In search of a predictive molecular-based model of nematic solutions

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Abstract

The athermal model of a binary rectangular-parallelepiped fluid, continuous in translations and discrete in orientational distribution, is used for calculations of infinite dilution activity coefficients, γ^∞, of nonmesogenic solutes dissolved in nematic and isotropic phases of model nematogens. The particles having D_{2h} symmetry were chosen so as to model molecules of *meta-* and *para*-xylenes (nonmesogens) and the first five homologues of 4,4′-alkyloxyazoxybenzenes (nematogens). The calculations of γ_i^∞ ($i = m, p$ denotes isomers of xylene) for various values of the relative temperature, $t*$, have explicated different characters of the functions $\gamma_i^\infty(t*)$ for the isotropic and nematic phases. The ratio $\gamma_m^\infty / \gamma_p^\infty$ is less than 1 and practically constant in the isotropic phase, whereas in the nematic phase it holds that $\gamma_m^\infty / \gamma_p^\infty > 1$, the ratio increasing with a decrease in $t*$. These features agree with experimentally established regularities and confirm the significance of the effect of the particle biaxiality in interpreting the separation of structural organic isomers with the aid of nematic sorbents. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The problems of molecular modelling of mixtures containing nematic liquid crystals (NLC) are focused on understanding mechanisms governing the long-range orientational ordering of particles as well as on the search of the possible ways for their practical application. The development of methods capable to predict structural and thermodynamic properties of nematic mixtures on the molecular level is motivated by the requirements for the materials consumed in LC-display technologies [1–3]. An important area of the research into thermodynamics of NLC mixtures concerns the study of these materials as high-selectivity stationary phases in gas—liquid-crystal chromatography as well as the

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determination of thermodynamic dissolution characteristics of substances, having various chemical nature, in isotropic and anisotropic phases of NLC [4–7]. Furthermore, the items of the theory of mesomorphic solutions are of great interest for interpreting data on spectroscopic study of solute–solvent interactions, which serves the elucidation of intermolecular forces in mesomorphic systems [8–11].

The statistical-thermodynamic treatment of binary nematic systems is presently performed on the basis of a mean-field theory [9,10], lattice models [12–14] and a generalized van-der-Waals theory [15–17]. Because of a pronounced asymmetry in molecular shape of real mesogens, an important issue of modelling NLC mixtures is the elaboration of approaches towards systems of particles having polar asymmetry or biaxiallity of molecular shape.

The present study is influenced by modern microscopic theories of the mesogenic state, which attribute the correlation structure in nematics to the anisotropy of intermolecular repulsion forces [1,13,15]. This concept initiated model investigations of mixtures of particles having solely hard-core repulsion [18]. Among them the simplest model of a binary fluid of biaxial molecules seems to be represented with a system of hard rectangular parallelepipeds [13,19,20]. Herein we focus on the effect of shape of molecules of solvent and solute on the orientational behavior of nematic solutions as well as on the solute activity coefficients. The special emphasis on the limit of the infinite solute dilution is due to the application of the model results to one of the chromatographic problems, namely, the mechanism of separation of organic structural isomers based on nematic stationary phases. The correlation between the solvent and solute order parameters is also of importance as it would serve the development of interpretation of data obtained from the spectroscopic techniques concerning dilute nematic solutions, the descriptions adding to the current mean-field theories.

The calculations are based on the off-lattice model of a binary rectangular-parallelepiped fluid, continuous in translations and discrete in orientational distribution; three-particle correlations are taken into account. This model, suggested earlier in Refs. [19,20], proved to be successful in studying the thermodynamic properties of nematics and the stability of biaxial nematic phases [21,22]. The present study aimed to elucidate the role of steric interactions in the trends of thermodynamic and structural behavior of real NLC, viz., 4,4′-alkyloxyazoxybenzenes, nonmesogenic admixtures being anthracene and isomers of xylene, molecules of which could be modeled with hard plates having various shapes.

2. Formalism of the off-lattice model for a binary nematic hard-particle mixture

A nematic mixture was modeled with a fluid of $N = N_1 + N_2$ blocks. The constituent particles were specified with volumes ν_l and linear dimensions (edges) $A_1^{(l)} \geq A_2^{(l)} \geq A_3^{(l)}$ (the index $l = 1,2$ labels components). The unit vectors $\vec{e}_i^{(l)}$ ($i = x, y, z$) of the molecular coordinate frame are aligned along the edges $A_1^{(l)}, A_2^{(l)}, A_3^{(l)}$ of a parallelepiped of kind l. Let the director, $\vec{n}$, of the mesophase coincide with the axis Z of the laboratory frame XYZ. If axes of the molecular frame of coordinates are confined to be parallel to axes X,Y,Z of the laboratory frame, then each particle of symmetry D_{2h} ('biaxial') could be adopted into the space in six distinguishable orientations [23,24]. A procedure of labelling orientations with numbers α ($\alpha = 1, \ldots, 6$) can conveniently be performed so as to hold [14,22,24] $\alpha = 2i - 1$; $2i$ ($i = 1,2,3$), if $|(\vec{n}, \vec{e}_i^{(l)})| = 1$. The distribution of particles over orientations

can be described by a set of values $\{s_{\alpha l}\}$ ($s_{\alpha l} = N_{\alpha 1}/N_l$), fractions of particles of sort l having orientation α ($\sum_{\alpha=1}^{6} s_{\alpha l} = 1$).

For a uniaxial nematic phase one has in accord with adopted labelling:

$$s_{1l} = s_{2l}, \ s_{3l} = s_{4l}, \ s_{5l} = s_{6l} \tag{1}$$

In the case of a discreet-orientation model the ordering of the unit vectors $\vec{e}_1^{(l)}$ with respect to $\vec{n}$ is usually defined in terms of statistical averages [14,19,20,23,24]:

$$S^{(l)} = 3s_{1l} - 1/2; \ D^{(1)} = 3(S_{3l} - S_{5l}) \tag{2}$$

referred to as the order parameter and the parameter of biaxiallity $D^{(l)}$. For each of the components in an isotropic phase one has $s_{\alpha l} = 1/6$, $S^{(l)} = 0$, $D^{(l)} = 0$.

In the frame of the off-lattice model, the pressure equation of state for a mixture of rectangular blocks with D_{2h} symmetry is given by:

$$\frac{Pa^3}{kT} = \sum_{l=1}^{2} \frac{\varphi_l}{f_1(\overline{V}-1)} + \sum_{i=1}^{3} \frac{a_i b_i}{(\overline{V}-1)^2} + \frac{2}{(\overline{V}-1)^3} \prod_{i=1}^{3} a_i \tag{3}$$

where V is the volume of a system, $\overline{V} \equiv V/\sum_{l=1}^{2} N_l v_l = 1/\eta$, η is the density (the packing fraction), $a_i = \sum_{l=1}^{2} \varphi_l \sum_{\alpha=1}^{6} s_{\alpha l}/f_{\alpha l}^{(i)}$, $b_i = \sum_{l=1}^{2} \varphi_l \sum_{\alpha=1}^{6} s_{\alpha l} f_{\alpha l}^{(i)}/f_l$, x_l and $\varphi_l = x_l v_l/\sum_{k=1}^{2} x_k v_k$ are the mole and volume fractions of the component of kind l, a is the unit length, $f_l = v_l/a^3$, and $f_{\alpha l}^{(i)}$ is the dimensionless length of an edge of a molecule of a component l with orientation α constrained to be parallel to the direction i.

Given the system is in the orientational equilibrium, the following thermodynamic constraints are necessarily obeyed:

$$\mu_l = \mu_{\alpha l}, \ \alpha = 1,\ldots,6, \ l = 1,2, \tag{4}$$

where $\mu_l = (\partial F_c/\partial N_l)_{T,V,N_{k \neq l}}$ is the chemical potential per molecule of a component l and $\mu_{\alpha l} = (\partial F_c/\partial N_{\alpha l})_{T,V,N_{\beta k \neq \alpha l}}$ is the chemical potential per molecule of a component l having an orientation α.

Accounting for the usual definition of an infinite dilution solute activity coefficient, γ_2^{∞} (taking pure fluid 2 as a reference state), one has:

$$\ln\gamma_2^{\infty} = \ln\left(\frac{s_{\alpha 2}^{\infty} v_2}{s_{\alpha 2}^{0} v_1}\right) + \Phi_1 \frac{v_2}{v_1} - \Phi_2 + \sum_{l=1}^{2} h_l \left\{ \frac{1}{\overline{V}_l - 1} \times \sum_{i=1}^{3} \left[f_{\alpha 2}^{(i)} a_i^{(l)} + \frac{f_2}{f_{\alpha 2}^{(i)}} b_i^{(l)} \right] \right.$$

$$\left. + \frac{1}{(\overline{V}_l - 1)^2} \sum_{i=1}^{3} \prod_{i=1}^{3} a_i^{(l)} \sum_{i=1}^{3} \frac{f_2}{f_{\alpha 2}^{(i)} a_i^{(l)}} \right\} \tag{5}$$

where $h_1 = -h_2 = 1$; $\overline{V}_l = 1/\eta_l$; $a_i^{(l)}, b_i^{(l)}$ are the values of a_i, b_i for a pure component of sort l($\varphi_l = 1$),

$$\Phi_l = \frac{Pa^3 f_l}{kT} = \frac{Pv_l}{kT} \tag{6}$$

η_l and Φ_l are the density and compressibility factor of a fluid of sort l; the superscripts 0 and ∞ denote the orientational state of a pure nematogen and that of a component of sort 2 dissolved in a nematogen.

Since in the athermal model the internal energy of the system is identically zero, thermodynamic properties may be expressed as functions of the reduced temperature [13,22,23]:

$$T* = \frac{kT}{Pv_l} \tag{7}$$

the relationships being independent of the separate variables P and T. Using Eqs. (6) and (7) one can define the relative temperature $t*$, normalized with respect to the reduced temperature of the nematic–isotropic $(T*_{NI})_1$ transition of a pure component 1, as follows:

$$t* \equiv T*/(T_{NI}*)_1 = (\Phi_{NI})_1/\Phi_1 \tag{8}$$

where $(\Phi_{NI})_1$ relates to the point of the NI transition.

3. Computational procedure

It could be seen from Eq. (5), that the behavior of an athermal nematic mixture at infinite solute dilution is governed by the density and orientational properties of the pure solvent, as well as by the ratio v_2/v_1 and by the linear dimensions of particles. In the present study the input model parameters are volumes of particles and their axial ratios, which are defined as $\Gamma_1^{(l)} = A_1^{(l)}/A_2^{(l)}$, $\Gamma_2^{(l)} = A_2^{(l)}/A_3^{(l)}$ ($l = 1,2$ for NLC and nonmesogen, respectively).

The comparison of model particles with real molecules of 4,4′-alkyl-oxyazoxybenzenes (labelled as I—*para*-azoxyanisole; II—*para*-azoxyphenetole; III—4,4′-dipropoxy-; IV—4,4′-dibuthoxy-; and V —4,4′-dihexyloxyazoxybenzene) and isotropic solutes can be performed solely in a simplified manner. The molecular volumes of NLC as well as of solutes were estimated on the base of the Bondi Tables [25]. In the case of nematogens the size of their molecules in the direction of the *para*-axis, $A_1^{(1)}$, was set equal to the distance between the farthest apart carbon atoms of the opposite terminal chains accounting for the dihedral angles between the phenylene rings in the aromatic conjugated core (around 4°) and the conformation of the chains predicted by the CNDO estimations. The value $A_2^{(1)}$ was set equal to twice the radius of revolution of the most distanced carbon atom around the *para*-axis. Consequently, $A_3^{(1)} = v_1/(A_2^{(1)} \cdot A_1^{(1)})$. Thus, e.g., for NLC I it follows that, $v_1 = 0.2324$ nm³, $\Gamma_1^{(1)} = 2.76$, $\Gamma_2^{(1)} = 1.82$. The models of homologous substances following NLC I in the series under study were built by an increment in the molecular volume corresponding to two methylene groups, increasing the longitudinal axis $A_1^{(1)}$ and holding the value of $\Gamma_2^{(1)}$ constant. It should be noted that in the case of real conventional rod-like nematogens the even–odd alternation of macroscopic properties with respect to the carbon number is observed. This results from the alternation of anisotropy of polarizability combined with alternation of axial ratios, both phenomena stemming from the change in longitudinal size of NLC molecules [1]. Hence, the present procedure of constructing the geometrical analogues of 4,4′-dialkyloxyazoxybenzenes may reproduce the trends in

molecular sizes in subseries: I and III and subseries: II, IV and V (in *trans*-conformation).Volumes of *meta*- and *para*-xylenes (denoted by *m* and *p*) and athracene (*a*) are set equal to 0.1174; 0.1174 and 0.1651 nm^3, respectively. As for the axial ratios, they are: $\Gamma_1^{(2)} = 1.81$; 2.41 and 1.73; $\Gamma_2^{(2)} = 1.96$; 1.69 and 2.37, respectively.

4. Results and discussion

The results of computations of properties of the infinitely diluted solutions, including solute activity coefficients, $\gamma_p^{\infty}\gamma_m^{\infty}$, and the order parameters of the model xylenes in the coexisting phases of the pure NLC are presented in Table 1. It is seen that for all the solutes at the nematic–isotropic (NI) transition

$$\frac{\gamma_2^{\infty,N}}{\gamma_2^{\infty,I}} > 1 \tag{9}$$

The inequality (9) has been established for nonmesogens belonging to various chemical classes (normal and branched alkanes, alkenes, dienes, aromatic hydrocarbons, etc.) dissolved in NLC of miscellaneous chemical nature [6,26,27]. Comparing the quantity $\gamma_2^{\infty,N}/\gamma_2^{\infty,I}$ for the model analogues of xylene we infer that the inequality (9) weakens in the case of *para*-substitution, i.e., in the case of a more elongated molecule. This property of nematic mixtures has been observed for real solutions of xylenes in Schiff bases [28], 4,4'-dialkyloxyazoxybenzenes [26] and other NLC [27]. It is also seen that an increase in the longitudinal sizes of model analogues of xylene following the *para*-substitution results in an increase of $S_{\infty}^{(2)}$ and in a decrease of $D_{\infty}^{(2)}$. The similar regularity on $S_{\infty}^{(2)}$ has been observed experimentally for many dyes dissolved in NLC media [29].

Now we turn to specific features of the dependencies of $\gamma_p^{\infty}(t*)$ and $\gamma_m^{\infty}(t*)$ in connection with structural properties of real solutions of *meta*- and *para*- xylenes. These characteristics are of significance for analyzing the factor $\mathbf{S}_{m/p} = \gamma_m^{\infty}/\gamma_p^{\infty}$, coefficient of selectivity of the nematic stationary phase [4,6,28].

Inspection of Table 1 shows, that in all the model systems studied, the inequality $\gamma_m^{\infty} < \gamma_p^{\infty}$ ($\mathbf{S}_{m/p} < 1$) holds at the point of the NI transition of the nematic solvent. In the isotropic solutions, the value of $\mathbf{S}_{m/p}$ is practically independent of $t*$. However, as is seen in Fig. 1, the value of $\mathbf{S}_{m/p}$

Table 1
Limiting values of the activity coefficients and characteristics of the orientational ordering of model xylene isomers in the coexisting phases of model fluids

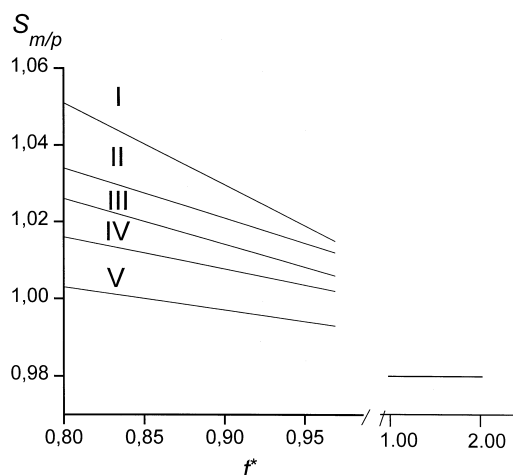| NLC	*para*-(*meta*-)xylenes				
	$\gamma_2^{\infty,I}$	$\gamma_2^{\infty,N}$	$S_{\infty}^{(2)}$	$D_{\infty}^{(2)}$	$\gamma_2^{\infty,N}/\gamma_2^{\infty,I}$
I	0.9435 (0.9328)	0.9947 (0.9895)	0.2145 (0.1684)	0.1221 (0.1595)	1.0543 (1.0608)
II	0.9195 (0.9079)	0.9980 (0.9935)	0.2157 (0.1689)	0.1215 (0.1589)	1.0854 (1.0943)
III	0.8933 (0.8813)	0.9952 (0.9892)	0.2084 (0.1638)	0.1179 (0.1579)	1.1141 (1.1224)
IV	0.8676 (0.8552)	0.9881 (0.9804)	0.1988 (0.1558)	0.1134 (0.1477)	1.1389 (1.1464)
V	0.8266 (0.8147)	0.9740 (0.9640)	0.1784 (0.1399)	0.1039 (0.1347)	1.1783 (1.1833)

Fig. 1. The factor $\mathbf{S}_{m/p}$ vs. $t*$ for infinitely diluted solutions of the model *meta-* and *para-*xylenes in NLC I–V.

grows surpassing a value of unity, if $t*$ is decreased causing an increase of the orientational ordering in NLC. Therefore, a significant feature of nematic fluids is in that following a decrease in $t*$ the positive deviations from the ideal behavior in the solutions of *meta-*substituted molecules having lower symmetry are more pronounced compared to solutions of *para-*isomers. This feature seems to be coupled with the different character of the dependencies $S_\infty^{(2)}(t*)$ and $D_\infty^{(2)}(t*)$ for *meta-* and *para-*isomers.

Indeed, as is seen in Fig. 2 the absolute value of the derivative $|dS_\infty^{(2)}/dt*|$ for *para-*isomer is greater than for *meta-*isomer, whereas in the case of $|dS_\infty^{(2)}/dt*|$, the situation is reverse. Hence, the
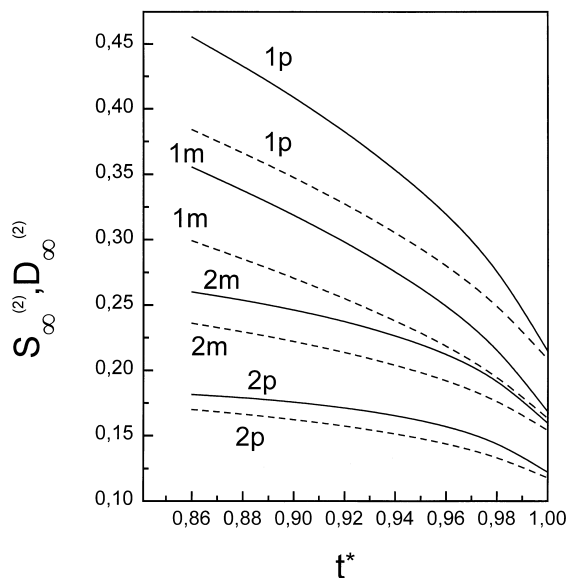

Fig. 2. Order parameters $S_\infty^{(2)}$ (1) and biaxiallity parameters $D_\infty^{(2)}$ (2) of the model analogues of *meta-* (*m*) and *para-* (*p*) xylene in nematic fluids I (solid lines) and III (dashes).

correlation between the long molecular axes of NLC and the *para*-isomer solute may be enhanced with a decrease in $t*$ faster compared to the *meta*-isomer in a nematic matrix. Employing the main ideas of the Onsager theory of nematic ordering in hard-body fluids [30], one may suppose that the predominant entropy contribution to the activity coefficient is the one due to the translational motions, its quantity increasing more steeply with a decrease in $t*$ for *para*-isomer compared to the *meta*-one. As for the orientational entropy, its different variations with temperature for different isomers seem to be of minor significance. It results in that the magnitude of γ_p^∞ becomes smaller compared to γ_m^∞, the value $\gamma_m^\infty - \gamma_p^\infty$ increasing with a decrease in $t*$. Thus, the coefficient $\mathbf{S}_{m/p}$ increases in comparison with its value at the clarification point and is greater than unity, the inequality $\mathbf{S}_{m/p} > 1$ increasing with a decrease in $t*$. The latter agrees with numerous experimental data on solvents of various nature, viz., azoxyethers, azines, azo-derivatives, and esters [4,6,26–28].

As is also seen in Fig. 1 the coefficient $\mathbf{S}_{m/p}$ for fixed $t*$ decreases with a growth in elongation of model NLC particles. These trends agree with experimental observations. We cite the values of $\mathbf{S}_{m/p}$ for NLC homologues under discussion from Ref. [4] (numbers in parenthesis denote temperature of observation/clarification temperature, K): I—1.040 (391.2/408.5); II—1.09 (413.2/439.9); III—1.019 (386.2/398.2); IV—1.069 (375.2/411.3).

One of the basic reasons for this phenomenon involves the manifestation of anisotropy of steric interactions in solutions of NLC characterized with the same transverse sizes but different elongation. It is actually seen in Fig. 2 that the orientational behavior of model xylenes dissolved in fluids I and III, as well as in fluids II and IV, are subject to a depression of $t*$ to a different extent. For a given isomer of xylene under constant $t*$ with transition from NLC I to III and with transition from II to IV, the parameter $D_\infty^{(2)}$ changes insignificantly whence the order parameter $S_\infty^{(2)}$ observably diminishes. This fact, seeming by unusual, may be explained by lowering of density in the model NLC resulting from the elongation of molecules, although the order parameter $S^{(1)}$ grows. Indeed, at the NI transition, η_1 as well as $S^{(1)}$ are 0.3284; 0.2635 and 0.3564; 0.4808 for NLC I and III, respectively; 0.2937; 0.2399 and 0.4290; 0.5202 for NLC II and IV, respectively. Thus, the propensity for parallel alignment of long axes of the solvent and solute, for the less dense media may weaken. A contribution to the entropy of solutes, resulting from this alignment, could be minor compared to that due to an increase in volume of space, where molecules of solutes can move about. This effect seems to be especially pronounced for *para*-xylene and eventually explains a decrease of the value $\gamma_m^\infty - \gamma_p^\infty$ and of the coefficient $\mathbf{S}_{m/p}$, concurrent with an elongation of NLC molecules.

A special point worth mentioning is reproducing in our model estimations the experimentally established linear character (the tangent spanning 0.48–1.25) of the correlation $S_\infty^{(2)}(S^{(1)})$ over the whole temperature interval of the nematic phase for admixtures of various shape and size (anthracene, nitroxides and dyes) in homologous 4,4′-di-*n*-alkyoxyazoxybenzenes, 4-*n*-alkyl-4′-*n*-alkoxytolanes [11]. For example, for the systems I + *a* and III + *a*, the linear dependency $S_\infty^{(2)}(S^{(1)})$ is characterized with tangents 0.6476 and 0.5573, respectively (the coefficient of correlation ≥ 0.995).

5. Conclusions

The present results demonstrate that the off-lattice model provides an adequate approximation for comprehending the influence of the hard-core anisotropy of solvent–solute interactions on the

orientational ordering and on the infinite dilution solute activity coefficients in nematic mixtures composed of biaxial molecules. The main motivation for considering a fluid of hard rectangular parallelepipeds is its relative simplicity and, we believe, its relevance for being employed as a reference system in subsequent inclusion of attractive interactions into the molecular-statistical treatment.

However, the present model is restricted with the case when the molecules of both the solvent and solute are rigid. This is far from a realistic description of concrete nematogens, which typically have flexible terminal and side chains and can undergo conformational transitions. Since at present the multitude of such factors could hardly be incorporated into a molecular model useful for practical calculations, it is important to discriminate the most essential among them and to understand the minimum number of factors required for a model of solutes in nematic solvents, the approach being simultaneously efficient and based on a molecular level.

Acknowledgements

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