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The liquid-crystalline state of salt melts containing organic ions

T A Mirnaya, V D Prisyazhnyi, V A Shcherbakov
Institute of General and Inorganic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

ABSTRACT. The present review deals with the latest achievements in the chemistry of ionic melts and liquid crystals (LC). New liquid crystals, formed by salt melts containing organic ions, have been described. The characteristics of their thermodynamic and transport behaviour, structure, and optical properties have been examined. The part played by electrostatic interactions and the parameters of the cations and anions in the stabilisation of the ionic mesophase has been demonstrated. The dependence of the production of liquid crystals in binary salt mesogenic systems on the nature of the interionic interactions has been analysed. The possible practical applications of this new class of liquid crystals have been discussed.

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I. Introduction

The most remarkable of the states of aggregation of matter, namely the liquid-crystalline state, is produced as a result of the specific breakdown of the crystal lattice on fusion (thermotropic LC) or solution (lyotropic LC) of a mesogenic substance.

The basic problem in the chemistry of liquid crystals is to determine which characteristics of the structure of the molecules of mesogens and their interactions determine the existence of the mesomorphic phase. Ionic liquid-crystalline melts, in which the principal role in the stabilisation of the liquid-crystalline state is played by the electrostatic factor,[1] are of particular interest in this connection.

The term melt is used to describe that part of the range of the liquid state of matter which can be described by the quasi-crystalline approach.[1,2] The structure and properties of salt melts consisting of simple ions have been studied in detail. They can be regarded as unique model systems, but the intensive study of melts containing monatomic ions has been stimulated not only by the possibility of carrying out simple experiments and the unambiguous interpretation of the results, but also by their extensive practical application.[2,3] Physical chemists have recently begun to study salt melts containing polyatomic ions. This has been due not only to the necessity of developing the theory of the liquid state but also to a number of technological requirements of modern industry. Research workers have been attracted by the low melting points, the ease of formation of salt glasses, and other properties of melts containing complex ions.[4–6]

Until recently, mainly inorganic salt melts were studied although organic salts provide a much wider and more varied range of materials for study and application. Since the shape and size of the repulsion envelope of the organic ion,† and the magnitude and distribution of the density of the Coulombic charge on it, can be easily varied, organic salt melts make it possible to obtain liquids with different inter-particle interactions, with expected and sometimes unusual properties.

The main obstacle to the extensive study and application of organic salt melts has been their low thermal stability. The instability of salt melts is both "internal", determined by the energy of the interatomic bonds within the ion, and "external", determined by the perturbing influence of impurity ions, molecules, and atoms.[4]

In most cases, the instability of organic ionic melts is "external", so that it can be avoided. Ubbelohde and co-workers[7,8] determined various impurities influencing the stability of melts containing organic ions, and formulated the requirements to be satisfied in the synthesis and study of these salts. Thus the basic conditions for working with molten organic salts include the absence from the melt of molecular or atomic oxygen and impurity transition metal ions and OH^- ions.

Thorough precautions in experiments with organic salt melts have made it possible to accumulate fairly extensive data on their physicochemical properties.[9–12]

Melts formed by the salts of n-alkanoic acids have been studied most systematically. Many representatives of this class of salt show unique properties. Thus in a definite temperature range, from the melting point (T_f) to the clearing temperature of the mesophase (T_{cl}), most of them exist in a viscous optically anisotropic state completely analogous to liquid crystals.[13]

A liquid crystal is a liquid with a constant anisotropy of the physical properties, having one-dimensional (nematic, cholesteric) or two-dimensional (smectic) order in space.

Liquid crystals play an important role in present-day science and technology.[14–27] Considerable interest is shown in all new data on liquid-crystalline substances, particularly data refuting the previously accepted view that the ability to form liquid crystals or mesophases

†The repulsion envelope of a polyatomic ion is the surface extending round the spheres of repulsion of the outer atoms in the complex ion; the radius of the sphere of repulsion of an atom, according to Ubbelohde, is equal to its crystal-chemical radius for the given type of bond and coordination (see the bibliography in Ubbelohde's book[1]).

is shown only by complex organic molecules with clearly defined anisometry.[14,15]

In fact, mesogens (that is substances forming liquid crystals or mesophases) are most frequently long rod-shaped or cylindrical, and also disc-shaped, molecules. At an early date, however, Frederiks,[16] one of the founders of the physics of liquid crystals, warned against overestimation of the part played by the anisometry of mesogens: "... since there are known cases of liquids with long molecules which do not form an anisotropic liquid phase, a comparatively elongated molecule is undoubtedly not a sufficient condition for the existence of an anisotropic phase. In fact, it cannot even be stated that this is a necessary condition".

Mesogenic substances with non-traditional structure and molecular shape, such as organic and inorganic compounds with ionic structures, are now increasingly encountered among liquid crystals.[1,13,20,21] These mesogens are extending the range of existence of mesogenic substances from organic into inorganic chemistry.

The liquid-crystalline properties of salts of carboxylic acids were detected as early as 1910 by Vorlaender on fusion of the long-chain homologues of soaps.[14] The mesophases of these salts are similar to liquid soaps, and by analogy were called smectic, from the Greek work "smektos"—soap-like. It was later found that the smectic form of liquid crystals is often encountered in substances of other (non-salt-forming) classes. Having given their name to the type of liquid-crystalline system showing two-dimensional order, however, the carboxylic acid salt mesophases themselves subsequently attracted practically no attention from research workers for many decades. Many aspects of the structure of the mesophases and the mechanism of fusion of the salts of the higher homologues of aliphatic acids became clear only after the work of Vold and co-workers[28,29] and Skoulios and co-workers.[30–33]

The liquid crystals formed by soaps show no distinctive features compared with smectic liquid crystals of other types, and show the same regularities; their molecules have clearly defined anisometry (the length to width ratio is greater than 5) and have a constant dipole at right angles to the long axis of the molecule.[14]

Ubbelohde's discovery[34] of the liquid-crystalline properties of the salts of the lower homologues of the alkanoic acids (from propanoic to octanoic) was unexpected and even sensational.

Table 1. Characteristics of the polyatomic anions of various mesogenic and non-mesogenic salts.[8]

Anion	Radius of repulsion envelope, Å	Charge/(number of atoms) ratio
SCN^-	2.20	1:3
NO_3^-	2.32	1:4
ClO_4^-	2.36	1:5
$CH_3CO_2^-$	2.60	1:7
$C_2H_5CO_2^-$	2.82	1:10
$n\text{-}C_3H_7CO_2^-$	3.04	1:13
$iso\text{-}C_4H_9CO_2^-$	3.28	1:16

Firstly, the particles making up these mesophases are quasi-globular ions: inorganic cations and carboxylate anions, whose length to width ratio does not exceed 2. Thus the principal geometric requirement satisfied by the particles of all previously known mesogenic substances[14] is not satisfied in this case.

Secondly, in contrast to the classic liquid crystals formed by electrically neutral molecules, the salt mesophases have a high ratio of the electrostatic charge to the total number of atoms. Moreover, the radii of the repulsion envelopes of the carboxylate anions of the group of salts being considered differ little from those of the polyatomic anions of inorganic non-mesogenic salts (Table 1). Thus salt mesophases are anisotropic ionic melts.

Thirdly, in most cases there is a marked difference in the radii of the repulsion envelopes of the cations and the carboxylate anions, that is $r_c/r_a < 1$ (Table 2). By analogy with inorganic salts, this ratio of the dimensions of the cation and the anion should favour the stepwise positional ordering of first the cation sub-lattice and then the anion sub-lattice of the crystal, and hence lead to the existence of a highly conducting solid phase (solid electrolyte).

Table 2. Ratio of the radii of the cation and the anion and the difference in the specific conductance of the melt and the crystal at T_f for non-mesogenic salts and T_{cl} for mesogenic salts.[8]

Salt	r_c/r_a	γ_l/γ_s	Characteristic of thermal behaviour
AgCl	0.62	30	solid electrolyte
AgBr	0.57	20	ditto
$C_2H_5CO_2Na$	0.35	13	mesogenic salt
$iso\text{-}C_4H_9CO_2Na$	0.30	8	ditto
$n\text{-}C_3H_7CO_2Na$	0.32	—	»

These facts, together with electrical conductivity data (Table 2), led Ubbelohde[8] to suggest that the mesophases of the salts of the lower carboxylic acids are not true liquids but highly plastic solid forms in which only the anions are organised in a crystal lattice, while the cation sub-lattice is disordered. Measurements of the shearing stresses showed unambiguously,[35] however, that salt mesophases are true liquids throughout the temperature range of their existence from T_f to T_{cl}, and that they are liquids with constant anisotropy of the physical properties. Similar anisotropic melts with the structure of the smectic form of type A were subsequently detected among salts of aromatic acids and alkali metals[36] and the lower homologues of n-alkylammonium halides.[37]

Ionic anisotropic melts have been called ionic liquid crystals (ILC). They could be defined as thermodynamically equilibrium liquids with constant anisotropy of the physical properties, consisting of oppositely charged ions. The basic structural unit of ILC, in contrast to molecular LC, is a mesogen ion, and not a mesogen molecule. Since the existence of a mesophase requires clearly defined anisotropy of the inter-particle interactions,[15] it follows that in molecular liquid crystals, in which the predominant intermolecular interaction is van der Waals interaction, an anisotropic shape is a necessary characteristic of the mesogen molecule, whereas in ILC, in which the predominant inter-particle interaction is electrostatic, the necessary characteristic of the mesogen ion should be the anisotropy of the distribution of the Coulombic charge, and the geometry of the ion is now not the decisive factor.

Table 3. Parameters of the fusion and clearing of non-mesomorphic and mesomorphic salts and classic LC.

Compound	T_f, K	T_{cl}, K	ΔH_f, kJ mol^{-1}	ΔH_{cl}, kJ mol^{-1}	ΔS_f, J mol^{-1} K^{-1}	ΔS_{cl}, J mol^{-1} K^{-1}	$\Delta V_f/V_s$, %	$\Delta V_{cl}/V_{lc}$, %	$\Delta V^*/V_s$, %	Refs.
Non-mesomorphic salts										
$NaNO_3$	577		14.6		25.3		10.7			[1]
NaCl	1075		30.1		28.0		25.0			[1]
CH_3CO_2Na	603		17.9		29.7		3.9			[8]
Ionic liquid crystals										
n-$C_3H_7CO_2Na$	529	597	6.2	1.5	11.7	2.5	6.8	3.4	17.4	[8]
iso-$C_4H_9CO_2Na$	461	553	4.2	0.8	9.1	1.3	3.9	3.6	13.6	[8]
n-$C_4H_9CO_2Na$	408	631	10.9	2.0	21.8	3.2				[12]
n-$C_6H_{13}NH_3Cl$	490	526	6.6	2.2	13.4	4.2				[37]
n-$C_4H_9CO_2Tl$	455	487	5.4	3.0	12.1	6.3				[12]
n-$C_3H_7CO_2K$	626	677	10.8	5.0	17.3	7.4				[12]
Classic liquid crystals										
p-Azoxyanisole	391	409	29.4	0.6	75.3	1.4	11.0	0.4		[12, 27]
p-Azoxyphenetole	303	441	26.9	1.4	88.7	3.1	8.4	0.6		[14, 27]
Cholesteryl propionate	371	385	23.1	0.4	62.3	1.1				[23]
Sodium stearate	387	553	21.7	2.2	56.0	3.8				[12]
Cadmium myristate	374	400	43.0	1.6	115.0	4.0				[38]

Note. $\Delta V_f = V_m - V_s$, where V_m is the volume of the mesophase at T_f, and V_s the volume of the solid phase at T_f; $\Delta V_{cl} = V_l - V_{lc}$, where V_l is the volume of the isotropic melt at T_{cl}, and V_{lc} the volume of the mesophase at T_{cl}; $\Delta V^* = V_l - V_s$.

The properties of this new class of liquid crystal, the structural characteristics of typical representatives, and the relationship between the mesomorphism and the nature of the ionic components of the melt can now be considered.

II. The thermodynamic properties of ionic mesogens

The study of the thermodynamic functions of liquid crystals and the changes which they undergo in mesomorphic phase transformations is an important step in the determination of the nature of the inter-particle interactions and the mechanisms of the phase transformations. Most available data on the thermodynamic properties of organic salts have been fully dealt with in a review by Franzosini and Sanesi.[12] Nevertheless, the tendency of most salts with organic ions to form supercooled and metastable states complicates considerably the interpretation of the thermodynamic data obtained; a large number of ambiguous results and results which have not been reproduced have been published.

The temperatures of the phase transformations have been most fully studied; this applies to the homologous series of the alkanoates of the alkali metals, thallium, ammonium, various metals of the second main group of the periodic system, and various transition metals (zinc, cadmium, lead, manganese, etc.), and various salts of aromatic carboxylic acids.[12,36] The enthalpies and entropies of the fusion and clearing of the mesophase have been studied for the alkanoates of the alkali metals, thallium, and various transition metals, and for mono-substituted n-alkylammonium chlorides,[12,37–41] but a complete picture of the thermal change in the thermodynamic properties has been obtained for only two salts from the ILC group, sodium isovalerate and butyrate.

A comparative analysis of the parameters of the fusion and clearing of the mesophase (Table 3) for three groups of substance, namely non-mesogenic inorganic salts, ILC, and molecular LC, leads to several important conclusions.

1. Ionic mesogens have relatively low enthalpies of fusion, like molecular LC and salts without conformationally flexible chains.[42]

2. The values of ΔS_f for ionic mesogens are extremely low (9–20 J mol^{-1} K^{-1}) compared with ΔS_f for molecular LC ($\sim$70 J mol^{-1} K^{-1}) and inorganic salts ($\sim$25 J mol^{-1} K^{-1}). They are often even lower than ΔS_f for the inert gases ($\sim$14 J mol^{-1} K^{-1}).

3. The values of ΔH_{cl} and ΔS_{cl} for ILC are of the same order of magnitude as for ordinary LC.

4. The values of ΔS_{Cl} for ILC are lower than ΔS_f by factors of 2–5.

5. The relative changes in volume in the fusion and clearing of ILC are approximately equal, whereas for molecular LC the relative change in volume at T_{cl} is smaller by an order of magnitude than that at T_f. The relative change in the volume of ionic mesogens in the transformation between the crystal and the isotropic melt via the mesophase ($\Delta V^*/V_s$, see Table 3) is of the same order of magnitude as the relative change in volume in the transformation between the crystal and the isotropic melt for ordinary inorganic salts.

The low enthalpy and entropy of fusion of ILC are indications of positional ordering, characteristic of a crystal containing quasi-spherical molecules consisting of a small number of atoms.[42] However, the fact that ΔS_f for ionic liquid crystals is often lower than the value 14 J mol^{-1} K^{-1} characteristic of the formation of simple positional defects apparently indicates cooperative positional disordering of the crystal lattice at T_f.[42]

In the fusion of ionic mesogens, the features of the cooperative positional disordering may be that each group of neighbouring ions and their component atoms are displaced collectively from their equilibrium positions in the crystal, forming local structures or domains with liquid-crystalline ordering. If smectic ILC are formed on fusion, the arrangement of the ions in these domains should preserve the long-range orientational order combined with translational periodicity in two dimensions. An indirect thermodynamic indication of the preservation of partial positional

order in ILC is the extremely marked increase in volume of T_{cl} for sodium butyrate and isovalerate, comparable with the change in volume on fusion.

A characteristic feature of the ILC studied is the absence of mesomorphic polymorphism (only one LC phase exists).

The influence of the length of the aliphatic chain of the anion or cation on the thermodynamics of the mesomorphic state has been studied for the homologous series of n-alkanoates of the alkali metals, thallium, and various transition metals, and for mono-substituted n-alkylammonium chlorides.[12,36-41]

Fig. 1 gives the dependence of the thermodynamic parameters of the phase transformations (T_{cl}, ΔS_f, ΔS_{cl}) on the length of the aliphatic chain of the mesogen ion (n) in various homologous series of ILC. Analysis of these data shows that:

1) there is an odd–even alternation of the thermodynamic parameters of the transformation betweeen the ILC and the isotropic melt, which is smoothed out with increase in the length of the alkyl chain n;

2) the dependence of T_{cl} on n shows a flat maximum at n = 5–8;

3) there is no simple dependence of ΔS_f on n;

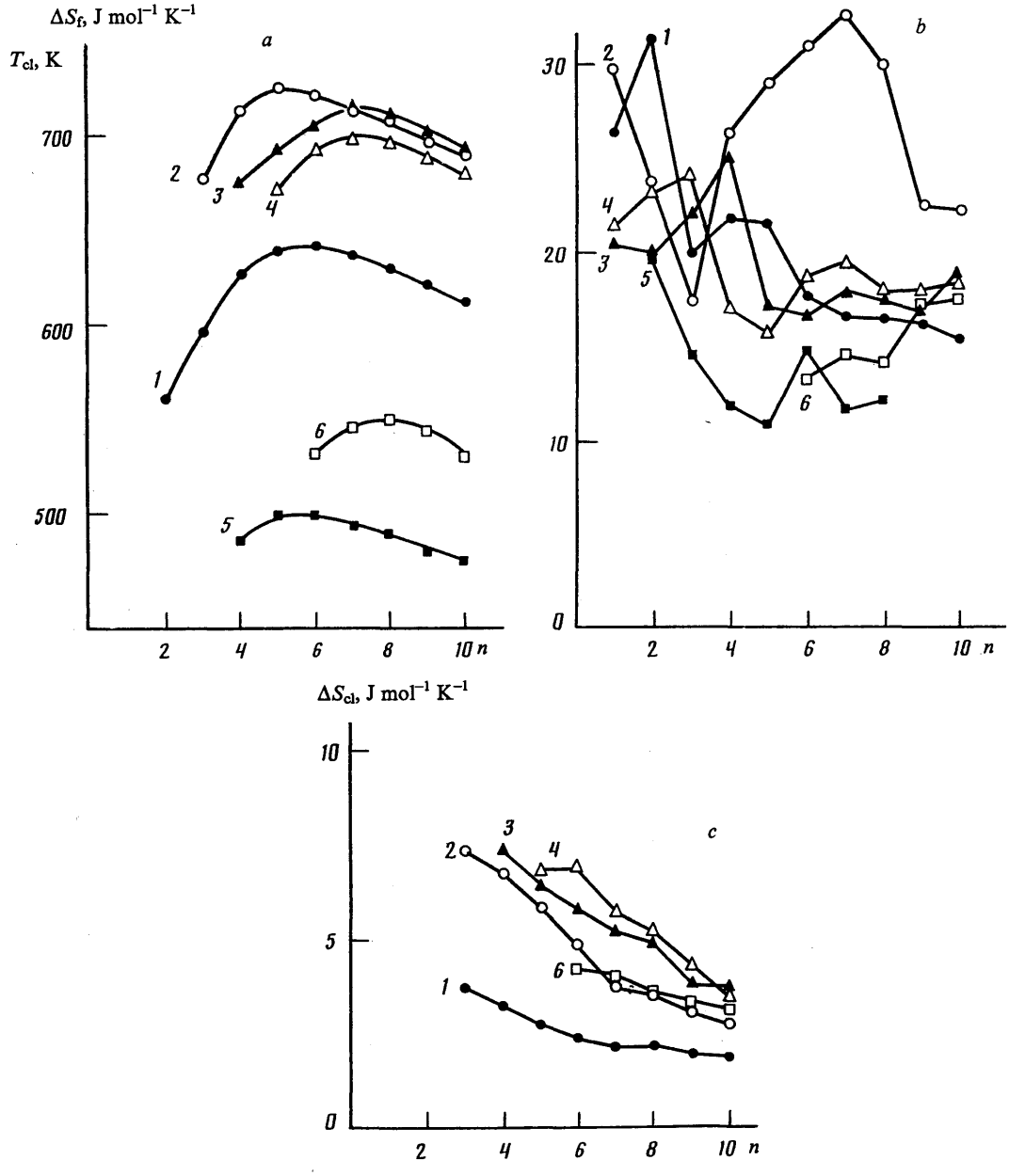


Figure 1. Dependence of the clearing temperature (*a*), the entropy of fusion (*b*), and the entropy of clearing (*c*) of the mesophase on the number of carbon atoms in the aliphatic chain of the mesogen ion for homologous series of salts: *1*, $C_nH_{2n+1}CO_2Na$; *2*, $C_nH_{2n+1}CO_2K$; *3*, $C_nH_{2n+1}CO_2Rb$; *4*, $C_nH_{2n+1}CO_2Cs$; *5*, $C_nH_{2n+1}CO_2Tl$; *6*, $C_nH_{2n+1}NH_3Cl$.[12,37]

4) ΔS_{cl} and ΔH_{cl} decrease regularly with increase in the length of the alkyl chain of the mesogen ion.

These regularities are qualitatively the same as the general regularities in the thermodynamic behaviour of known homologous series of classic smectic liquid crystals,[43] since in all cases a decisive role is played by the dimensions of the alkyl group. Thus the odd–even alternation is a consequence of the difference between the contributions of an odd and an even carbon atom to the length and polarisability of the hydrocarbon chain of the ion or molecule.

The decrease in ΔS_{Cl} and ΔH_{Cl} with increase in n may be due either to a relative increase in the ordering of the isotropic melt or to a decrease in the ordering of the mesophase close to T_{cl}. X-Ray diffraction data for thallium alkanoates[44] indicate an increase in the ordering of the alkane chains of the anions in the mesophase close to T_{cl} with increase in n.

The few published studies of the total change in the entropy of organic salts on going from the crystalline state at 0 K or 298 K to the isotropic liquid state indicate a definite increase in $\Sigma\Delta S$ with increase in the length of the alkyl group.[40] This increase in the total entropy in homologous series of flexible molecules is due predominantly to the increase in the configurational component of the entropy. Thus for the long-chain homologues of alkanoates and alkylammonium salts, the main mechanism of fusion involves disordering of the alkane chains.

For the homologues of salts with short alkyl groups ($n \leqslant 7$), in which the predominant interionic interaction is electrostatic, the mechanism of fusion is apparently slightly different, and will be discussed later in relation to structural data for ILC. The fact that the electrostatic interaction makes the principal contribution to the total energy of stabilisation of the ionic mesophase explains the high sensitivity of the thermal stability of ILC to the nature of the component ions. Thus Fig. 1*a* shows that the LC state is not realised in lithium carboxylates; in the homologous series of the salts of the other alkali metals, the existence of the mesophase depends on the length of the alkyl group; for example, the salts form a mesophase at $n \geqslant 2$ for sodium, at $n \geqslant 3$ for potassium, at $n \geqslant 4$ for rubidium, and at $n \geqslant 5$ for caesium.

Parameters of the cations and the carboxylate anions making up the salt mesophase, namely the polarising power of the cations z_c/r_c^2 and the ratio of the radii of the cations and anions r_c/r_a, have been analysed.[45] This analysis made it possible to formulate the following empirical relationship: an ionic mesophase can exist in molten salts of alkanoic acids if

$$z_c/r_c^2 \leqslant 1.05 \text{ and } r_c/r_a \leqslant 0.4. \quad (1)$$

This relationship is naturally approximate, but it applies satisfactorily to 12 homologous series of monovalent and divalent metal n-alkanoates.[45] The main value of the expressions (1) is that they show the relationship between the possible production of LC ordering in a salt melt and the nature of cations and anions.

III. The structure and optical properties of ionic mesogens

Although the structure of ILC has not yet been established in sufficient detail, a model of the structure of the ionic mesophase has now been proposed, based on the results of polarisation, X-ray diffraction, and NMR studies of sodium butyrate and isovalerate,[46–48] potassium hexanoate,[49] thallium and sodium n-alkanoates,[44,50–52] and sodium methylpentanoates.[53]

Optical polarisation studies have established unambiguously that the mesophases of the salts of lower alkanoic acids are homogeneous liquid-crystalline phases of the smectic A type;[44,48] the existence of only one smectic phase throughout the temperature range of stability of the ILC is also indicated by the ^{23}Na NMR spectra of sodium alkanoates. Thus in all the sodium salts studied, the quadrupole coupling constant, calculated from the first-order quadrupole splitting of the ^{23}Na NMR spectrum, shows a smooth temperature dependence.[47,51,53]

The basic principle of the arrangement of the ions of the salts of carboxylic acids in the condensed state is determined by the combination of the strong electrostatic interactions of the cations and the anions and the weak van der Waals interactions of the organic chains of the anions. The ionic groups should be in contact with one another, but in such a way that the bulky non-polar organic parts of the carboxylate anions are close-packed. This condition is satisfied by electrostatic "sandwich" layers of metal cations, situated close to the negatively charged carboxyl groups of the alkanoate anions (Fig. 2). This layer segregation of the ions practically excludes the unfavourable interaction of the Coulombic charges with the aliphatic chains, whose dielectric constants are low

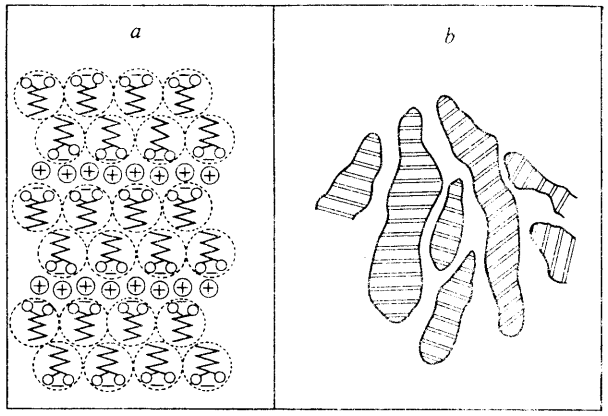


Figure 2. Schematic representation of the layer structure of an ionic liquid crystal (from published data[46–48]): *a*, relative arrangement of the carboxylate anions and the metal cations in LC domains; *b*, possible preferred orientation of the cation–anion layers forming the domains in the ionic mesophase.

Thus in a liquid-crystalline carboxylate melt, the first coordination sphere of the cation contains only anions, in accordance with Temkin's model of the structure of ionic melts,[42] whereas the first coordination sphere of the anion contains both cations and anions. The energy of the Coulombic interaction of two adjacent cations in the same electrostatic layer will naturally be much greater than the energy of this interaction between the cations belonging to two neighbouring electrostatic "sandwiches".

The arrangement of the electrostatic "sandwiches" in space may be different in different salts, since the packing of the ions is determined by the Coulombic forces acting both [illegible] sandwich"

and between neighbouring "sandwiches". The magnitude of these forces should apparently depend both on the nature of the metal cations and on the size of the hydrocarbon chain of the carboxylate anion, shielding the electrostatic interactions between neighbouring "sandwiches". In ionic liquid-crystalline melts, the Coulombic interactions involve more than ten thousand ions,[8] and this facilitates their mutual ordering. Thus the strength of the electrostatic interactions should also influence the size of the LC domains in salt melts, and the parameters of the order in the ILC.

Optical polarisation studies of lower sodium carboxylates[48] have shown that in the series of homologues from sodium butyrate to sodium heptanoate there is a considerable change in the size of the LC domains (Table 4). The size of the domains decreases with a relative increase in the organic part of the carboxylate anion in the series of related compounds, reflecting the increase in the shielding of the electrostatic field. No obvious simple criteria have yet been found, however, for estimating the absolute dimensions of the LC domains in other homologous series. Thus no complete explanation has yet been given for the marked increase (by a factor of ~ 25) in the size of the domain on going from sodium butyrate to sodium isovalerate, which is similar in many respects but which has a lower mesophase thermal stability (Table 4).

Table 4. Size of the LC domain and the thermal stability of the ionic mesophase of sodium carboxylates.

Salt	Size of domain $\times$ 10^6, m (Ref.48)	T_{cl}, K (Ref.12)
iso-$C_4H_9CO_2Na$	500	556
n-$C_3H_7CO_2Na$	20	597
n-$C_4H_9CO_2Na$	15	626
n-$C_5H_{11}CO_2Na$	10	631
n-$C_6H_{13}CO_2Na$	7	634

A characteristic feature of salt mesogens is the preservation of the long lattice constants of the crystals (d) on fusion. Thus non-branched sodium and thallium alkanoates[44,46] show an abrupt decrease in d at the melting point, and further increase in temperature leads to an even greater gradual compression of the cation–anion layers. Sodium isovalerate at the melting point shows a sharp increase in the long period, which in the mesophase remains constant and independent of temperature (Fig. 3).

According to Duruz and Ubbelohde,[46] the difference in the thermal behaviour of the long periods d of the mesophases of sodium butyrate and isovalerate is due to a difference in the thermal flexibility of the two alkane chains and the difference in their reaction to increasing torsional thermal vibrations with increase in temperature. Using data on the molar volume V, the authors cited[46] estimated the area occupied by the electrostatic cation–anion layers ($A = V/d$) in sodium butyrate and isovalerate, with the approximate assumption that these layers are packed in columns with no spaces between them. It was found that if one imagines cylinders being cut from the sequence of layers formed by identical numbers of cations and anions in the structures of the two salts, then at a temperature slightly below T_f the butyrate cylinder will be higher and will have a smaller basal area than the isovalerate cylinder. At T_f, the area of the base of the butyrate cylinder increases abruptly (by $\sim 8\%$), and its length decreases (by $\sim 1.6\%$). For the isovalerate cylinder, however, the length increases abruptly (by $\sim 7\%$), and the area of the base decreases (by $\sim 2.2\%$). Further increase in temperature from T_f to T_{cl} leads to a gradual increase in the area of the base of both cylinders, while the length of the isovalerate cylinder remains constant and that of the butyrate cylinder gradually decreases.

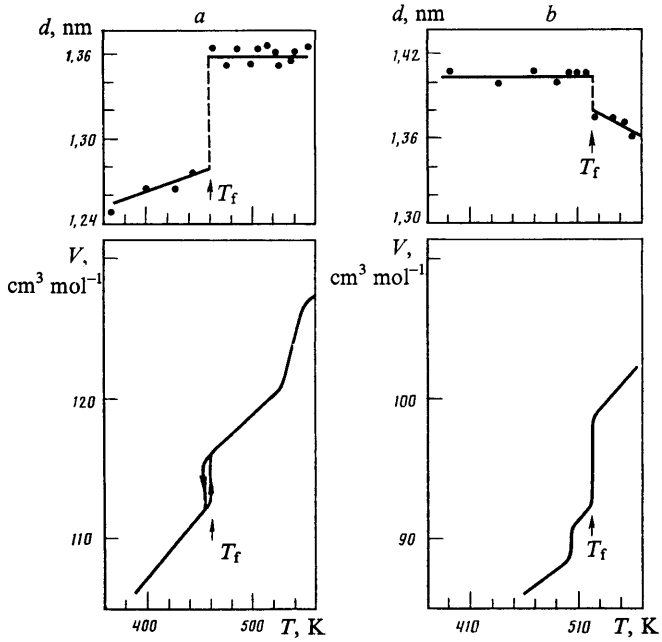


Figure 3. Temperature dependence of the lattice parameter d and molar volume V in the crystal and mesophase of sodium isovalerate (a) and butyrate (b).[46]

Thus a common feature of the thermal behaviour of salt mesophases containing organic ions is that the packing of the ions is loosened in a direction parallel to the plane of the electrostatic layers. In the direction at right angles to the plane of the smectic layers, however, the strong electrostatic attraction tends to compress the layers. The greater the possibility of a configurational change in the alkane chains of the mesogen ion, the greater the relative compression of the cation–anion layers in the mesophase. Thus for the homologous thallium n-alkanoates, the relative compression of the layers in the mesophase β ($\beta = (2L - d)/2L$, where L is the length of the carboxylate anion) is directly proportional to the length of the alkane chain of the anion n.[44] When a configurational change in the alkane chain of the anion is hindered, as in sodium isovalerate,[46] the inter-layer distance in the mesophase remains practically unchanged with increase in temperature.

The results of structural and thermodynamic studies of ILC indicate that the mechanism of the fusion of ionic mesogens involves cooperative positional disordering of the crystal lattice of the salt, accompanied by configurational ordering of the alkane chains of the

mesogen ions, and at T_{cl} the electrostatic layers probably undergo positional and other types of ordering.

A molecular model of the structure of ILC, essentially quasicrystalline, was first proposed by Ubbelohde and Duruz,[46] and was later developed in more detail from the results of polarisation and NMR studies by Jonas and co-workers.[47,48,51–53] According to this model, the structure of smectic ILC is described by a space filled by sequences of parallel cation–anion layers forming LC domains (see Fig. 2). These domains may take all possible configurations and be subjected to the orienting influence of different fields. In the opinion of Jonas and co-workers,[52] the organic chains of the anions in the LC domains either rotate "in a cone" with angle of 35° about the normal to the cation–anion layer or are ordered along the normal to the charged layer, but undergo *trans–gauche* isomerisation. Local structure formation, corresponding to the isotropically oriented layer domains, are preserved in the isotropic melts.[53] The type of ordering of the carboxylate anions in the layers may apparently be different for different salts, and, as noted by Jonas and co-workers,[53] is determined by the size and structure of the crystal lattice defects, and also by the structure of the carboxylate anions. No change in the size of the domains in carboxylate ILC with change in temperature was observed.[48]

In contrast to the above quasi-crystalline model of the structure of the mesophases of molten salts of alkanoic acids, an attempt has been made to describe them using the so-called R-theory of aqueous amphiphilic mesophases.[39] The basic postulates of this theory were analysed by Winsor.[24] The R-theory describes the structure of the mesophases on the basis of the balance between intermolecular forces which tend on the one hand to make the amphiphilic layer of molecules convex with respect to the lypophilic environment, and on the other hand to make it convex with respect to the polar medium. The postulates of this theory can obviously be applied satisfactorily only to systems with a low density of Coulombic charges, for example to the molten salts of the higher homologues of n-alkanoic acids. In ILC, where powerful Coulombic forces operate, this balance of intermolecular forces apparently does not play a decisive role in the stabilisation of the LC order.

An important characteristic of LC is the degree of long-range orientational order or the order parameter S, introduced by Tsvetkov[25] and defined by the equation:

$$S = {}^1/_2(3\overline{\cos^2\theta} - 1),$$

where θ is the angle between the direction of the director‡ of the LC and the long axis of the molecule, and $\cos^2\theta$ is the value obtained by averaging over all orientations of the molecules. In an ideal crystal, $S = 1$, and in an isotropic liquid, $S = 0$. For molecular LC, the maximum value of S in nematic crystals is 0.6–0.8, and the value for smectic crystals reaches 0.9 and changes little with change in temperature.

In the ionic smectic melts of sodium isovalerate and n-alkanoates, the order parameter is much smaller than in molecular smectics, and depends on temperature. Thus with increase in temperature from T_f to T_{cl}, the value of S changes from 0.65 to 0.1 in sodium isovalerate and from 0.38 to 0.1 in sodium butyrate.[47,48]

‡The director of the LC is the unit vector which indicates the direction of the preferred orientation of the long molecular axes, coinciding with the optical axis of the LC (for more details see Pikin's book[26]).

A characteristic feature of ILC is negative birefringence.[48,50] Pelzl and Sackmann[50] studied the birefringence of the LC phases formed by homologous thallium n-alkanoates. They established that the lower homologues (n = 5–9) show negative birefringence, which decreases with increase in the length of the alkane chain and with decrease in the temperature of the mesophase. For the middle homologues (n = 10–12), the sign of the birefringence changes from negative to positive. The higher homologues ($n > 12$) show only positive birefringence, which increases with increase in the length of the alkane chain of the anion and with decrease in the temperature of the mesophase. The difference between the optical behaviour of the lower and higher homologues of the n-alkanoates can be attributed to the characteristics of the structures of their smectic mesophases.

The magnitude and sign of the birefringence of LC are determined by the magnitude of the anisotropy of the polarisability. For salt mesophases, the anisotropy of the polarisability is determined by two structural factors: 1) the monoaxial layer arrangement of the polar groups, and 2) the group and mutually consistent configuration of the alkane chains between the cation–anion planes. The first factor determines the negative anisotropy of the polarisability, that is the polarisability in a direction perpendicular to the optical axis ($\alpha_\perp$), which is greater than the polarisability in a direction parallel to the optical axis ($\alpha_\parallel$), that is $(\alpha_\parallel - \alpha_\perp) < 0$, and the second factor determines the positive anisotropy of the polarisability, that is $(\alpha_\parallel - \alpha_\perp) > 0$.[50] In ILC, where the ratio of the charge to the number of atoms is high, the first factor predominates, so that negative birefringence is observed, whereas for the long-chain homologues of thallium alkanoates, the second factor is decisive, and positive birefringence is observed.[50]

As already noted, increase in the temperature of the mesophase of the salts of n-alkanoic acids leads to compression of the cation–anion layers and to loosening of the packing of the ions in a direction parallel to the cation–anion layers, and this leads to a decrease in $\alpha_\parallel$ and an increase in $\alpha_\perp$. Since the refractive index for the extraordinary ray n_e is directly proportional to $\alpha_\parallel$, and the refractive index for the ordinary ray n_o is directly proportional to $\alpha_\perp$, increase in temperature leads to an increase in the negative value of the birefringence $(n_e - n_o)$ for ILC, and to a decrease in its positive value for the LC phases of the higher homologues of thallium alkanoates. Thus the optical behaviour of ionic mesophases is described satisfactorily in terms of the above quasi-crystalline model of their structure.

IV. The transport properties of ionic mesophases

The transport properties of LC materials are very sensitive to their anisotropy and orientation. Unfortunately, for ILC there are practically no published data on completely oriented single-domain specimens, although these studies are necessary to establish the relationship between the dynamics and structure of the ionic mesophases.

Viscosity. ILC apparently have very high viscosities, since they are smectic forms (usually type A). Approximate data are available for only two mesophases, sodium butyrate and isovalerate.[12] Close to T_{cl}, the viscosity of both mesophases is ~10 Pa.s; on going to the isotropic melt, the viscosity decreases to ~0.04 Pa.s for sodium isovalerate and to ~0.01 Pa.s for sodium butyrate. Thus the viscosities of the isotropic melts of ionic mesogens are comparable with those of molten inorganic salts.[1,2,5]

Nuclear magnetic relaxation times and diffusion. Jonas, Bonekamp, and co-workers[47,51–54] have carried out NMR studies (^{1}H, ^{2}H, ^{23}Na) of the smectic mesophases of molten sodium carboxylates throughout the temperature range of stability of the LC phases. It was established that the mechanism of proton relaxation in the salt mesophase reduces to the self-diffusion of the anions and fluctuations in the ordering of their orientation; the first mechanism determines the frequency dispersion of the spin–lattice proton relaxation time T_1, and the second determines that of the spin–rotation relaxation time $T_{1\rho}$. The values of the self-diffusion coefficients D for the butyrate and isovalerate anions in the mesophase, estimated by the authors cited, are about 10^{-7} to 10^{-6} cm^2 s^{-1}, which coincides with the values predicted by theory for smectics of type A.[55]

The temperature dependence of the coefficients of self-diffusion of the anions in the mesophase and in an isotropic melt obey the Arrhenius law, with a break at T_{cl}. The NMR data can be used to estimate the averaged coefficient of three-dimensional diffusion.[54] It is assumed, however, that in smectic domains there is two-dimensional diffusion, which, according to the calculations,[54] is characterised by a value of D 1.5 times that measured by NMR. These differences in the absolute values of the diffusion coefficients, however, do not influence the estimation of the activation energy of diffusion, which has the values 37.7 kJ mol^{-1} and 37.2 kJ mol^{-1} for the butyrate and isovalerate anions respectively.

For sodium isovalerate, good agreement was established between the activation energies of viscosity and diffusion in the isotropic melt (50.6 kJ mol^{-1} and 48.1 kJ mol^{-1} respectively).

The absolute value of D calculated from the viscosity data using the Stokes–Einstein equation is smaller by two orders of magnitude than the values of D measured by NMR.[54] The explanation apparently is that the viscosity of the salt mesopahse is determined by slow interactions between the LC domains, whereas the rate of NMR relaxation reflects the rapid diffusion within domains of macroscopic dimensions.

The spin–lattice relaxation times T_1 (^{23}Na NMR) in the mesophases of molten sodium carboxylates increase regularly with increase in temperature, and have values of 10^{-4}–10^{-2} s. Because of the large difference in the dimensions of the carboxylate anion and the sodium cation, the correlation times (τ_c) for the fluctuations in the electric field gradient at the sodium cation, calculated by Bonekamp and co-workers,[47] reflect the fluctuations as a consequence of the diffusion of the sodium cation, and not the anion. The values of the activation energy for τ_c (16.7 kJ mol^{-1} for sodium butyrate and 32.3 kJ mol^{-1} for sodium isovalerate), obtained by Bonekamp and co-workers,[47] are much smaller than the values of the activation energy of diffusion of the anion. Thus the principal charge carrier in the ionic mesophases of molten carboxylates is the cation, and the conductivity in the mesophase of sodium butyrate should be higher than that in the mesophase of sodium isovalerate.

Electrical conductivity. A basic characteristic of the liquid-crystalline phases of salt melts is their intrinsic ionic conductivity.[8,56–59] In the isotropic melts of the carboxylates of monovalent and divalent metals, the activation energy of the electrical conductivity is not sensitive to change in the length of the alkane chain of the anion n.[57,58,60] At the same time, the absolute value of the electrical conductivity of the melt (measured at a temperature 5 K above T_{cl}) decreases regularly with increase in n.[57] These data indicate that the predominant charge carriers in carboxylate melts are the metal cations. This is also indicated by the size of the ionic components and by the NMR relaxation data for the salt mesophases. In the isotropic melt–mesophase and mesophase–crystal transformations, there is an abrupt change in the electrical conductivity, and the magnitude of these sharp stepwise changes depends on the length of the alkane chain of the anion and is greatest for the lower homologues of the alkanoates.[56,57]

The values of the specific conductance of the ILC studied are 10^{-1}–10 S m^{-1}, but most published electrical conductivity data relate to multi-domain non-oriented LC specimens. The results obtained by Duruz and Ubbelohde,[61] and also by Meisel and co-workers,[56,57] indicate marked anisotropy of the electrical conductivity of ILC. Thus the electrical conductivity of the mesophase of sodium isovalerate, obtained by cooling the isotropic melt with the application of a magnetic field ($\sim$10 kG) perpendicular to the electrical field, was found to be twice that of the mesophase obtained by cooling the isotropic melt in the absence of a magnetic field.[61] It has been shown[57] that the electrical conductivity of thallium carboxylates is influenced by differences in the degree of orientation of the LC phase, obtained by applying mechanical shearing stresses to the mesophase or by producing it in the field of a varying temperature gradient.

The most convincing proof of the anisotropy of ion transport, however, was obtained by Meisel and co-workers,[57] who determined the electrical conductivity of a homeotropically oriented (smectic layers parallel to the supports) LC specimen of thallium laurate in two mutually perpendicular directions. According to their data, the electrical conductivity of the mesophase in a direction parallel to the smectic cation–anion layers was much greater than that in the perpendicular direction (by a factor of $\sim$3). The electrical conductivity along the cation–anion layers in the oriented single-domain salt mesophase was found to be even higher than in the isotropic melt at a higher temperature, and at the point corresponding to the change from the mesophase to the isotropic melt, a marked abrupt decrease in the electrical conductivity was observed. In the direction perpendicular to the smectic layers, however, the electrical conductivity in the mesophase was much lower than that in the isotropic melt, and on going from the mesophase to the isotropic melt the usual abrupt increase in conductivity was observed. These data, and the values of the activation energies of the electrical conductivity in the salt mesophase (in the case of isovalerate, 7.6 kJ mol^{-1} for the non-oriented mesophase and <4 kJ mol^{-1} for the oriented mesophase), lead to the following conclusions.[61]

1. Charge transfer in the salt mesophases apparently involves the movement of ions along channels in the electrostatic layers.
2. The barriers preventing this movement are due to changes in the local electrostatic potential, so that they are extremely low (<4 kJ mol^{-1}) and comparable with the barriers controlling the migration of the ions in aqueous electrolytes.
3. The less oriented the LC specimen, the higher the activation energy of the electrical conductivity, as a consequence of the additional barriers preventing the transfer of ions from one LC domain to another.

The fact that the electrical conductivity in the oriented single-domain mesophase in a direction parallel to the smectic layers is higher than that in the less viscous isotropically-liquid phase at a higher temperature is apparently due to the marked difference in the heights of the energy barriers controlling ion migration in these two phases (the activation energy of the electrical conductivity in the isotropic carboxylate melt is $\sim$28 kJ mol^{-1}).

The further study of the anisotropy of the electrical conductivity of oriented thin-layer single-domain ILC specimens will yield new data on the dynamics and structure of this unusual class of LC materials, which will be useful for their practical application.

V. Binary systems of ionic mesogens

As already noted, a characteristic of the ionic mesophase is that its stabilisation depends to a considerable extent on electrostatic factors. For salts of carboxylic acids, it follows from Fig. 1*a* and the empirical relationship (1) that a decisive role in the stabilisation of the mesophase is played by the size of the ions and the polarising power of the cation. The relationship between the nature of the interionic interactions in the salt melt and the stability of the mesophase is most clearly revealed in binary salt systems, in which the formation of mixed melts is accompanied by a change in the nature of the interionic interactions.[45]

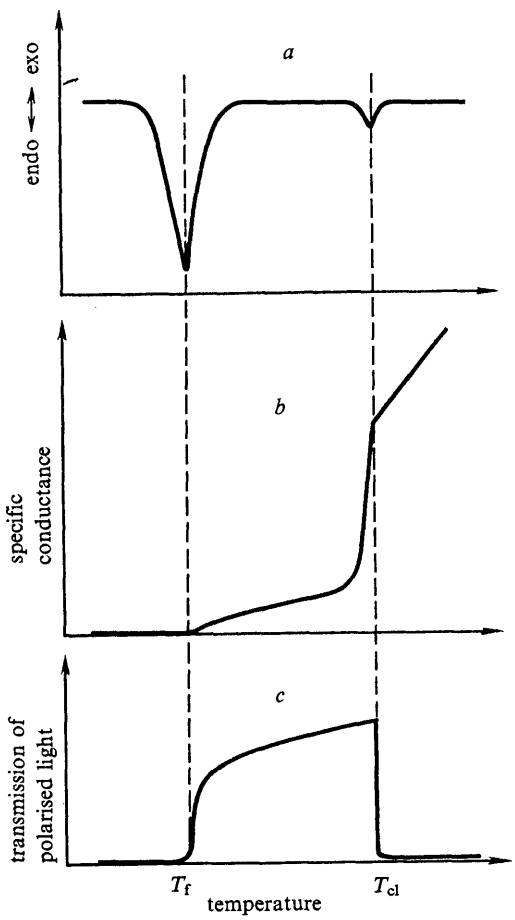


Figure 4. General form of the temperature dependence of the physicochemical properties of ionic mesogenic systems observed on heating; thermodynamic transitions from the crystal to the mesophase at T_f and from the mesophase to the isotropic melt at T_{cl}: *a*, differential thermal analysis curve; *b*, temperature dependence of the specific conductance; *c*, temperature dependence of the intensity of polarised light passed through a specimen of a salt LC system.[45]

In general, the formation of multicomponent systems provides interesting possibilities for extending the range of existence of the LC phase and even for the production of a mesophase in mixtures of components which are potentially mesogenic but individually non-mesomorphic, as a result of a marked decrease in T_{cl} for the system.[23] This last feature was first pointed out and confirmed experimentally in the early nineteen-huundreds by Bogoyavlenskii and Vinogradov.[62,63] Fifty years later, it was confirmed repeatedly by many workers.[23] The study of the stability of the mesophase with change in the ionic composition of the LC melt is of particular interest.

Mirnaya[45] studied the temperature range of existence of a binary salt mesophase by three independent methods: by studying the differential thermal analysis (DTA) curve, the temperature dependence of the specific conductance, and the transmission of polarised light by the LC specimen. Fig. 4 shows that all three methods made it possible to determine reliably the melting point of the crystal and the clearing temperature of the mesophase; DTA gives T_{cl} most accurately, and the other two methods are highly sensitive to the change from the isotropic liquid to the mesophase.

Unfortunately, very few binary salt mesogenic systems have been studied, and most of these contain the butyrate anion as the mesogen ion. All the salt LC systems studied can be provisionally divided into two groups.

The first group consists of systems in which continuous LC solutions are formed. They are characterised by a smooth change in T_{cl} with change in concentration, with positive or *S*-shaped deviations from additivity. These systems include binary mixtures of salts with a common mesogen anion and symmetrically charged cations, for example Na, K$|C_3H_7CO_2$; Na, Cs$|C_3H_7CO_2$; Cs, $NH_4|C_3H_7CO_2$; and Na, Tl$|C_3H_7CO_2$ (Fig. 5).

The second group consists of systems in which the formation of the mixed melt leads to marked destabilisation and disappearance of the mesophase. These systems include binary systems with a common mesogen anion and asymmetrically charged cations, for example K, Zn$|C_3H_7CO_2$; Na, Mg$|C_3H_7CO_2$, and also systems with a common cation, for example Na$|C_3H_7CO_2$, NO_3; Na$|C_3H_7SO_2$, SCN (Fig. 6).

In the ionic mesogenic systems studied, T_{cl} in most cases deviates considerably from additivity, whereas in molecular LC systems of two components without specific interaction, T_{cl} obeys the additivity law, that is it is a linear function of the composition:[14,24]

$$T_{cl} = T_1 + x_2(T_2 - T_1),$$

where T_1 and T_2 are the clearing temperatures of the mesophases of the individual components, and x_2 the mole fraction of the second component. In only a few cases are slight deviations from additivity ΔT_{cl} (mainly negative) observed, when the molar volumes of the components differ considerably. This behaviour of molecular LC mixtures is described satisfactorily by the statistical theory of Luckhurst and Humphries.[64]

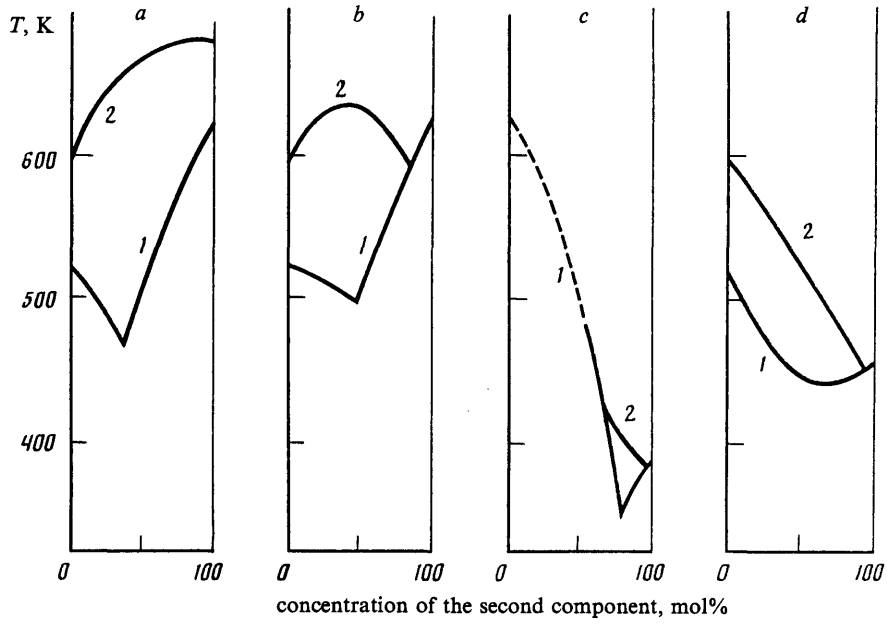


Figure 5. Melting point (*1*) and clearing temperature (*2*) of the mesophase in binary salt systems: *a*, $C_3H_7CO_2Na-C_3H_7CO_2K$; *b*, $C_3H_7CO_2Na$–$C_3H_7CO_2Cs$; *c*, $C_3H_7CO_2Cs$–$C_3H_7CO_2NH_4$; *d*, $C_3H_7CO_2Na$–$C_3H_7CO_2Tl$.[45]

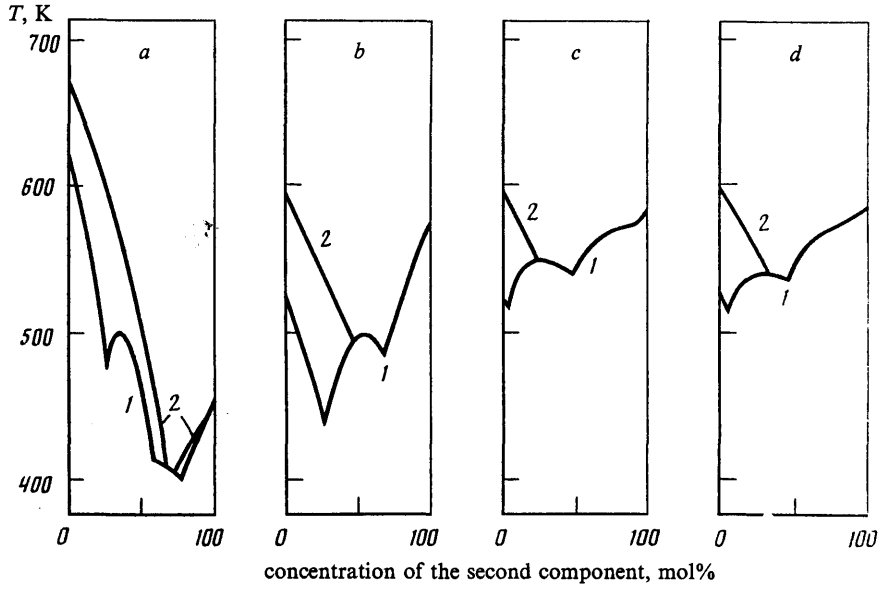


Figure 6. Melting point (*1*) and clearing temperature (*2*) of the mesophase in binary salt systems: *a*, $C_3H_7CO_2K$–$(C_3H_7CO_2)_2Zn$; *b*, $C_3H_7CO_2Na$–$(C_3H_7CO_2)_2Mg$; *c*, $C_3H_7CO_2Na$–$NaNO_3$; *d*, $C_3H_7CO_2Na$–NaSCN.[45]

The formation of continuous LC solutions in salt systems of the first group made it possible to estimate the thermal stability of a mixed ionic mesophase using the approximate model of ionic solid solutions.[65] This approach led to the following expression:

$$\Delta T_{cl} = 2x_1x_2E/R,$$

where R is the universal gas constant, and E the energy of stabilisation of the mesophase, which is the orientational component of the enthalpy of mixing of the system corresponding to one mole of the vapour of the interacting non-equivalent cations.

In systems in which one or both of the components containing the mesogen ion are individually non-mesomorphic, ΔT_{cl} was estimated using the values of the latent T_{cl}, determined by extrapolation.[45,66]

The value of E is extremely sensitive to the nature of the interionic interactions in the mesomorphic systems. Thus in the systems formed by alkali metal carboxylates with a common mesogen anion, for example Na, K|$C_3H_7CO_2$ or Na, Cs|C_3H7CO_2, where the predominant type of inter-particle interaction is the Coulombic interaction of the non-equivalent cations, $E > 0$. This leads to a unique characteristic of systems of this type, namely the marked positive deviation of T_{cl} from additivity, reaching several tens of degrees. The energy of stabilisation in these systems is practically independent of the concentration of the components, and shows a linear correlation with the parameter of the interionic interactions Δ^2 [$\Delta = (r_1 - r_2)/(r_1 + r_2)$, where r_1 and r_2 are the cation–anion distances in the individual components].[65] The authors cited[65] established the interesting fact that the stabilisation of the ionic mesophase in the binary system, is higher, the greater the difference in the sizes of the metal cations of the two salts.

For salt melts, the parameter of the interionic interactions determines the intensity of the enthalpy changes on formation of the mixed melt,[67] so that the stabilisation of the carboxylate mesophase takes place as a result of the enthalpy factor, that is the increase in the energy of the orientational interaction of the non-equivalent ions relative to the energy of their thermal motion.

Another type of binary mesogenic system in the first group corresponds to the systems formed by monovalent metal and ammonium carboxylates with a common mesogen anion, for example Ca, NH_4|$C_3H_7CO_2$ (see Fig. 5). A distinguishing feature of interionic interactions in these systems is the formation of hydrogen bonds (H-bonds) between the ammonium cations and the carboxylate anions. A linear change in E with change in concentration was established for systems of this type.[68] The relative increase in the concentration of the monovalent metal cation in the mixed melt leads to an increase in E, and a directly proportional relationship is observed between the value of E and the increase in the ^{1}H NMR chemical shift (δ) of the ammonium ion as a result of the formation of H-bonds in the system.[45]

Thus the energy of stabilisation of the mixed salt mesophase is higher, the greater the number of ions forming H-bonds in the melt, and the greater strength of these bonds.[45,68] Naturally, the formation of H-bonds in the salt melt will facilitate the production of LC order only if appreciable anisotropy of the electrostatic interactions is preserved or created in the system.

In the systems formed by ammonium and monovalent metal butyrates, the values of the energies of formation of the H-bonds and the stabilisation of the mesophase are determined by the nature of the metal cation. The strength of the H-bond between a carboxylate anion and the ammonium cation in a salt melt is a complex function of two parameters of the metal cation, namely its size and its polarising power.[69] Increase in the polarising power of the metal cation is accompanied by a decrease in the strength of the H-bond as a result of the decrease in the electron-donor power of the carboxyl group of the anion, and increase in the size of the metal cation is accompanied by an increase in the steric barriers preventing the formation of the H-bond. According to Mirnaya and co-workers,[68] in the salt mesophases studied the last factor predominates, and with increase in the size of the metal cations in the LC melt, the energy of stabilisation of the mesophase generally decreases.

The first group of salt mesogenic systems also includes the binary systems formed by thallium and alkali metal carboxylates with a common mesogen ion, for example Na, Tl|$C_3H_7CO_2$ (see Fig. 5). In these systems, one component, namely the thallium(I) carboxylate, provides a non-Coulombic component of the cation–anion bond, so that their behaviour is determined by both the Coulombic and the exchange repulsion interaction. In the presence of the strongly polarising lithium and sodium cations, the covalent character of the bond formed by the thallium cation with the counter-ion decreases, whereas in the presence of other alkali metal cations it increases, the increase being greater, the larger these cations.[70] The increase in the covalent character of the bond formed by the thallium cation with the butyrate anion in the salt mesomorphic melt is equivalent to an increase in the probability of formation in the melt of long-lived paired cation–anion associates, that is uncharged quasi-globular particles, which decrease the electrostatic stabilisation of the LC phase; E may then have negative values and actually determine the energy of destabilisation of the mesophase. It is this factor which apparently is responsible for the destabilisation of the ionic mesophase observed in the systems formed by thallium and alkali metal carboxylates,[45] since the stability of the mesophase decreases with increase in the size of the alkali metal cation (Fig. 7). With increase in the concentration of the alkali metal salts in systems of this type, stabilisation of the ionic mesophase takes place in addition to its destabilisation. The stabilisation is due to an increase in the anisotropy of the electrostatic interactions with increase in the total number of Coulombic charges, and also to the decrease in the total energy of the system. At definite component ratios in the systems formed by thallium and alkali metal carboxylates, the stabilisation of the salt mesophase predominates, so that the overall concentration dependence of E is S-shaped (Fig. 7).

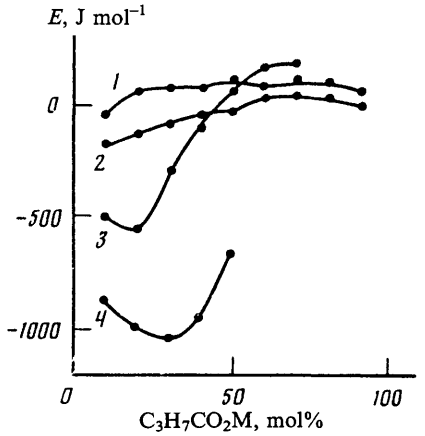


Figure 7. Concentration dependence of the energy of stabilisation of the ionic mesophase in the binary systems $C_3H_7CO_2Tl$–$C_3H_7CO_2M$, where M = Na (*1*), K (*2*), Rb (*3*), Cs (*4*).[45]

Unlike the mesogenic systems of the first group, where the formation of the mixed mesophase in most cases stabilises the LC phase, the mesogenic systems of the second group are characterised by breakdown of the LC order when the components are mixed. This behaviour is similar to that of molecular LC systems with one non-mesomorphic component. For the latter, the decrease in the thermal stability of the mesophase when the

non-mesomorphic component is added is greater, the greater the volume and mass and the smaller the anisometry of the non-mesogen molecules.[23,43]

In salt mesogenic systems with a common cation, for example $Na|C_3H_7CO_2$, NO_3 or $Na|C_3H_7CO_2$, SCN (see Fig. 6), the introduction of the anions of the second component into the cation–anion layers of the LC domains depresses T_{cl}. The rate of the decrease in the thermal stability of the salt mesophase is greater, the higher the symmetry and the larger the size of the added anion. Thus the anions studied[45] can be arranged in the following order of increasing ability to break down the LC order in molten sodium butyrate:

$$iso\text{-}C_4H_9CO_2^- < C_2H_5CO_2^- < SCN^- < NO_3^- < CH_3CO_2^-.$$

The mechanism of the observed breakdown in the LC order in the binary systems formed by carboxylates with a common mesogen anion and asymmetrically charged cations, such as K, $Zn|C_3H_7CO_2$ or Na, $Mg|C_3H_7CO_2$ (Fig. 6), is apparently the same as in systems with a common cation. This is due to appreciable local ion association and complex formation in these salt melts.[45] Thus as a result of the formation of the fairly stable anionic complexes $[Zn(C_3H_7CO_2)_4]^{2-}$, the K, $Zn|C_3H_7CO_2$ system can be regarded as a system with a common cation, in which one anion is the mesogenic butyrate anion, and the other the non-mesogenic anionic complex, that is $K|C_3H_7CO_2$, $[Zn(C_3H_7CO_2)_4]$.

The non-mesogenic character of the ionic complexes formed in salt melts is related to their quasi-globular form and the isotropic distribution of the Coulombic charge. These factors are responsible for the fundamental difference between ionic mesogenic systems and molecular systems in relation to the influence of complex formation on the thermal stability of the LC phase. In molecular LC systems with donor–acceptor interaction between the components, the thermal stability of the mesophase increases, apparently as a result of the increase in the anisotropy of the intermolecular interactions when molecular complexes with a higher anisotropy of the molecular form,[71,72] compared with the individual components, are formed. In individual cases, the donor–acceptor interaction between the components may be insufficient for the formation of a molecular compound, but when the nematic or isotropic solution is cooled, this interaction may lead to partial ordering of the molecules and to the formation of smectic or nematic phases, not observed for the components.[73,74] Thus complex formation in binary molecular systems makes it possible not only to obtain new LC phases but also to increase their stability.

Molten salt systems in which the ionic complex formed is mesogenic can also probably exist, and this should lead to an increase in the stabilisation of the ionic mesophase or to the appearance of LC order in a salt melt consisting of two individually non-mesomorphic components. Salt systems of this kind are not yet known, although searches are being carried out in this direction.[45,75]

Glass formation is an interesting characteristic of LC melts of salts of carboxylic acids with asymmetrically charged ions.[45] Among the great variety of problems in the physics and chemistry of liquid crystals, a unique position is now occupied by the problems of obtaining and detecting metastable LC phases, or, in Shubnikov's words, the problems of "obtaining homogeneous mesomorphic systems of sufficiently large volume in the supercooled vitreous solid state".[76] The aim in the production of these LC glasses is to extend the range of the practical application of LC to lower temperatures, and also to study the fundamental properties of the LC state.[26,77] The research interest is due to the fact that in LC glasses, all the characteristics of the macro-structure corresponding to the mesomorphic form will be revealed more clearly as a consequence of the marked decrease in the mobility of the LC molecules. The preparation and study of known molecular LC glasses is complicated, however, by the fact that their softening temperatures are usually much lower than room temperature.[26] In contrast to molecular systems, in ionic LC systems LC glasses with high softening temperatures (> 300 K) are formed.[45]

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In conclusion it should be noted that binary ionic systems provide additional possibilities for controlling the stability of the ionic mesophase and for the production of new LC phases as a consequence of the high sensitivity of the salt mesophase to the nature of its component ions. High- and medium-temperature smectic ILC (range of existence 313–673 K) have now been studied, but it is also possible to produce low-temperature ILC using an appropriate combination of cations and anions in the salt melt.

It is not difficult to predict the future practical applications of this new class of LC. In contrast to classic smectics, ionic smectic LC should show optical sensitivity with respect to even weak electric fields. This is due to the high values of the components of the dielectric constant tensor of the ionic melt, the appreciable anisotropy of the electrical conductivity, and the small size of the cations and anions making up the ILC. In addition to the long-term memory and the possibility of local erasure of information,[18] characteristic of ordinary smectics, a basis for new non-traditional applications of ILC should be provided by the characteristic ionic channel electrical conductivity and its sensitivity to the degree of orientation of the LC specimen, and also by the possibility of controlling the optical properties of ILC by ion exchange and electrochemical transformations. The use of ILC as an anisotropic medium for the synthesis of organic and inorganic compounds, and also as an isotropic vitreous matrix for various spectroscopic purposes, is also of interest.

References

1. A R Ubbelohde *The Molten State of Matter* (Translated into Russian), Izd. Metallurgiya, 1982, 376 pp
2. Yu K Delimarskii *Khimiya Ionnykh Rasplavov* (The Chemistry of Ionic Melts), Izd. Naukova Dumka, Kiev, 1980, 328 pp
3. D Inman, D G Lovering (Editors) *Ionic Liquids*, Plenum Press, New York–London, 1981, p.450
4. A R Ubbelohde *J. Chim. Phys., Numéro spécial*, 1969, 59
5. H Rawson *Non-metallic Solids. Vol. 2. Inorganic Glass-forming Systems* (Translated into Russian), Izd. Mir, Moscow, 1970, 312 pp
6. C A Angell, J C Tucker *Phys. Chem. Process Metallurgy: Abstr. of Richardson Conf. L: Inst. Mining Metallurgy Publ.*, 1974, p. 207
7. F J Hazlewood, E Rhodes, A R Ubbelohde *Trans. Faraday Soc.*, 1966, **62** 3101
8. J J Duruz, H J Michels, A R Ubbelohde *Proc. R. Soc. London A*, 1971, **322**(1550) 281
9. J E Gordon *Techniques and Methods of Organic and Organometallic Chemistry*, Acad. Press, New York, 1969, p. 51

10. J E Lind, Jr. *Advances in Molten Salt Chemistry,* Plenum Press, New York–London, 1973, Vol. 1, p. 1
11. P Tissot *Molten Salt Techniques* (Edited by D G Lovering, R J Gale), Plenum Press, New York–London, 1983, Vol. 1, p. 137
12. *Thermodynamic and Transport Properties of Organic Salts,* (Edited by P Franzosini, M Sanesi), Pergamon Press, New York, etc., 1980, 370 p
13. A R Ubbelohde *Rev. Int. Htes Temp. Refract.,* 1976, **13** 5
14. G W Gray *Molecular Structure and the Properties of Liquid Crystals,* Acad. Press, London–New York, 1962, 314 pp
15. Yu B Amerik, B A Krentsel' *Khimiya Zhidkikh Kristallov i Mezomorfnykh Polimernykh Sistem* (The Chemistry of Liquid Crystals and Mesomorphic Polymeric Systems), Izd. Nauka, Moscow, 1981, 288 pp
16. V K Frederiks *Zh. Fiz. Khim.,* 1936, **7**(6) 889 [English translation in *Russ. J. Phys. Chem.,* 1936(6)]
17. *Primenenie Zhidkikh Kristallov v Vychislitel'noi Tekhnike* (The Use of Liquid Crystals in Computer Technology), Izd. Naukova Dumka, Kiev, 1980, 172 pp
18. S A Gadzhiev, A Kh Zeinally, A N Nasrullaev, D F Aliev *Termo- i Elektro-opticheskie Svoistva Smekticheskikh Kristallov* (The Thermo- and Electro-optical Properties of Smectic Crystals), Preprint Akad. Nauk Azerbaidzhan. SSR, Baku, 1985, 24 pp
19. S M Arakelyan, Yu S Chilingaryan *Nelineinaya Optika Zhidkikh Kristallov* (The Non-linear Optics of Liquid Crystals), Izd. Nauka, Moscow, 1984, 360 pp
20. V A Shcherbakov, L L Shcherbakova *Radiokhimiya,* 1984, 26(5) 708
21. L L Shcherbakova, V A Shcherbakov *IV Vsesoyuznoe Soveshchanie po Spektroskopii Koordinatsionykh Soedinenii. Tezisy Dokladov* (Summaries of Papers Presented at the Fourth All Union Conference on the Spectroscopy of Coordination Compounds), Krasnodar, 1986, p. 64
22. P G De Gennes *The Physics of Liquid Crystals* (Translated into Russian), Izd. Mir, Moscow, 1977, 400 pp
23. S I Zhdanov (Editor) *Zhidkie Kristally* (Liquid Crystals), Izd. Khimiya, Moscow, 1979, 328 pp
24. *Liquid Crystals and Plastic Crystals,* (Edited by G W Gray, P A Winsor), Wiley, New York, 1974, Vol. 1, 383 p; Vol. 2, 314 p
25. A S Sonin *Vvedenie v Fiziku Zhidkikh Kristallov* (Introduction to the Physics of Liquid Crystals), Izd. Nauka, Moscow, 1983, 319 pp
26. S A Pikin *Strukturnye Prevrashcheniya v Zhidkikh Kristallakh* (Structural Transformations in Liquid Crystals), Izd. Nauka, Moscow, 1981, 336 pp
27. A P Kapustin *Eksperimental'nye Issledovaniya Zhidkikh Kristallov* (Experimental Studies of Liquid Crystals), Izd. Nauka, Moscow, 1978, 368 pp
28. R D Vold, M J Vold *J. Am. Chem. Soc.,* 1939, **61** 808
29. M J Vold, M Macomber, R D Vold *J. Am. Chem. Soc.,* 1941, **63** 168
30. A E Skoulios, V Luzzati *Nature,* 1959, **183** 1310
31. A E Skoulios, V Luzzati *Acta Crystallogr.,* 1961, **14** 278
32. B Gallot, A E Skoulios *Acta Crystallogr.,* 1962, **15** 826
33. B Gallot, A E Skoulios *Mol. Cryst.,* 1966, **1** 263
34. A R Ubbelohde, H J Michels, J J Duruz *Nature,* 1970, **228** 50
35. A R Ubbelohde, H J Michels, J J Duruz *J. Phys. E: Sci. Instrum.,* 1972, **5** 283
36. D Demus, H Sackmann, K Seibert *Wiss. Z. Univ. Halle, M,* 1970, **19**(5) 47
37. V Busico, A Scopa, M Vacatello *Z. Naturforsch., A,* 1982, 37(12) 1466
38. I Konkoly-Thege, I Ruff, S O Adeosun, S J Sime *Thermochim. Acta,* 1978, **24** 89
39. S O Adeosun, S J Sime *Thermochim. Acta,* 1976, **17** 351
40. S O Adeosun *J. Therm. Anal.,* 1978, **14** 235
41. S O Adeosun *Can. J. Chem.,* 1979, **57**(2) 151
42. A R Ubbelohde *Melting and Crystal Structure* (Translated into Russian), Izd. Mir, Moscow, 1969, 420 pp
43. A G Morachevskii, E P Sokolova, in Ya M Kolotyrkin (Editor) *Fizicheskaya Khimiya. Sovremennye Problemy* (Physical Chemistry. Current Problems), Izd. Khimiya, Moscow, 1984, p. 77
44. J Lindau, S Diele, H Krüger, H-D Dörfler *Z. Phys. Chem. (Leipzig),* 1981, **262**(5) 775
45. T A Mirnaya, Candidate's Thesis, Institute of General and Inorganic Chemistry, Ukrainian SSR Academy of Sciences, Kiev, 1984
46. J J Duruz, A Ubbelohde *Proc. R. Soc. London,* 1972, **330**(1580) 1
47. J E Bonekamp, T Eguchi, S Plesko, J Jonas *J. Chem. Phys.,* 1983, **79** 1203
48. J E Bonekamp, B Hegemann, J Jonas *Mol. Cryst. Liq. Cryst.,* 1982, **87** 13
49. H J Michels, A R Ubbelohde *J. Chem. Soc., Perkin Trans. II,* 1972, (12), 1879
50. G Pelzl, H Sackmann *Mol. Cryst. Liq. Cryst.,* 1971, **15** 75
51. J E Bonekamp, I Artaki, M L Phillips, et al. *J. Phys. Chem.,* 1983, **87** 4991
52. M L Phillips, T M Barbara, S Plesko, J Jonas *J. Chem. Phys.,* 1986, **4** 5143
53. S Plesko, M L Phillips, R Cassell, J Jonas *J. Chem. Phys.,* 1984, **80** 5806
54. M Wolfe, J E Bonekamp, J Jonas *J. Chem. Phys.,* 1979, **70** 3993
55. G J Krüger *Phys. Rep.,* 1982, **82** 229
56. J Roth, T Meisel, K Seybold, Z Halmos *J. Therm. Anal.,* 1976, **10** 223
57. T Meisel, K Seybold, J Roth *J. Therm. Anal.,* 1977, **12** 361
58. S O Adeosun, S J Sime *J. Chem. Faraday, Trans. I,* 1979, **75** 953
59. S O Adeosun, M O Illori, H A Ellis *Thermochim. Acta,* 1980, **39** 125
60. M E Ekwunife, M U Nwachukwu, F P Rinehart, S J Sime *J. Chem. Soc., Faraday Trans. I,* 1975, **71** 1432
61. J J Duruz, A R Ubbelohde *Proc. R. Soc. London,* 1976, **347**(1650) 301
62. A Bogoyavlenskii, N M Vinogradov *Z. Phys. Chem.,* 1907, **60** 433
63. A Bogoyavlenskii, N M Vinogradov *Z. Phys. Chem.,* 1908, **64** 229
64. R L Humphries, G R Luckhurst *Chem. Phys. Lett.,* 1973, **23** 567
65. T A Mirnaya, V D Prisyazhnyi *Ukr. Khim. Zh.,* 1983, **49** 1023
66. J M Lohar, D S Shan *Mol. Cryst. Liq. Cryst.,* 1974, **25** 145
67. J Braunstein *Ionic Interactions,* Vol. 1, *Equilibrium and Mass Transport,* S Petrucci (Editor), Acad. Press, New York–London, 1971, p. 179

68. T A Mirnaya, V D Prisyazhnyi, V N Mirnyi *Ukr. Khim. Zh.*, 1984, **50** 359
69. V N Mirnyi, V D Prisyazhnyi, T A Mirnaya *Termodinamicheskie i Elektrokhimicheskie Svoistva Ionnykh Rasplavov* (The Thermodynamic and Electrochemical Properties of Ionic Melts), Izd. Naukova, Dumka, Kiev, 1984, p. 54
70. Y Nakamura, Sh Shimokawa, Y Kitazawa, M Shimoji *Proc. I Intern. Symp. on Molten Salt Chemistry and Technology, Kyoto, Japan*, 1983, p. 387
71. J W Park, C S Bak, M M Labes *J. Am. Chem. Soc.*, 1975, **97** 4398
72. A C Griffin, R F Fisher, S J Havens *J. Am. Chem. Soc.*, 1978, **100** 6329
73. K Araya, Y Matsunaya *Bull. Chem. Soc. Jpn.*, 1980, **53** 3079
74. R S Gupta, R A Vora *Mol. Cryst. Liq. Cryst.*, 1984, **106** 147
75. V Busico, T Tartaglione, M Vacatello *Thermochim. Acta.*, 1983, **62** 77
76. A V Shubnikov *Kristallografiya*, 1960, **5**(1) 3
77. O P Kevdin, Candidate's Thesis, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1983