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Effect of Specific Intermolecular Interactions on the Properties of Cyano-Substituted Nematics Mixed with Azoxy Compounds of Low Polarity†

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Phase transition temperatures, densities, rotational viscosities and their activation energies are determined for 4-cyano derivatives of biphenyl (4-cyano-4′-pentylbiphenyl and 4-cyano-4′-heptylbiphenyl) and phenylcyclohexane (trans-4-heptyl-(4′-cyanophenyl)-cyclohexane and trans-4-pentyl-(4′-cyanophenyl)- cyclohexane) mixed with azoxy compounds (4-butyl-4′-methoxyazoxybenzene and 4-butyl-4′-heptanoyloxyazoxybenzene). Macroscopic properties of the mixtures comprising 4-cyano-4′-alkylbiphenyls (CB) as the polar compounds are found to differ significantly from those comprising trans-4-alkyl-(4′-cyanophenyl) cyclohexanes (PCH). The results obtained are discussed in terms of specific intermolecular interactions and associate formation.

1. INTRODUCTION

In recent years extensive studies have been made on nematic mixtures containing components of different polarities. Cyano derivatives of different chemical classes are commonly used as high-polarity components, while the other components are chosen from alkyl- or alkoxysubstituted azo- and azoxybenzenes, benzylidene anilines and

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other compounds of relatively low polarity. Such systems are characterized by a number of macroscopic parameters showing anomalous behaviour.[1,2] One of the unusual properties is the possibility of induced smectic phase formation.[3,4] This phenomenon is generally interpreted in terms of the formation of intermolecular associates or complexes as a result of specific interactions between the molecules of different components.[5] Little, however, is definitively known about the intermolecular interactions, and knowledge of the greatest possible number of parameters affected by the interaction is needed to enlighten the situation.

Earlier[6-8] we reported on clearing temperatures T_c, rotational viscosities γ_1, activation energies E, and elastic constant ratios K_{33}/K_{11} versus concentration for mixtures of 4-heptyl-(4′-cyanophenyl)cyclohexane (PCH-7) with nematic azoxy compounds. Essential non-additivity of the above-mentioned properties was tentatively explained by a possible formation of intermolecular associates. This system proved to be convenient for investigation due to its broad nematic range and the absence of any smectic phases up to -5°C for all concentrations of the cyano derivative.

In this paper results of our further studies are reported. Assuming the molar volume V to be strongly influenced by intermolecular interactions, we carried out density measurements in several liquid crystalline mixtures. It was noted earlier that the intermolecular interactions may differ significantly with biphenyl and phenylcyclohexane cyano derivatives;[6,9] therefore, to enable a comparison we made measurements with both PCH and CB as polar components.

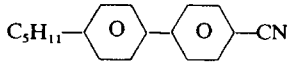
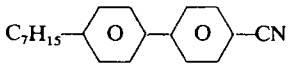
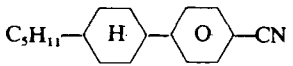
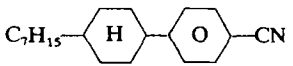
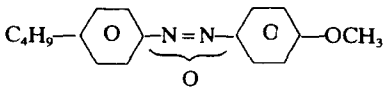
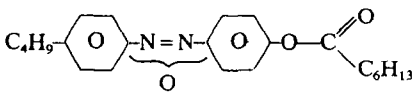
2. EXPERIMENTAL

The structural formulae, clearing temperatures (T_c), molecular mass (M), van-der Waals volumes of the molecules (V), molecular packing coefficients K of the substances studied are given in Table I. 4-cyano-4′-alkylbiphenyls 5CB and 7CB and trans-4-alkyl-(4′-cyanophenyl) cyclohexanes PCH-5 and PCH-7 were chosen as components of high polarity. The low-polarity components used were azoxycompounds 1OBAB, 6COBAB and their mixture (2:1 by weight). One should note that 1OBAB is an alkyl-alkyloxy derivative, while 6COBAB is an alkyl-acyloxy one. Phase transition temperatures were determined using a "Mettler-5" hot stage with a polarizing microscope.

Rotational viscosities γ_1 were determined from the relaxation time of Freederiks transitions in the planar NLC layer deformed by an

TABLE I

Liquid crystalline substances and their properties

Nomenclature	Structural formula	Chemical designation	T_m, °C	T_c, °C	M	V $10^{-24}cm^3$	K (40°C)
CB-5		4-cyano-4′-n-pentyl-biphenyl	24	35.3	249,358	268.4	0.6523 (isotropic phase)
CB-7		4-cyano-4′-n-heptyl-biphenyl	30	42.8	277.412	302.6	0.6507*
PCH-5		trans-4-pentyl-(4-cyanophenyl)-cyclohexane	30	57	255.406	283.2	0.6333
PCH-7		trans-4-heptyl-(4-cyano-phenyl)-cyclohexane	30	55	283,460	317.4	0.6224**
1OBAB		4-butyl-4′-metoxyazoxy-benzene	19	71	284.363	284.0	0.6597
6COBAB		4-butyl-4′-heptanoyloxy-azoxybenzene	37.9	79.4	382.509	371.3	0.6228
MxBAB	Mixture 1OBAB and 6COBAB (2:1 weight)		−5	72	310.939***	307.6***	0.6447

*Calculated according to ref. 12.
**Calculated using a ratio of the densities of PCH-5 and PCH-7 according to ref. 14.
***Calculated according to the properties of components.

external electric field.[10] The activation energies E were determined by the slopes of the $\ln\gamma_1$ - T^{-1} Arrhenius plot, assuming the relationship $\gamma_1 \sim \exp(E/kT)$ to hold at temperatures of 5-10° below T_c.

Density (ρ) measurements were carried out in standard picnometers of 3 cm^3 volume with the accuracy of $\pm 2 \cdot 10^{-4} g/cm^3$. The ρ values obtained agree well with those reported in.[11-13] Absolute ρ values for PCH substances presented in [14] appear to be over-estimated, presumably due to calibration errors, though relative density values for different series members are the same as ours.

3. RESULTS AND DISCUSSION

Temperature dependences of densities ρ were obtained for PCH-5 + MxBAB, PCH-5 + 1O BAB, PCH-5 + 6COBAB systems in all the concentration range and for the 5CB + MxBAB system in a mixture containing 40wt.% of 5CB. The character of intermolecular interactions in mixtures is more clearly reflected by values of some related properties than of density itself, namely, by deviations of the molar volume $V = M/\rho$ isotherm from the ideal behavior (i.e., by excess the volume V^E, if both components and their mixtures are in the same phase at a certain temperature, or by the volume of isothermal mixing V^S, if the components and mixtures are in different phases at the temperature of interest). We have analyzed V^E values, which were compared sometimes with V^S values. Excess volumes were calculated from the relationship $V^E = V - (V_1x_1 + V_2x_2)$, where V is the experimental molar volume for the mixture containing, respectively x_1 and $x_2 = (1 - x_1)$ mole fractions of each of the components, their molar volumes as individual substances being V_1 and V_2. The accuracy of V^E determinations was estimated as $\Delta V^E = \pm 0.1 - 0.2$ cm^3/mol.

$V^E(x)$ isotherms for PCH-5 + MxBAB and 5CB + MxBAB systems are shown in Figure 1. In the nematic phase $V^E > 0$, and the concentration dependence has a maximum at $x_{PCH} \approx 0.5$. The maximum becomes less pronounced at higher temperatures. In the isotropic phase $V^E < 0$, and the concentration dependence $V^E(x)$ has a minimum at $x_{PCH} \approx 0.5$. The fact of V^E having opposite signs in the nematic and isotropic phases, to our knowledge has not yet been reported. For similar mixtures of 5CB with 4,4'-dipentylazoxybenzene (DPAB) and 4-ethyl-4'-pentylazoxybenzene (EPAB) V^E (or V^S) values were negative for both nematic and isotropic phases[13] (Figure 1, curve 5,5', 6, 6'). Our V^E values for 5CB + MxBAB mixtures are also negative.

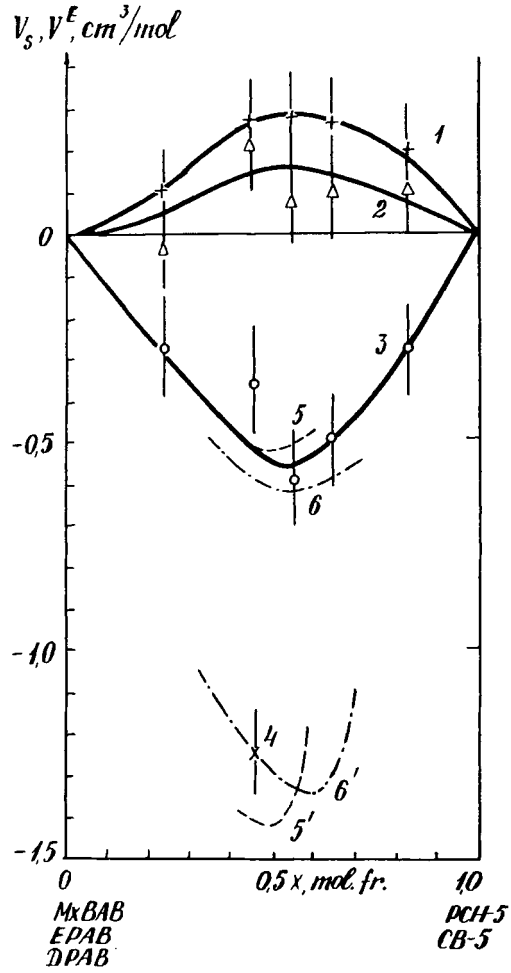


FIGURE 1 Isotherms of the excess volume V^E (curve 1-6) and the volume of the isothermal mixing of the solution V^S (curves 5',6') for the mixtures of cyanoderivatives with liquid crystalline azoxybenzenes.
1,2,3, - PCH-5 + MxBAB (1 (+) – t = 40°C, 2 (△) – t = 50°C, nematic phase; 3 (○) – t = 75°C, isotropic phase); 4(x) – CB-5 + MxBAB (t = 75°C, isotropic phase); 5, 5' – CB-5 + EPAB (5 – t = 75°C, isotropic phase; 5' – t = 52°C – nematic phase); 6,6' – CB-5 + DPAB (6 – t = 75°C – isotropic phase; 6' – t = 30°C – nematic phase). Curves 5,5', 6,6' are taken from 13.

The presence of extrema on the $V^E(x)$ curves is an indication of specific intermolecular interaction which can lead, as it is argued in [13], to the formation of associates composed of the molecules of different polarity. The character of this interaction is, however, quite different in the nematic and isotropic phases of the PCH-5 + MxBAB

system. Positive V^E values in the nematic phase imply that the presumed mixed associates occupy greater volume than needed by the constituent molecules in the absence of specific interactions.In the isotropic phase the picture is reversed, i.e., associate formation leads to an increase in packing density. Consequently, the associates in the nematic phase of PCH-5 + MxBAB may be called "loosening" and those in the isotropic phase "condensing". In the mixtures involving biphenyls, associates are "condensing" in both phases, being relatively more "loosening" in the isotropic phase.

The difference between V^E (or V^S) concentration dependences obtained in the PCH and CB mixtures may be tentatively explained in terms of steric factors due to the different associate shapes. In fact, with CB mixtures a rod-like associate shape may be naturally assumed, due to the fact that both CB and azoxy compounds possess conjugated bond systems, with a possibility of the π-electron clouds of interacting molecules overlapping. Such associates with coplanar phenyl rings were considered in ref. 5. This special configuration is stericly favourable in the orientationally ordered nematic phase. Above the nematic—isotropic transition such associates are naturally getting more "loosening" because of greater freedom of molecular orientations. In the case of PCH molecules, the extent of conjugation is shorter, and the volume of cyclohexane ring is somewhat greater than that of phenyl one. The associate shape may be consequently different (e.g., long axes of the constituent molecules may not be parallel). Then in the nematic phase such an associate would be sterically unfavourable, i.e. "loosening". In the isotropic phase the same associate may become "condensing" because mutual attractions of constituent molecules are no longer hindered by orientational order. Above we have considered that the shape of the associate structure is invariable. But one should note that the associate shape itself may be influenced by short-range order.

The difference described above of the associate structure in the MxBAB + PCH -5 and MxBAB + 5CB mixtures is supported also by the concentration dependences of clearing temperatures T_c (Figure 2). Both systems are characterized by positive deviations from additivity, which supports the idea of associate formation. For the PCH mixtures these deviations are noticeablly smaller, implying, apart from weaker specific interactions, a negative influence of steric factors upon molecular packing and orientational order. A comparison of T_c (x) curves for PCH-7 and PCH-5 shows that the effect of alkyl chain length is but a minor one.

Rotational viscosity and its activation energy data presented in

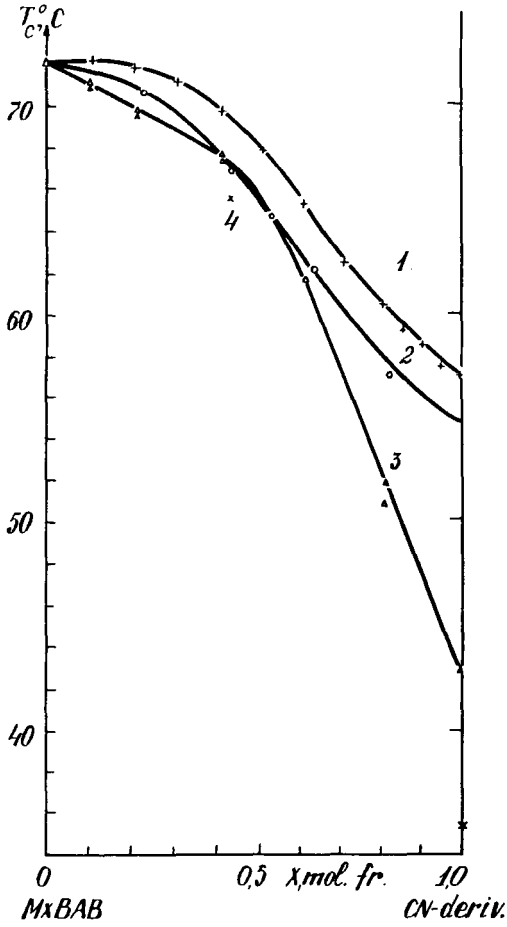


FIGURE 2 Clearing temperatures of the mixtures:
1 – PCH-7 + MxBAB (+ – +); 2 – PCH-5 + MxBAB (O – O); 3 – CB-7 + MxBAB (△ – △); 4 – CB-5 + MxBAB (x).

Table II also point to weaker specific interactions in the PCH-5 + MxBAB system as compared with the 5CB + MxBAB one. The E values in mixtures are lower than in the pure components, reflecting changes in intermolecular interaction (a complete set of experimental data on E and γ_1 concentration dependences in the PCH-7 + MxBAB system is presented in refs. 6 and 7). The change in the E value is less pronounced with the PCH mixture, which is obviously due to the factors explained above.

A matter of additional interest for the present investigation is

TABLE II

Rotational viscosity γ_1 and its activation energy of the cyanoderivatives nematic liquid crystals and its mixtures with MxBAB

NLC	E, eV	γ_1, Poise (25°C)
CB-5	0.55	0.82
PCH-5	0.41	0.97
MxBAB	0.435	1.95
40 weight % CB-5 + 60 weight % MxBAB	0.37	1.25
40 weight % PCH-5 + 60 weight % MxBAB	0.36	1.23

to eliminate the effects caused by MxBAB being a mixture of two components—1OBAB and 6 COBAB (see Table I), the molecules of which differ both in length and in structure of one of the end chains. Phase diagrams for mixtures of these substances with PCH-5 are presented in Figure 3. It can be seen that introducing $O-C(=O)-C_6H_{13}$ instead of $-O-CH_3$ does substantially increase the molecular polarizability and its anisotropy, leading, apart from the induced smectic-A phase formation, to a large increase in T_c.

Concentration dependences of excess volumes, presented in Figure 4, also differ from each other substantially. V^E values in both nematic and isotropic phases are negative in the main for PCH-5 + 1OBAB mixtures and positive for PCH + 6COBAB mixtures. PCH-5 and 1OBAB molecules, being of practically equal volume (Table I), form associates which are packed more densely than would be the case of ideal mixtures.

The exceptions are the PCH-5 concentrations less, than 0,4 in the nematic mixture or less than 0,2 in the isotropic phase, where a "loosening" is observed. At present we can not comment on the fact. Let us only note, that the "condensing" and "loosening" effects in the nematic mixtures of PCH-5 + 1OBAB (for $t > 30°C$ $|V^E| < 0{,}3$ cm^3/mol) are weak and the V^E concentration dependence assumes a complicated form. In the case of 6COBAB + PCH-5 mixtures, due to the size difference of specifically interacting molecules and greater flexibility of the heptanoyloxy group, more empty space can be left, causing an increase in the molar volume of the mixture. Although the $V^E(x)$ isotherms are different, the two systems, may be described in principle by the same reasoning as applied to the mixed PCH-5 + MxBAB systems. This is reflected by the inequalities V^E(nem.) >

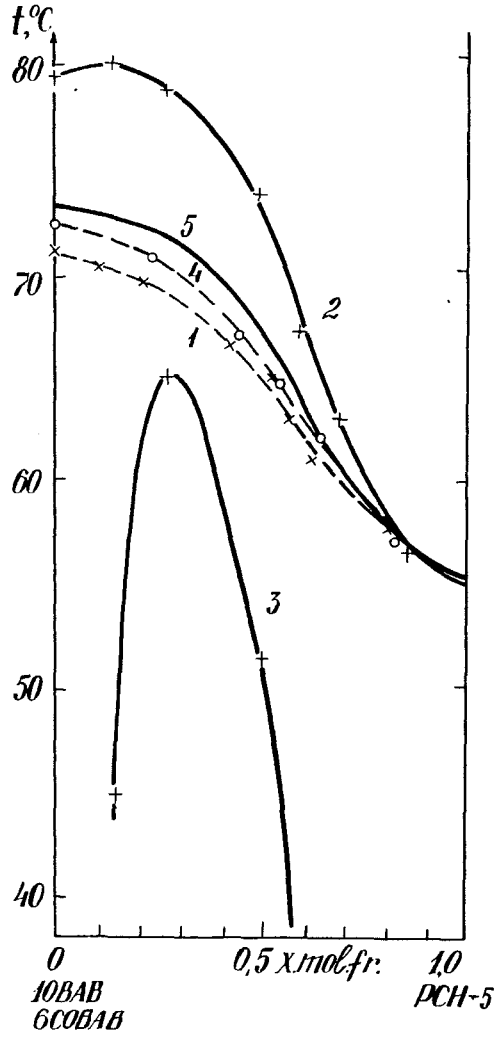


FIGURE 3 Phase diagrams of the mixtures PCH-5 with the components of MxBAB. 1) T_c of the mixtures 1OBAB + PCH-5; 2) T_c of the mixtures 6COBAB + PCH-5; 3) T_{SN} of same mixtures; 4, 5) T_c of the mixtures PCH-5 + MxBAB (4 – measured, 5 – calculated from the curves 1,2).

V^E(iso) remaining true in all the cases, i.e., associates of PCH-5 and azoxy molecules "loosening" the nematic mesophase. Therefore, no direct comparison is possible for the PCH-5 + 1OBAB system and, e.g., 5CB mixtures with 4-dialkyl-4'-azoxy-benzenes.[13]

The "loosening" effect of the nematic phase in comparison with

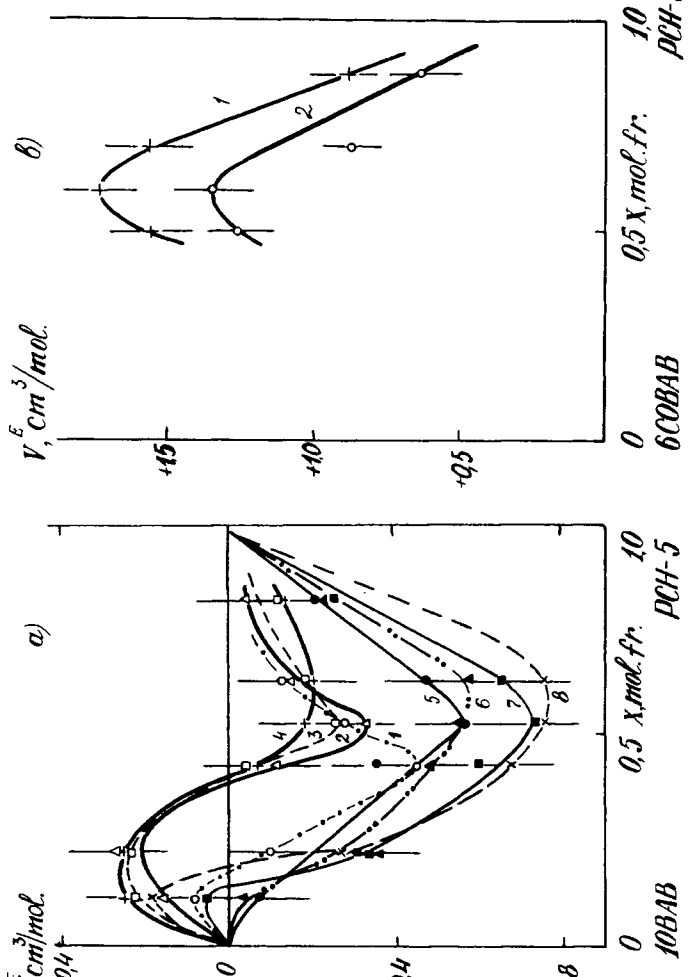


FIGURE 4 Isotherms of the excess volume of the systems
a) PCH-5 + 10BAB and b) PCH-5 + 6COBAB.
a) 1–4—nematic phase: 1 (○—·—·—○) – t = 20°C; 2(Δ—Δ) t = 30°C; 3(□——□) – t = 40°C; 4(+——+) – t = 50°C; 5–8—isotropic phase: 5(●——●) – t = 75°C; 6(▲—▲) – t = 80°C; 7(■——■) – t = 85°C; 8 – (×——×) – t = 90°C;.
b) 1(+——+) – t = 50°C – nematic phase; 2(○—○) – t = 85°C – isotropic phase.

the isotropic one (V^E(nem) > V^E(iso)) is described, e.g. for the mixture system of 4-ethoxy-4′-pentanoyl- and 4-ethoxy-4′-nonanoyloxyazobenzene [15]. V^E concentration dependencies are similar to these ones for the PCH-5 + 1OBAB system (figure 4a). In this case, the authors explain the observed phenomena mainly due to the steric factors.

One should note that properties of PCH-5 + MxBAB mixtures cannot be regarded as a linear superposition of the properties of PCH-5 + 1OBAB and PCH-5 + 6COBAB mixtures. Thus, the would-be additive $T_c(x)$ is higher than that observed in reality (Figure 3). Besides that, V^E values, calculated for the PCH-5 + MxBAB system from the data of Figure 4, also exceed the experimental ones. The latter seems to take place due to the large negative excess volume of the mixture MxBAB itself V^E (40–80°C) = -1.10 ± 0.20 cm^3/mol.

Considering V^E (x) changes with temperature, we note that for the 1OBAB + PCH-5 system in the nematic phase ($0 <$ xPCM-5 $< 0{,}6$), V^E is increased when the temperature is increased ($dV^E/dT > 0$); in the isotropic phase the sign is reversed. For the 6COBAB + PCH-5 system V^E is temperature independent within the limits of our experimental error. Positive $\frac{dV^E}{dT}$ values in the nematic phase are presumably caused by orientational disordering upon heating, while negative $\frac{dV^E}{dT}$ in the isotropic phase may be due to the gradual weakening of specific interactions.

The location of the V^E extreme points on the $V^E(x)$ concentration curves for the PCH-5 + 1OBAB, PCH-5 + 6COBAB systems shows the approximate stoichiometry 1:1 of associates formed by PCH-5 and azoxycompounds molecules, as well as for the PCH-5 + MxBAB system (figure 1). However, we should note, that the $T_{SA\text{-}N}$ maximum in the 6COBAB + PCH-5 system is observed for the concentration $X_{PCH\text{-}5} \approx 30$ mole %. The same shift is observed in the PCH-7 + 4-hexyloxyphenyl-4′-pentylbenzoate.[16]

As we have shown, the excess volume data allowed us to make some conclusions about the nature of specific intermolecular interactions. Further information can be obtained from the molecular packing coefficient K, which is defined, according to ref. 17, as

$$K = \frac{N_A v}{V},$$

where N_A is Avogadro's number, and v is the van-der-Waals volume of the molecule. The value of v was calculated from the increments of van-der-Waals volumes of the atoms;[18] the v value for —N=N—

group was estimated using the mean values of atomic van-der-Waals radii and averaged chemical bond lengths.[18]

Van-der-Waals volumes of the molecules and molecular packing coefficients K for the substances studied are presented in Table I. Addition of two- —CH_2— groups to the alkyl chain leads to a decrease in K by about 0.01. This is understood in terms of lateral group interaction and greater alkyl chain flexibility. One should note a substantial decrease of K when the phenyl ring is replaced by cyclohexane one. It appears to be a consequence of at least two reasons. Firstly, there is a change in the character of specific intermolecular interaction due to weaker attractions in the absence of π-electrons, and secondly, the size of cyclohexane ring is somewhat greater, resulting in less dense packing and increased free volume.

4. CONCLUSIONS

In the mixtures of polar 4-cyano substituted nematogens with azoxy compounds of low polarity, mixed associate formation does occur. The nature of the associates depends upon the mixture composition; consequently, differences in macroscopic properties may be discussed in terms of differences in specific intermolecular interaction and packing facilities.

When a phenyl ring is replaced by a cyclohexane one in a 4-cyano substituted namatogen, the molecular packing coefficient decreases. In the mixtures with azoxy compounds the following changes are noted: deviations of clearing temperatures from additivity are decreasing, concentration-dependent minima of rotational viscosity activation energies become less pronounced, excess volumes in the nematic phase change sign and become positive ("loosening" of the nematic phase). When in an azoxy compound a short alkoxy group is replaced by a longer and more polarizable acyloxy group, the molecular packing coefficient decreases, and in the mixtures with p-cyano substituted nematogens induced smectic phase formation occurs, the excess volumes change sign from negative to positive in both nematic and isotropic phases, and deviations of clearing temperatures from the additive values become more pronounced.

Further research is needed to obtain complete sets of macroscopic parameters for different mixtures of alkyl-, alkoxy- and acyloxyazobenzenes with 4-substituted nematics of different chemical classes. Such data would enable clearer understanding of intermolecular interaction phenomena in mesophases.

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