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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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To cite this Article Mirnaya, T. A. and Volkov, S. V.(1994) 'Electrostatic stabilization of liquid crystalline ordering in binary melts of sodium and potassium alkanooates', *Liquid Crystals*, 16: 4, 687 – 692

To link to this Article: DOI: 10.1080/02678299408036540

URL: <http://dx.doi.org/10.1080/02678299408036540>

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Electrostatic stabilization of liquid crystalline ordering in binary melts of sodium and potassium alkanooates

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(Received 3 March 1993; accepted 18 August 1993)

The mesophase electrostatic stabilization energy (E) has been examined by using the ionic continuous solid solution model for binary systems of sodium and potassium alkanooates with a common anion. It is found that E increases with a decrease in chain length of the alkanooate anion and that there is an inverse proportionality between E and the square of the mesophase bilayer spacing. The electrostatic stabilization factor is shown to be responsible for the formation of an ionic mesophase in binary acetate and propionate systems derived from two non-mesomorphic components.

1. Introduction

Thermotropic liquid crystal phases of short chain alkanooic acids salts have long been known as a special family of so-called ionic liquid crystals [1], because the bilayer smectic structure of these mesophases is stabilized by electrostatic forces acting between the ions, rather than through a large molecular length to width ratio normally considered essential for the existence of liquid crystals. The effect of the electrostatic factor upon the ionic mesophase formation can be demonstrated by the empirical regularity of behaviour found by us for pure alkanooate salts [21] for which cation and anion parameters have been correlated with the possibility of ionic mesophase appearance. Thus, we have noted that pure anhydrous metal alkanooates may form enantiotropic mesophases and also have latent mesogenic properties when the metal cation polarizing ability is less than 1.05 and the ratio of cation radius to anion radius does not exceed 0.4 or 0.5 for the salts with real or latent mesomorphic properties, respectively.

The influence of electrostatic interactions on the ionic smectic mesophase stability for molten metal alkanooates is most pronounced in binary systems with a common alkanooate anion. As shown earlier [3], continuous liquid crystalline solutions were formed in binary systems of sodium, potassium, rubidium and caesium butyrates or valerates, the mesophase clearing temperatures of the mixtures exhibiting large positive deviations from an additivity law, i.e. from the straight line joining the clearing temperatures of the two components. These deviations (ΔT) were used to estimate the mesophase electrostatic stabilization energy (E) in the framework of the solid solution model as follows [3]:

$$E = \Delta TR / 2x_1x_2, \quad (1)$$

where R is the gas constant, and x_1 and x_2 are the mol fractions of the components (detailed derivation and theoretical substantiation of equation (1) may be found in [3]).

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The physical meaning of E is the orientational constituent of the mixing energy resulting essentially from the cation–cation repulsion energy change; the changes in energy of all other interactions (dispersion, anion polarization, etc.) on mixing molten salts with a common anion is well known [4] to be negligible compared with the change due to electrostatic cation–cation interaction. The above change is greater the larger the difference in cation radii [4].

As results from [3], the enhancement of mesophase thermostability in binary alkali metal alkanoate systems becomes greater as the energy of electrostatic interaction between the dissimilar cations increases, i.e. there happens to exist a direct proportionality between the value of E and the difference in the radii of the two components alkali metal cations. Therefore ionic binary mesophase stabilization must be a function of both the difference between the dissimilar cationic radii and the distance between these cations.

Hence it would be interesting to elucidate the effect of alkanoate anion chain length on the ionic mesophase electrostatic stabilization energy. Towards this end, we have estimated the values of E for binary systems of sodium and potassium alkanoates, Na , $\text{K}[\text{C}_n\text{H}_{2n-1}\text{O}_2]$, and have established the dependence of E upon the mesophase bilayer spacing (d) as the shortest distance for cation–cation interaction across the smectic layers.

2. Experimental

Sodium and potassium salts of acetic (NaC_2 and KC_2), propionic (NaC_3 and KC_3), butyric (NaC_4 and KC_4), valeric (NaC_5 and KC_5), isovaleric ($\text{Na}i\text{-C}_5$ and $\text{K}i\text{-C}_5$), hexanoic (NaC_6 and KC_6) and heptanoic (NaC_7 and KC_7) acids were prepared in our laboratory by a generally accepted method [5]. Substances were dried in vacuum at 120°C during 48 h. IR-spectra of the salts synthesized showed the absence of any water. All the pure salts other than the acetates and propionates exhibited enantiotropic smectic A phases in accord ($\pm 1^\circ\text{C}$) with literature data [1]. Sodium propionate is known to have a latent (virtual) mesophase clearing temperature [6]. Potassium propionate and also potassium and sodium acetate are expected to possess latent mesomorphic properties as they are subject to the empirical rule concerning the relationship for cation–anion radii [2].

The mesophase clearing temperatures and, in some special cases quoted below, the melting temperatures were determined using a polarizing microscope equipped with a hot stage.

The mesophase bilayer spacings were measured by using small angle X-ray diffraction (Ni filtered CuK_α radiation).

The preparation of binary mixtures and their investigation were carried out in an inert atmosphere.

3. Results and discussion

There is some information on mesophase–isotropic liquid transition temperatures for binary systems of potassium and sodium butyrate, valerate, iso-valerate and hexanoate [7,8]. Analysis of the data has shown positive deviations of the experimental clearing temperatures for the binary mesophases from the straight line joining the clearing temperatures of the pure components. By way of a typical example, we have presented in figure 1 the curve of the mesophase clearing temperatures for the binary system of NaC_4 with KC_4 from [8]. In order to estimate the values of E for binary systems of NaC_n with KC_n in the framework of the ionic solid solution model

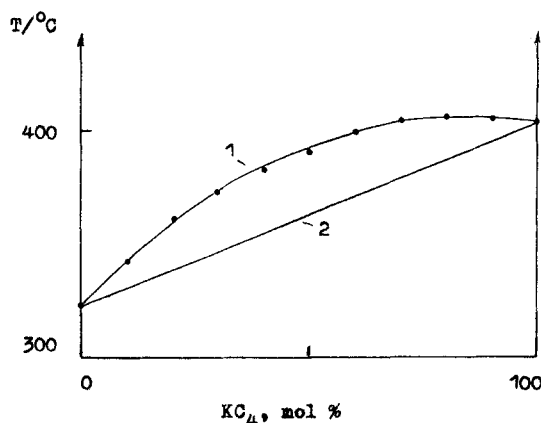


Figure 1. Mesophase clearing temperatures for the binary system of sodium and potassium butyrate; (1) experimental values [8], (2) values calculated according to additivity law.

Mesophase electrostatic stabilization energies (E) and bilayer spacings (d) for binary systems of sodium and potassium alkanates, clearing temperatures (T) for pure components and for their equimolar mixtures, and deviations of clearing temperatures from additivity (ΔT) for equimolar mixtures.

System	$T_{\text{Na}}/^{\circ}\text{C}$	$T_{\text{K}}/^{\circ}\text{C}$	$T_{\text{Na}+\text{K}}/^{\circ}\text{C}$	$\Delta T/^{\circ}\text{C}$	$E/\text{J mol}^{-1}$	$d/\text{\AA}$ at 300°C
Na, K C ₇	369	439	413	9	150	19.5
Na, K C ₆	366	449	420	13	216	17.8
Na, K C ₅	356	444	416	16	265	15.8
Na, K i-C ₅	286	406	367	21	349	14.3
Na, K C ₄	324	404	391	27	448	14.0
Na, K C ₃	274†	287†	318	38	632	11.4

† Latent mesophase clearing temperatures estimated by extrapolation (q.v., text).

using equation (1), the mesophase clearing temperatures of the pure components (T_{Na} and T_{K}) and their equimolar mixture ($T_{\text{Na}+\text{K}}$) were measured; these transition temperatures were consistent with literature data [1, 3, 5–8]. The deviation of $T_{\text{Na}+\text{K}}$ from additivity (ΔT) was calculated as follows:

$$\Delta T = T_{\text{Na}+\text{K}} - 1/2(T_{\text{Na}} + T_{\text{K}}). \quad (2)$$

The table lists the experimental values of T_{Na} , T_{K} and $T_{\text{Na}+\text{K}}$ as well as the calculated values of ΔT and E for all of the systems studied; the latent clearing temperatures were used for the pure components in the case of the propionate system.

It will be noted that while both components of the binary propionate system are not apparently mesomorphic, a mixture of the two is found to give the induced mesophase over a fairly wide concentration range. We have studied the mesophase clearing temperatures and melting temperatures for this system, and the phase diagram is displayed in figure 2. The induced mesophase is proven to be of the type smectic A. On cooling the isotropic melt, we observed through the polarizing microscope the appearance of the bâtonnets at the clearing temperatures, followed immediately by the formation of a confocal-conical texture. The latter is typical for smectic A phases of short chain alkali metal alkanates. Moreover, in our experiments, the propionate

mesophase showed continuous miscibility with the known smectic A phases of pure sodium butyrate or valerate. The latent mesophase–isotropic liquid transition temperatures for sodium and potassium propionate were estimated by extrapolation of the clearing temperature curve to 0 mol per cent KC_3 ($T_{\text{Na}} = 274^\circ\text{C}$) and 0 mol per cent NaC_3 ($T_{\text{K}} = 287^\circ\text{C}$), respectively, the value of T_{Na} being in good agreement with available data [6]. One can easily see from figure 2 that $T_{\text{Na+K}}$ for the propionate system is higher by 38°C than the straight line joining the latent clearing temperatures of the two components.

The powder X-ray diffraction patterns of all the mesomorphic salt mixtures studied were characterized by just a single line, fairly sharp and intense, corresponding to the 001 reflection, i.e., the bilayer spacing (d). The table lists the mesophase bilayer spacings for equimolar molten mixtures of NaC_n with KC_n at 300°C . The data obtained were found to correlate reasonably with known X-ray diffraction data on bilayer spacings for mesophases of pure sodium alkanooates [9, 10]. As can be seen from the table, the energy of mesophase electrostatic stabilization E increases with decrease in the bilayer spacings d , i.e. with decrease in the alkanooate anion chain length.

We have supposed, as mentioned above, that this additional energy of mesophase stabilization has arisen from the electrostatic interaction of dissimilar metal cations in the molten salt mixture. Since the energy of electrostatic interactions is known to change as the inverse square of the distance between interacting ions, it is interesting to analyse the relationship between E and $1/d^2$. As shown in figure 3, this relationship may be fairly described by a straight line. Thus the stabilization of the liquid crystalline phase in binary systems of alkali metal alkanooates with a common anion is found to obey the electrostatic laws. It is obvious that the action of electrostatic forces is the stronger, the shorter the alkanooate anion chain.

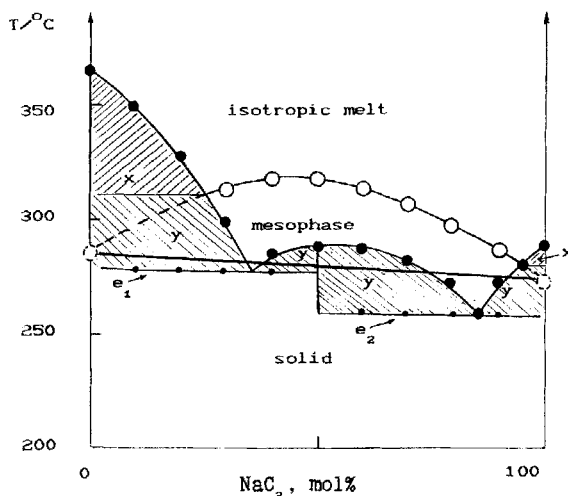


Figure 2. Phase diagram for the binary system of sodium and potassium propionate. The curve through the open circles is the mesophase clearing temperature curve. The curve through the larger dark circles is the melting temperature curve; the e_1 and e_2 lines are eutectic lines. The solid straight line joins the latent clearing temperatures of the pure components as determined by extrapolations of the clearing temperature curve (marked by the dotted lines). The shaded regions, x and y , are two phase regions where solid coexists with isotropic melt and mesophase, respectively. The boundary between x and y regions is purely conventional, and it is not established experimentally.

One can conclude from figure 3 that the influence of electrostatic interactions on the existence of the mesophase in systems consisting of NaC_n with KC_n becomes negligible when the carbon atom number of the unbranched aliphatic chain (n) is more than 8. This implies that the mesophases of alkali metal alkanooates in which the alkanooate anion length is as long as in the case of an unbranched aliphatic chain with $n > 8$, cannot be considered as ionic mesophases.

On the other hand, the sharp increase in E with decreasing d leads to the conclusion that a range of mesophase existence may be discovered in binary alkanooate salt systems with two non-mesomorphic components, if they are potentially mesomorphic, given a favourable combination of the following two facts: (1) the melting temperature curve becomes lower than the clearing temperature curve and (2) the latter curve tends to be markedly convex upwards. It is this situation which is found in the binary system NaC_3 with KC_3 . It will be noted, as can be seen from figure 2, that for this system we would observe liquid crystals induced only by the first factor over the narrow concentration range near to the eutectic point located at 87 mol per cent NaC_3 if it were not for the additional electrostatic stabilization of the mesophase, i.e., if the second factor were absent.

Another interesting example of probable ionic mesophase formation due to additional electrostatic stabilization may possibly be provided by the system NaC_2 with KC_2 . Sodium and potassium acetate are known to be non-mesomorphic salts, but they are expected, as mentioned above, to possess latent mesomorphic properties. Therefore a mixture of these salts may produce a mesophase under the two conditions defined above. Unfortunately there are many conflicting and irreproducible data relating to the phase diagram of this system [7], and nothing has pointed to the formation of any mesophase.

We have tried to estimate the latent mesophase electrostatic stabilization energy for the binary system consisting of NaC_2 with KC_2 by using the plot in figure 3. An approximate value for the bilayer spacing for probable domains in the acetate melt

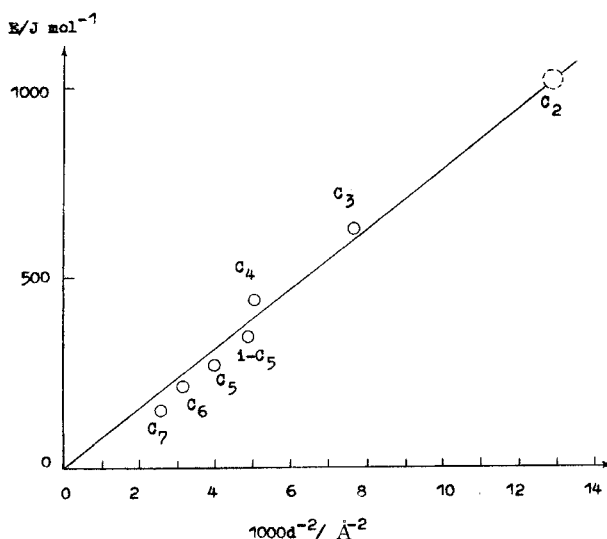


Figure 3. Plot of the mesophase electrostatic stabilization energy against the inverse square of the mesophase bilayer spacing for binary systems of sodium and potassium alkanooates Na, K[C_n .

accounts for 9.40 Å. This was calculated on the basis of the experimental value of d for the appropriate propionate melt ($d = 11.40$ Å) and the established fact that the bilayer spacing change accounts for ≈ 2.0 Å per methylene group on varying the alkanolate anion chain length [9, 10]. Based on the bilayer spacing obtained, we next estimated the mesophase electrostatic stabilization energy for the binary acetate system. It proved to be equal to ≈ 1 kJ mol⁻¹, which can cause a deviation of $T_{\text{Na+K}}$ from additivity by $\approx 60^\circ\text{C}$ according to equation (1).

Because of this very strong additional electrostatic stabilization of the latent ionic mesophase in the acetate melt, we decided to re-check the phase diagram for the system of sodium and potassium acetates with a view to finding any concentration and temperature range of mesophase existence. The results have confirmed our expectations. Indeed, we have found that the smectic mesophase does exist over the composition range of 45–60 mol per cent of NaC₂, the mesophase temperature interval being equal to 2–15°C. The detailed results of DTA and X-ray studies on this system will be published later.

Therefore, our investigation has shown that binary melts of short chain alkanolic acid salts allow new liquid crystal phases to be formed due to the electrostatic forces associated with interionic interactions in these systems composed of non-mesomorphic components.

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