for sodium — n — isovalerate in its mesophase, when measured in conventional capillary viscometers at moderate rates of flow.

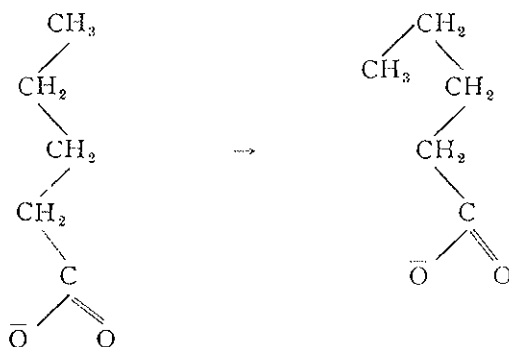
Above the second melting point, the organic ionic melt mesophases form the familiar clear optically isotropic liquids. The viscosity drops to about 0.1 poise in the clear melts.

#### *Structure and properties of ionic organic melts:*

As a general comment, this class of organic ionic melts may be expected to show other distinctive properties that are unfamiliar either in network liquids such as water or alcohols, or molecular liquids such as benzene or petrol or olive oil.

In molecular liquids forces of attraction and repulsion are short range, whereas in ionic organic melts both long range attractions and repulsion operate.

An enormous body of information is already available on aqueous solutions, or on hydrophobic solutions in which the forces between molecules are only fairly weak. With organic ionic melts of the group I am describing, we have to start from ground level to build up all the relevant information. Fortunately, certain guidelines are available that help the search for the more significant similarities and differences. Starting with the organic crystals, quite often these show solid/solid transformations of a lambda type, as is clear from specific volume or enthalpy measurements. Analogy with many other examples indicates that such transitions usually involve some kind of randomisation of orientation of parts of the alkane chain. Well known conformational isomerism arises from hindered rotation in the crystal of  $\text{CH}_3$  groups about the terminal C-C bond. A second kind of configuration isomerism arises from *syn-anti* flip-flop change about a C-C bond in a n-alkane chain such as in sodium n-butyrate



Researches are still in hand to determine which of these transformations may be operative in the solid state. A sur-



prising gap in our knowledge is that *x-ray crystallographic studies* on alkali salts of short chain carboxylic acids are practically unknown, particularly near their first melting points. At the first melting point, it is clear that organic ionic liquids of peculiar nature are found. Entropies of melting are of the order of only 3 eu in characteristic examples, pointing to positional disordering at Tf, but otherwise fairly close similarity between crystal packing and ion packing in the melts above Tf.

One of the most dramatic ways of showing this is from the ratio of electrical conductivity  $K$  of crystal and melt at Tf. Values (Ref. 5) illustrate that in conventional ionic crystals such as alkali halides, the ratio  $K_{liq.}/K_s$  is high, owing to the much greater mobility of ions in the melt, than in the crystal lattice. But in organic ionic melts, this ratio is even lower than in the silver halides, which are well known for their exceptional high cation mobility. Further insight into transport mechanisms in these organic ionic melts is obtained from ratios of parameters for ionic movement, and for momentum transfer. Present evidence suggests that actual ionic conductivities of organic ionic melts are distinctly low, compared with inorganic ionic melts which might be expected to show similar values (Ref. 5). Between the first melting point Tf and the clearing point, Tcl, if a mesophase appears at all its structure seems to lie between that of the crystals, and the isotropic ionic melts formed above Tcl. (A plausible sketch of its structure is illustrated in Ref. 6). This conclusion is already evident from *x-ray powder photographs* of the crystals, compared with *x-ray diffraction photographs* from the mesophase and from the ionic melts. The mesophase is however tolerant of greater configurational optimisation, in the packing of n-alkane molecules, than are the crystals. This probably explains why a flexible n-alkane chain actually contracts, at Tf and between Tf and Tcl, in the case of *sodium*

*n. butyrate*. An iso-alkane chain as in sodium isovalerate is thermally much less compressible. Its long spacings show the unusual property of remaining practically independent of temperature, over the interval of 80° or more between  $T_f$  and  $T_{cl}$  (Ref. 6).

These remarkable states of matter intermediate between conventional crystals and conventional liquids are in a sense examples of the "plastic" crystals to which attention was drawn already some years ago by TIMMERMANS. However, the examples previously known (cf. Ref. 1 UBBELOHDE 1965) were molecular crystals in which the forces between molecules are only comparatively weak. In molecular crystals interaction potentials  $\epsilon/kT$  seldom exceed 2 or 3. In organic ionic melt mesophases, on the other hand, intermolecular forces are strong, of the order of primary interionic forces. This profoundly affects mechanical and transport properties of the present group of "liquid" crystals. It probably explains why an elastic limit is observed at all, even though this is very low.

In conclusion, some guide lines may usefully be given about the properties of organic ionic melts as solvents. Although exploration of the solvent power of liquids with such a remarkable structure has only begun, some leading comments can already be made about ways in which they appear to be highly distinctive.

As has already been mentioned, when the ratio of charge/atom is high, as in the organic salts mainly studied so far, the electrostriction is high. This has important consequences for the properties of these liquids as solvents.

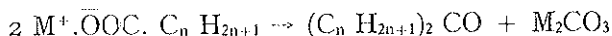
- 1) Their surface tensions may be expected to be large. Not many measurements are available to date, but the order of magnitude is similar to that of inorganic salts of low melting point.

TABLE I — *Surface tension dyne/cm for Potassium Salts at Tf*

	Tf°C	$\sigma$
F <sup>-</sup>	846	142
Cl <sup>-</sup>	770	97
Br <sup>-</sup>	730	89
I <sup>-</sup>	686	81
NO <sub>3</sub> <sup>-</sup>	400 d	113
CNS <sup>-</sup>	175	102
ClO <sub>3</sub> <sup>-</sup>	368	81
Cr <sub>2</sub> O <sub>7</sub> <sup>-</sup>	397	129

- 2) Neutral molecules would not be expected to show a high solubility, if this involves doing work against strong electrostatic forces. Molecules with strong dipoles and high polarisabilities should however show some exceptions. Measurements to date have not gone far enough to obtain quantitative values. In molten alkali nitrates solubilities of H<sub>2</sub>O near Tf are about 10<sup>-4</sup> moles/mole. Ionic species should on the other hand be fairly soluble. Again no quantitative information is yet available.
- 3) When these liquids are used as solvents in which to carry out reactions, strong neutral salt effects may be expected. The course of organic rearrangements when strongly influenced by local electrostatic fields may be profoundly modified in certain cases by such fields exerted at critical regions of a molecular skeleton.
- 4) Even if neutral molecules are not very soluble in these molten salts, they may be expected to sorb at the melt/gas interface. Systems in which the surface is deliberately enlarged, as in fluidised beds, may be necessary to reveal this effect. (Ref. 2).

At present, investigations are in hand on the course of organic decompositions of these salts, above the cracking temperatures. From the distribution of the molecular products, it is already clear that the classical ketone formation



occurs to only a small % of the whole — say 15 — 20%. Examination of other products points to the primary formation of free radicals, leading to many other species, including some of enhanced molecular weight, and tars.

I look forward to many developments in the chemistry as well as in the chemical physics of these interesting liquids.

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