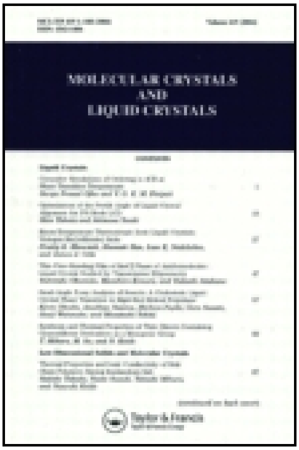

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Enthalpies of Mixing in Binary Systems of Nematic Liquid Crystals

T. G. Churjusova [a] & E. P. Sokolova [a]

[a] Institute of Chemistry, St. Petersburg State University, Universitetsky prosp., 2, St. Petersburg, 198904, U.S.S.R.

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Enthalpies of Mixing in Binary Systems of Nematic Liquid Crystals

T. G. CHURJUSOVA and E. P. SOKOLOVA

Institute of Chemistry, St.-Petersburg State University, Universitetsky prosp., 2, St.-Petersburg 198904, U.S.S.R.

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The mixing enthalpies of binary mixtures of nematic liquid crystals are studied using a Calvet calorimeter. The systems studied are: 4-ethoxybenzylidene-4′-*n*-butylaniline-4-*n*-pentylphenyl-4′-methoxybenzoate and 4-*n*-butyl-4′-methoxyazoxybenzene-4-*n*-pentyl-4′-cyanobiphenyl. In the second system the induced smectic A phase occurs in the medium concentration range.

The results are discussed in terms of molecular properties and interactions.

Keywords: nematic liquid crystals, binary systems, phase transitions, induced smectic A phase, enthalpy of mixing

INTRODUCTION

In recent years there have been many reports on physical properties of nematic liquid crystal (NLC) mixtures as a function of composition.[1–4] This arises from the fact that mixtures of liquid crystals are more suited for technological applications than pure materials. Another reason is that such systems are of considerable interest for theoretical studies in the field of molecular interactions.

It has been shown that the deviations from the ideal behavior of the mixtures containing molecules with strongly polar end groups can be attributed to the formation of different kinds of molecular associates (see, e.g.,[5,6] and references therein). Not only mixtures of terminal-polar compounds, but also the systems containing weakly polar mesogens should display a rich variety of thermodynamic properties owing to the strongly anisotropic molecular interactions. Recently, this has been confirmed with statistical mechanical methods based on hard particle theories,[7] and experimentally with volume-temperature studies for a binary system of weekly polar mesogens.[8]

Although several reports on mixing enthalpy (H^M)—composition studies in non-mesogen—NLC systems have been published,[9–13] studies for binary mixtures of mesogens have not been published up to now.

In the present study we have chosen two binary systems. The first system[14] contains two weakly polar compounds 4-ethoxybenzylidene-4′-*n*-butylaniline (EBBA) and 4-*n*-pentylphenyl-4′-methoxybenzoate (PPMB). In the second system the terminal non-polar 4-*n*-butyl-4′-methoxyazoxybenzene (BMAB) is combined with the strongly polar 4-*n*-pentyl-4′-cyanobiphenyl (PCB). In the latter system an induced smectic A phase (S_A) appears in the middle concentration range[15] although neither component possesses a smectic phase. The S_A-N phase boundary is practically of symmetric shape and passes through a maximum at 302 K.

EXPERIMENTAL

Transition temperatures and transition enthalpies of components and their mixtures were measured at scanning rates of 0.1, 0.5 and 1.0 K/min using a Setaram differential scanning calorimeter, model DSK-111. At least three scans were performed for each sample to check reproducibility. The accuracy of the transition enthalpies is estimated as 3–5%. In addition to the DSC-data the phase diagrams were studied using a Reichert polarizing microscope equipped with a heating stage. Transition properties of the substances studied and their dipole moments are listed in Table I, data in parentheses are taken from literature.

The measurements of mixing enthalpies were performed with a Calvet microcalorimeter, Setaram, France, using specimens with a mass of 0.5–5.0 g. Both components were placed in a metal calorimetric cell, one of the specimens being sealed in a glass ampoule. After destruction of the ampoule the components were mixed and the magnitude of the resultant heat flow was recorded. Destruction of the ampoule and stirring of the mixture were carried out with a fluoroplast disk attached to a stainless steel rod which passes through a lid of the cell. The H^M values were reproducible to within ±4% or better.

RESULTS AND DISCUSSION

The phase transition temperatures and the enthalpies of isothermic mixing versus mole fraction *x* are plotted in Figures 1(a, b) and 2(a, b), respectively. These

TABLE I

Temperatures and enthalpies of the N-I transition, the molecular mass (M) and the dipole moments (μ) of the substances under investigation

NLC	M	T_{NI} , K	ΔH_{NI}, $\frac{J}{mol}$	μ , D
EBBA	281,40	352,0(352,5)^{16}	587(586)^{16}	2,2^{21}
PPMB	298,38	315,1(316,1)^{16}	603(585,7)^{2}	2,0^{2}
BMAB	284,36	346,5(347,9)^{16}	426,5	-
PCB	249,36	308,0(308,16)^{16}	458,8(417,2)^{16}	4,8^{21}

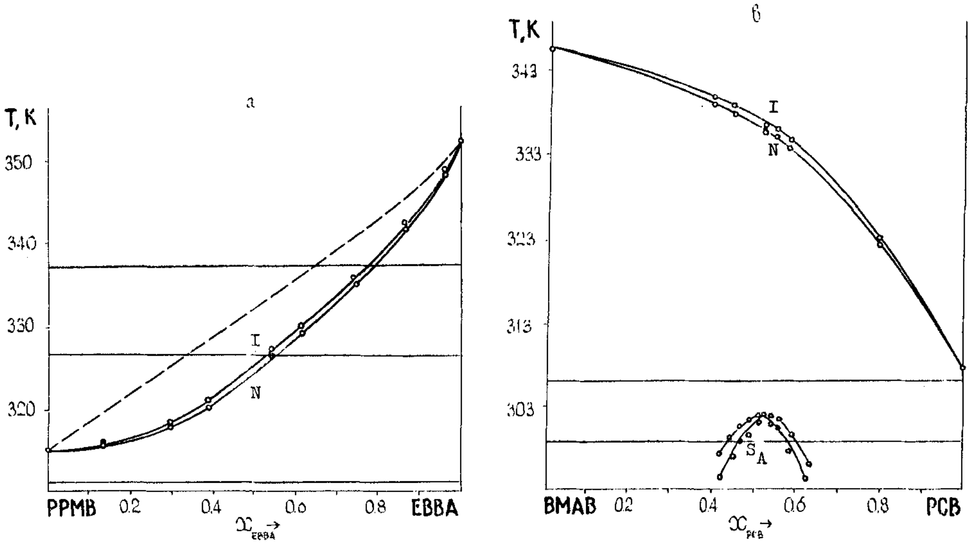

FIGURE 1 The phase diagrams for the EBBA-PPMB (a) and BMAB-PCB (b) systems. The experimental phase boundaries are indicated by solid lines (I, N, S_A designate the isotropic, nematic and smectic A phases, respectively). The dashed line is the dependence of $T_N(x)$ calculated from the van Laar equation. The isotherms under investigation, except 356 K, are marked with the horizontal lines.

enthalpies are equal to excess enthalpies H^E when both components and the solution are in the same phase. The boundaries of the N-I and S_A-N equilibria are marked in the Figure 2(a, b) with the vertical lines. Direct evidence of linearity of the curves $H^M(x)$ in heterogeneous regions is not available due to the smallness of the N-I coexistence range.

Let us discuss the results for both systems one after another. The mixing of EBBA with PPMB is accompanied by an endothermic effect. At 311 K, when both components and their mixtures are in the nematic state, the dependence $H^M(x)$ is a smooth curve of virtually symmetric shape. At 326 K and 337 K, when PPMB is in the isotropic state, it is possible to differentiate between three parts in the $H^M(x)$ curves. Two of the parts correspond to the isotropic and the nematic phases in the concentration ranges sufficiently far from the transition points. In the third part, i.e., in the vicinity of the stability boundaries, the curvature of the function $H^M(x)$ undergoes an abrupt change—the mixing enthalpy exhibits a strong decrease in the isotropic phase at 326 K and an enhancement in the nematic phase at 337 K as the transition to the two-phase region is approached.

There is no ready explanation at the moment for this behavior which is complicated by the fact that in the regions under discussion mixing effects and phase transitions are in superposition. The observed properties of the isotherms $H^M(x)$ near the boundary points require further experimental and theoretical studies.

The thermodynamic properties of the EBBA-PPMB system differ greatly from those of an ideal system, although the dipole moments as well as the size and shape of the molecules of both components are similar: the ratio of molecular volumes of EBBA and PPMB is 0.975 and the axial ratios are 3.12 and 3.15, respectively.[17] The non-ideality of the system is indicated by the considerable values of $|H^M|$ and

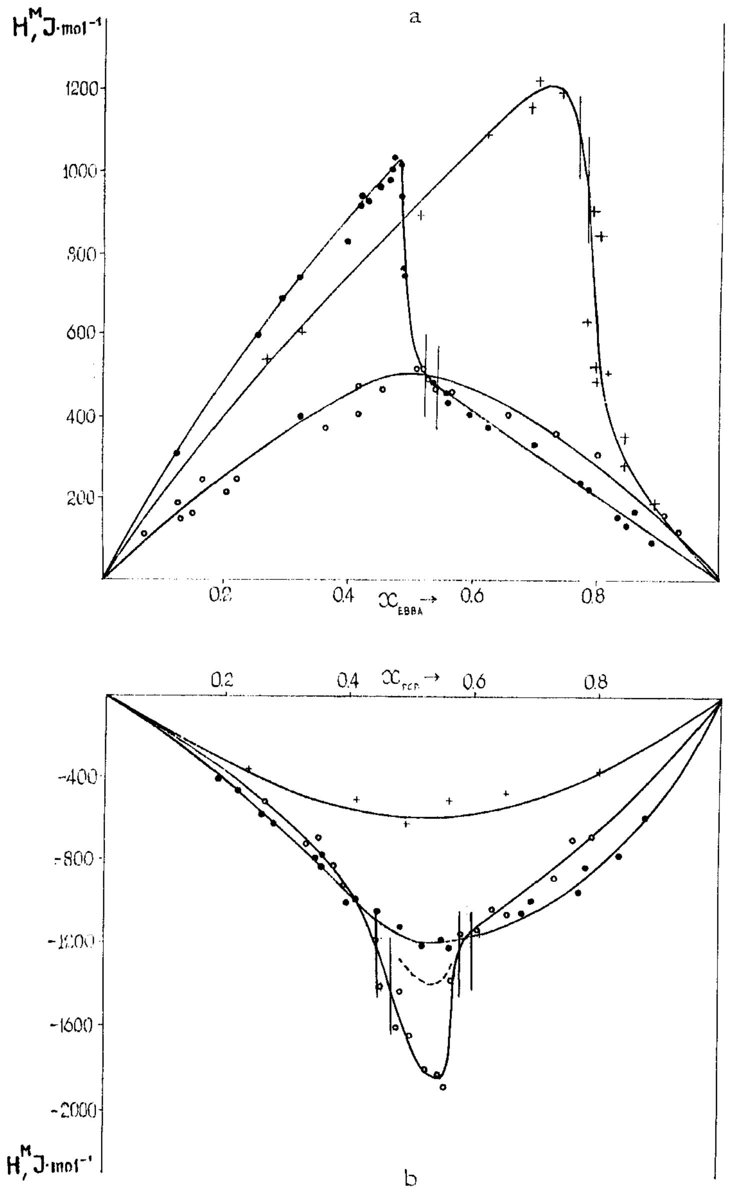

FIGURE 2 The mixing enthalpies as function of composition in the system EBBA-PPMB (a) at 311 (○), 326 (·) and 337 K (+) and in the system BMAB-PCB (b) at 299 (○), 307 (·) and 356 K (+). The dependence of $H^E(x)$ at 299 K is marked with the dashed line.

by the difference between the experimental dependence $T^N(x)$ and that calculated from the van Laar equation[18] (Figure 1a). The properties of the mixed phase of this system are probably mainly determined by energetic factors, in particular, by the character of electron density distribution in the molecules of asymmetric shape. In this connection it should be pointed out that the longitudinal α_l and the transverse

TABLE II

Enthalpies (J/mol) of the S_A-N transition in the system BMAB-PCB

x_{PCB}	0,472	0,500	0,522	0, 527	0,534	0,554	0,586
ΔH_{S_A-N}	380	451	468	462	457	458	388

α_t polarizabilities of both molecules are different; they are 41.9 and 34.2 (10^{-40} F · m^2) for EBBA and 57.3 and 32.5 (10^{-40} F · m^2) for PPMB, respectively.†

Non-ideal behavior of the EBBA-PPMB system may also be caused by a certain ability of each component to association. Such trend towards the local correlation of the neighboring dipole moments which are perpendicular to the molecular para-axis is obtained in Schiff bases, as it is estimated in Reference 21 according to the Fröhlich theory.

In contrast to the preceding case, the BMAB-PCB system shows an exothermic mixing enthalpy. At 356 and 307 K, when both components and the solution are in the same state, in the isotropic and nematic state, respectively, the $H^M(x)$ curves are symmetric with respect to the equimolar composition. The values of $|H^M|$ decrease considerably in the isotropic phase. The third isotherm of H^M was measured at 299 K. In the range of the induced S_A phase the exothermic effect increases abruptly, the minimum on the $H^M(x)$ curve corresponding to the composition $x_{PCB} = 0.53$.

In an attempt to estimate the excess enthalpies H^E in the smectic A region at 299 K the S_A-N transition heats have been determined calorimetrically using the differential scanning calorimeter (Table II). The excess enthalpies are evaluated approximately as $H^E = H^M + \Delta H_{S_A\text{-}N}$. A temperature dependence of $\Delta H_{S_A\text{-}N}$ was neglected. Figure 2(b) illustrates that the observed enhancement of H^M on passing to the smectic A phase is mainly due to the S_A-N transition.

The simplest thermodynamic model of binary mixtures exhibiting induced smectic phases considers them as an equilibrium mixture of dimers and monomers.[6] Trends in the nematic-smectic A transition temperatures have been investigated in Reference 6 in terms of a monomer-dimer equilibrium to account for the possibility of dimer formation between the two components and the self-association of the terminally polar compound. Due to the complexity of nematic mixtures, however, a quantitative description of their phase diagrams and the mixing functions is not feasible. Qualitatively speaking it seems that in the BMAB-PCB system the formation of the mixed complex is considerably responsible for the exothermic mixing provided the coupling between PCB and BMAB is energetically more favorable than the dimerization caused by dipole-dipole coupling of PCB.

It is evident that the behavior of mixtures of liquid crystals is much more com-

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† The α_l and α_t values of EBBA and PPMB were evaluated using the data of Table II[19] and Table IV.2[20] by assuming that the polarizability of an alkyl chain is given as a sum over the α_l and α_t values of every —CH_2— group.

plicated than a monomer-dimer equilibria. A quantitative description should account for the dependence of their properties upon the packing effects and attractive interactions between the molecular complexes.[6] Up to now the structural and excess thermodynamic properties have been calculated at a molecular level only for nematic-non-mesogenic mixtures within the quasi-chemical hole lattice model.[22]

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