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Nematic-Isotropic Transition in MBBA and its Mixtures with 4-Methoxybenzaldehyde: Applications to the Purity Control of Liquid Crystals

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Nematic-Isotropic Transition in MBBA and its Mixtures with 4-Methoxybenzaldehyde

Applications to the Purity Control of Liquid Crystals

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The nematic-isotropic transition temperatures of MBBA(1) + 4-methoxybenzaldehyde(2) mixtures (where MBBA = *N*(4-methoxybenzylidene)-4-*n*-butylaniline) for $0 \leqslant x_2 \leqslant 0.06$ and additionally the transition enthalpy of pure MBBA were measured by a calorimetric method. Straight lines were found for the $T^l(x_2)$ and $T^n(x_2)$ curves respectively where T^l and T^n are the upper and the lower limiting temperatures of the transition range for a given x_2. The results are compared with literature data on similar systems and confirm the wellknown rule that the decrease of the nematic-isotropic transition temperature with increasing x_2 depends more strongly on the size and the shape than on the polarity of component 2. From a plot of $\Delta T \equiv T^l - T^n$ against x_2 the mole fraction of impurity in the original sample can be extrapolated.

INTRODUCTION

Investigations of the influence of a non-liquid crystalline substance on the phase transition temperature of a liquid crystal are of considerable primary importance for the thermodynamics and the theory of liquid crystals.[1-4] They are also of fundamental interest for the delicate problem of purity control in liquid crystals.[4]

Results will be presented on the system MBBA(1) + 4-methoxybenzaldehyde(2) for $0 \leqslant x_2 \leqslant 0.06$. This impurity has been chosen because it is one of the hydrolysis products of MBBA samples. Since very high accuracy of transition temperatures is indispensable, the experiments were performed in a precision research calorimeter. Additionally the transition enthalpy of pure MBBA was determined.

EXPERIMENTAL

a) Apparatus and procedure

The transition temperatures T^{tr} and the enthalpy change ΔH^{tr} for the nematic–isotropic transition were determined with the isoperibolic reaction and solution calorimeter LKB 8721-1. For the measurements a sample of the liquid crystal or the mixture under test was heated from below up to above the transition range. Heating was performed by connecting the heater of the calorimeter vessel to a constant electrical power corresponding to a heating rate of about $4 \cdot 10^{-3}$ K · s^{-1}. In Figure 1 the resistance of the thermistor mounted in the calorimeter vessel is plotted against time for a characteristic run. The transition temperatures and ΔH^{tr} were obtained from the breaks *C* and *D* and from the slopes of the different branches of the curve. For details of experiments and calculations see Ref. 5.

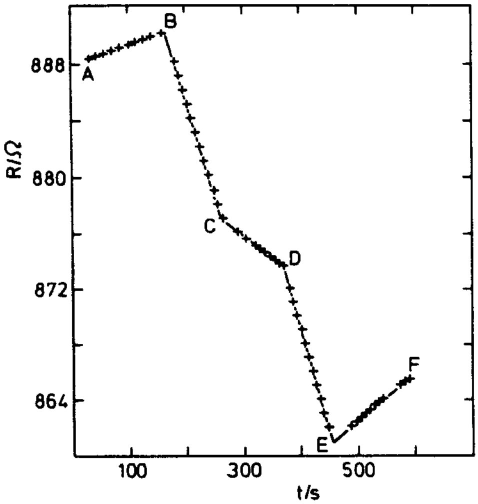

FIGURE 1 Calorimetric heating curve for a MBBA + 4-methoxybenzaldehyde mixture: Resistance of the thermistor (*R*) versus time (*t*) (*B* to *E* heating, *C* to *D* nematic–isotropic transition; see text).

b) Substances

MBBA was synthesized by condensation of freshly distilled 4-*n*-butylaniline with 4-methoxybenzaldehyde in boiling toluene and purified by recrystallizing it five times from pentane at low temperatures[6] in the absence of moisture. Finally all traces of the solvent were removed from the liquid crystal by applying a vacuum in a rotation evaporator at 293 K for several days. The MBBA was stored at 250 K in the dark under dried nitrogen.

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4-Methoxybenzaldehyde was purified by vacuum distillation and stored as described for MBBA.

RESULTS

a) Transition temperature and transition enthalpy of pure MBBA

For the MBBA purified according to the procedure described above the nematic–isotropic transition temperature $T^{tr} = (319.07 \pm 0.04)$ K and the nematic–isotropic transition enthalpy $\Delta H^{tr} = (1.02 \pm 0.04)\ \mathrm{J \cdot g^{-1}}$ were found; the transition range was (0.08 ± 0.04) K.

From the phase diagram of the system MBBA + 4-methoxybenzaldehyde (see Table II) a transition temperature $T^{*} = (319.80 \pm 0.05)$ K is extrapolated for a MBBA sample 100% pure. In Table I the values for T^{*} and ΔH^{tr} thus obtained are compared with data taken from the literature.

TABLE I

Transition temperature and transition enthalpy for MBBA

T^{tr}/K	$\Delta H^{tr}/\mathrm{J \cdot g^{-1}}$
320.01 Ref.[7]	2.30 Ref.[11]
319.75 Ref.[8]	1.56 Ref.[15]
319.65 Ref.[9]	1.55 Ref.[10]
319.0 Ref.[10]	1.17 Ref.[16]
317.0 Ref.[11]	1.05 Ref.[7]
316.95 Ref.[12]	1.02 this work
314.15 Ref.[13]	
312.65 Ref.[14]	
319.80 ± 0.05 this work	

b) Transition temperatures of MBBA containing small quantities of 4-methoxybenzaldehyde

The influence of small quantities of 4-methoxybenzaldehyde up to $x_2 = 0.06$ on the nematic–isotropic transition temperature of MBBA is represented in Table II.

Plots of T^{n} and T^{l} against x_2 give straight lines with the slopes $(\mathrm{d}T/\mathrm{d}x_2)^{l} = -188.4$ K and $(\mathrm{d}T/\mathrm{d}x_2)^{n} = -196.3$ K respectively with a standard deviation of 0.1 K. These values agree with results of other authors on similar systems.[3,9,17,18] As it has already been shown in the literature[4] the slopes of the $T^{l}(x_2)$ and $T^{n}(x_2)$ curves depend on properties of the pure liquid crystal and additionally the ratio of the activity coefficients of component 2 in the nematic

TABLE II

Transition temperatures for MBBA(1) + 4-methoxybenzaldehyde(2) mixtures
T^n nematic to two-phase transition temperature; T^i two-phase to isotropic transition temperature

x_2	T^n/K	T^i/K
0.01010	317.83	318.01
0.01126	317.55	317.71
0.01680	316.41	316.63
0.01858	316.13	316.36
0.02910	313.99	314.33
0.03810	312.23	312.75
0.04799	310.46	310.97
0.05431	309.10	309.69
0.05909	308.12	308.86

and the isotropic phases respectively. Similar values of this ratio have been found in gas-chromatographic experiments.[19,20] All these investigations confirm the well-known rule that the influence of a component added depends more strongly on its size and shape than on its polarity.

c) Determination of the amount of impurities in a liquid crystal

Because of their high instability against hydrolysis the most frequent impurities of liquid crystals will probably be their hydrolysis products. Since

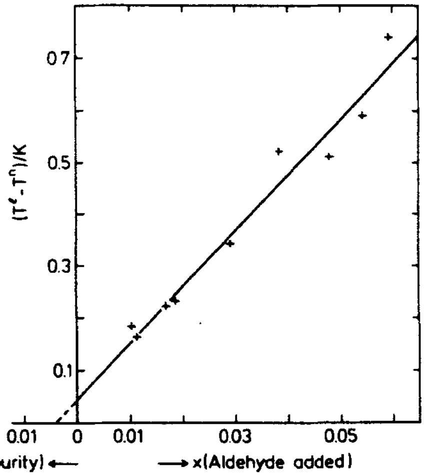

FIGURE 2 Purity control of liquid crystals from nematic–isotropic transition temperatures (see text).

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these hydrolysis products rather often resemble in size and shape, the ratio of the activity coefficients mentioned above can be assumed to be essentially the same for all impurities present in the liquid crystal and consequently the total amount of these impurities can be calculated from the phase diagram of mixtures of the liquid crystal with one of its hydrolysis products.

For purity control T^l and T^n are determined experimentally (e.g. by calorimetry) for the liquid crystal under test as well as for several mixtures (or at least one) with small but known mole fractions x_2 of one of its hydrolysis products (component 2). From the plot of $\Delta T \equiv T^l - T^n$ against x_2 the mole fraction of impurity in the original sample can be extrapolated at $\Delta T = 0$.

The procedure is illustrated in Figure 2 using results of this work. From Figure 2 a purity of 99.6 mol % is extrapolated for the MBBA used in analogy with a value deduced from DSC investigations by Sandrock.

The procedure is supposed to be applicable to other liquid crystals too. The advantages with respect to other methods are easy performance, little thermal decomposition, and others. For a similar method see Ref. 4.

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