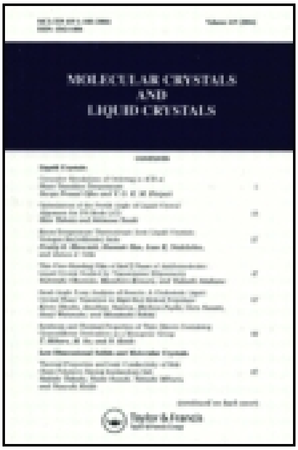

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A Van Der Waals Model for the Nematic Liquuid Crystal Mixtures

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A VAN DER WAALS MODEL FOR THE NEMATIC LIQUID CRYSTAL MIXTURES

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Abstract Phase diagrams and excess molar volumes of binary nematogenic mixtures are investigated in the frame of a van der Waals - type theory for systems made up of hard rectangular parallelepipeds. It is shown that the excess volumes can be positive or negative or can change sign depending on temperature and composition. In agreement with experiment the model predicts a coexistence of two nematic phases for mixture of rod-like and plate-like molecules.

A generalized van der Waals theory of nematic liquid crystal includes self-consistently both the repulsive and attractive pair-intermolecular interactions [1]. In the present paper the van der Waals approach is extended to the case of nematic mixtures of hard rectangular parallelepipeds with dimensions $A_{1K} * A_{2K} * A_{3K}$ (k is the index of component) with their principal axes constrained along the space-fixed directions. The steric contribution to the free energy is adopted from our earlier work [2]. The attraction term, F_{attr}, is evaluated by dividing the volume V of the system into cells of volume ΔV, the size $(\Delta V)^{1/3}$ of the cell being large compared to the range of intermolecular repulsion. Then in the mean-field approximation it holds [3,4]:

$$F_{attr} = -\frac{1}{2V}\sum_{K}\sum_{l} N_K N_l \sum_{\alpha}\sum_{\beta} s_{\alpha K} s_{\beta l} u_{\alpha K,\beta l}(\Delta V - v_{\alpha K,\beta l})$$

Here the $s_{\alpha K} = N_{\alpha K}/N_K$ are the fractions of particles of type k having orientation α, $u_{\alpha K,\beta l}$ and $v_{\alpha K,\beta l}$ are the effective attraction and the mutually excluded volume [3], respectively, for a pair of molecules whose orientations are α and β. For biaxially symmetric molecule six orientations are allowed, i.e. $\alpha = 1,\ldots,6$.

Recently, this approach was applied to binary systems with 4,4′-di-n-alkoxyazoxybenzenes and it was shown that the nematicisotropic temperatures were in a good agreement with the experimental data [4]. In the present study we examine excess volumes for mixtures of two nematic liquid crystals, since none of the models have described excess thermodynamic functions for such systems so far. The occurence of a coexistence region of two nematic phases for the liquid crystal mixture of rod-like and plate-like molecules is also demonstrated.

Here we consider the binary mixture of axially symmetric particles, i.e. $\alpha = 1,2,3$ for each kind of molecules. The contribution F_{attr} is estimated after use of decoupling of the intermolecular repulsions and attractions, i.e. it is assummed, that $\Delta v = \Delta V - v_{\alpha K,\beta \ell}$ does not depend on orientations of the particles.

Two types of attraction parameters were introduced in all the calculations: $u_{\alpha K,\alpha \ell} = u^{(K\ell)}$ and $u_{\alpha K,\beta \ell} = \delta^{(K\ell)} * u^{(K\ell)} (\alpha \neq \beta)$ are the effective attraction energies between parallel and perpendicular particles respectively. The molecular data and the calculated transition parameters for pure components are summarized in Table 1, where v (nm^3) and γ are the molecular volume and length-to-width ratio, η, ρ_N, ρ_I, $\Delta\Sigma/k$ are the order parameter, densities of coexisting phases and the entropy of transition, respectively; $C = \Delta v/kT_{NI}$. All the calculations were done at constant pressure of 1 atm. For convinience sake, the parameters $u^{(KK)}$ were chosen to produce the transition temperature T_{NI} = 409 K for all the components investigated.

TABLE 1 The parameters for the pure components.

	rods		plate		rods		plate
	1	2			1	2	
v	0.23	0.28	0.40	η	0.558	0.586	0.515
γ	1.6	1.8	0.6	ρ_N	0.6146	0.5571	0.5455
$Cu^{(KK)}$	22.1974	15.8614	25.8668	ρ_I	0.6114	0.5510	0.5408
$\delta^{(KK)}$	0.9739	0.9634	0.9514	$\Delta\Sigma/k$	0.308	0.360	0.301

In order to investigate the excess molar volumes V^E the effective attraction energies between different kinds of molecules are varied as fitting parameters. Numerical results are represented in terms of the parameters k_{12} and l_{12} specifying deviations from the geometric mean for attractive forces as follows: $u^{(12)} = k_{12} (u^{(11)} * u^{(22)})$, $\delta^{(12)} = l_{12} (\delta^{(11)} * \delta^{(22)})$. The V^E values for the mixture of rod-like molecules of species 1 and 2 are displayed in Figure 1 as functions of mole fraction x to-

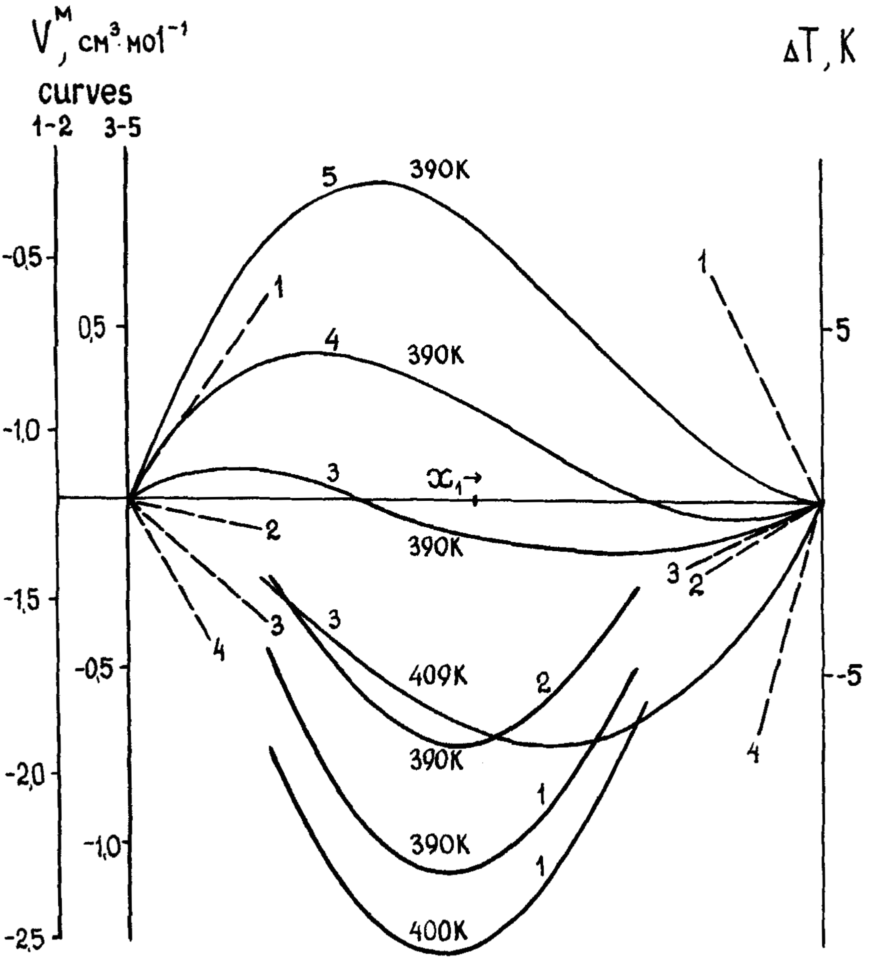

Figure 1 Isotherms of the excess volumes vs. mole fraction x. The limiting slopes of the nematic phase boundaries are shown as dashed lines. The slopes and curves 1 - 5 are calculated for the fixed pairs of values of k_{12}, l_{12}, respectively: 1 , 1; 1 , 1.0035; 0.95 , 1; 0.95 , 1.0035; 0.94 , 1.0035.

gether with limiting slopes of the nematic phase boundaries $\Delta T_N = x \cdot \lim_{x \to 0} (dT_N / dx)$.

As can be seen the binary mixtures studied exhibit different kinds of deviations from ideal behavior. If the geometric mean rule for attractive forces does hold ($k_{12} = l_{12} = 1$), $V^{\varepsilon} < 0$ in the whole composition range. The absolute magnitude of V^{ε} is found to decrease under the influence of the following factors: 1) as the temperature decreases, 2) as the attractions between parallel particles become weaker ($k_{12} < 1$), 3)as the attractions between perpendicular particles become stronger ($l_{12} > 1$). The latter factor stimulates sterically unfavourable configurations of molecules and therefore may cause the change of sign of the V^{ε}.

It is noteworthy that the present analysis provides decent agreement with experiment for the temperature and concentration dependence of the V^{ε} for systems without specific interactions. The decreasing of the V^{ε} upon decreasing of temperature and the change of the sign is a type of behavior of the V^{ε} observed by van Hecke and Theodore [5] in binary mixture of the low-polarity nematogen homologues.

The second aim of the present study is an application to the case of mixtures made up of rod-like and disk-like nematogens. The main prediction of several theoretical studies reported up to date concerned the occurence of a biaxial phase, which has not been, however, observed in any thermotropic system. Recently, Pratibha and Madhusudana found experimentally the coexistence of the nematic phases one relatively rich in rod-like molecules (N_R) and the other in plate-like molecules (N_P) [6]. The numerical evidence for the coexistence of the two types of nematics is to be seen from the phase diagram for the mixture of rod-like and plate-like molecules (see Table 1 for the pure components) pictured in Figure 2. In this case $k_{12} = 1.05$, i.e. the attractive forces tend to favour parallel configurations of molecular pairs

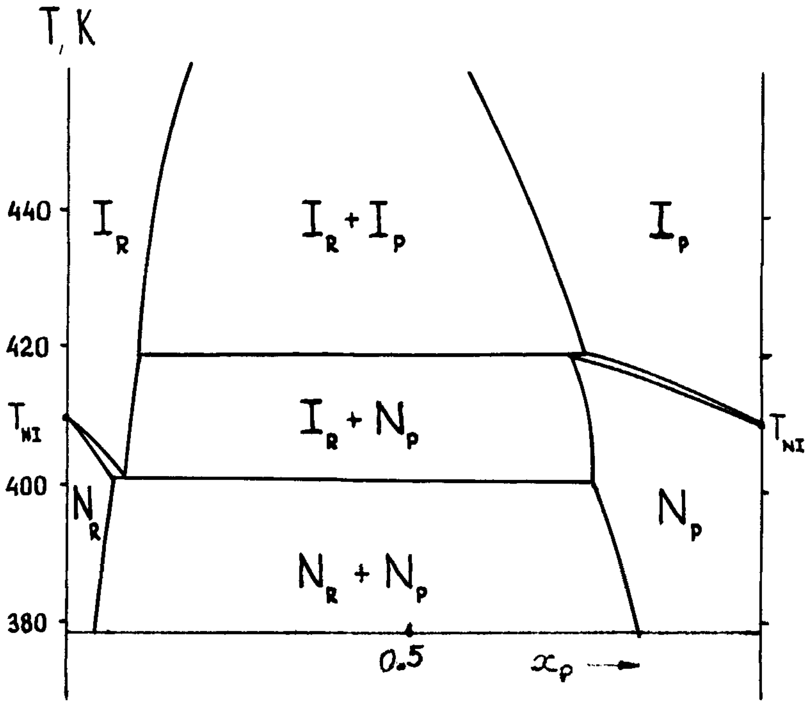

Figure 2 Phase diagram for mixture of rod-like (R, species 1) and plate-like (P) nematogens obtained for $k_{12} = 1.05$, $l_{12} = 1$.

composed of rod and plate. In the case $k_{12} = l_{12} = 1$ the components studied are almost immiscible in the nematic state.

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