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 descrete in orientational distribution is used for calculations of infinite dilution activity coefficients, γ^{∞}, of nonmesogenic solutes dissolved in a nematic and isotropic phases of model nematogens. The particles of nonmesogens having D_{2h} symmetry were chosen so as to model molecules of *meta*- and *para*-xylenes, the particles of nematic components modeled molecules of various homologues of 4,4'-alkyoxyazoxybenzenes. The calculations of γ_i^{∞} (i=m,p denotes isomers of xylene) for various values of the relative temperature, t^*, have explicated different character of the functions $\gamma_i^{\infty}(t^*)$ (i=m,p) 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 $\gamma_m^{\infty}/\gamma_p^{\infty}>1$, the ratio growing with a decrease in t^*. These features agree with experimentally established regularities and confirm the significance of the effect of the particle biaxiallity in interpreting the separation of structural organic isomers with the aid of nematic sorbents. It has also been shown that the correlation between order parameter of a solute and that of a solvent obey the linear law far below (about 35 K) the temperature of the nematic-to-isotropic transition, which agrees with experimental observations.

1. Introduction.

The problems of molecular modeling 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 stationery phases in gas - liquid-crystal chromatography as well as the 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 elucidation of intermolecular forces in mesomorphic systems [8-11].

The molecules forming liquid-crystalline phases often have complicated chemical structure: a lack in molecular symmetry, flexibility of chains attaining central core fragments, *etc*. Thereby practical statistical-thermodynamic treatment concerning systems of interest would inevitably be to a high extent approximate. Among the models presently applied for the study of binary nematic systems, lattice ones would seem embracing both intermolecular repulsion and attraction in the most explicit, although simplified, manner. Lattice models have proven to be useful and versatile in examining the effects of molecular size, shape and flexibility on thermodynamic functions of mixing and on the trends in nematic-to-isotropic (*NI*) transition properties of conventional nematic mixtures [12-14].

A more realistic approach is provided by a generalized van-der-Waals theory, developed for an off-lattice (continuous in mass centres of particles) model of binary mixture of spherical and rod-like molecules [15]. Other studies, which employ the ideas embodied in van-der-Waals-type theories, consider the problem of biaxial-phase formation [16] and the orientational behavior of admixtures in *NLC* solvents [17].

The molecules of real mesogens are often characterized with a pronounced asymmetry of shape. Because of that an important issue of modeling of *NLC* systems is the elaboration of approaches towards system of particles having polar asymmetry or biaxiallity of molecular shape. A substantial insight into the nature of intermolecular forces in mesogenic systems has been got in the frame of the mean-field theory, extended to the case of biaxial solute in a nematic solvent in the studies [9,10]. These theories based on the assumption that the nematic ordering mainly stems from the orientation-dependent intermolecular attractions, are mostly concerned with the analysis of orientational properties of nematic solutions.

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. 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 basing 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 diluted nematic solutions, the descriptions adding to the current mean-field theories.

The calculations are based on the model of muticomponent system of blocks, suggested earlier in ref. [19,20]. We used the off-lattice version of the corresponding theory, i.e. a mixture of parallelepipeds with continuous translation coordinates; three-particle correlations are taken into account. The off-lattice model under discussion has already proven to be successful in studying the trends of orientational ordering in nematic systems [21] and calculation of regions corresponding to the stability of biaxial nematic phases in mixtures of uniaxial rod-like and plate-like particles [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'-alkyoxyazoxybenzenes, a 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.

In this study a binary nematic mixture was modeled with a fluid of $N = N_1 + N_2$ rectangular parallelepipeds. The constituent particles were specified with volumes v_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 sort *l*. Let the axis of the preferential orientation of the mesophase (the director) $\vec{n}$ 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_{4h} (henceforth referred to as "uniaxial" particles) or that of symmetry D_{2h} ("biaxial") could be adopted into the space in 3 or 6 distinguishable orientations, correspondingly [23,24]. A procedure of labelling orientations with numbers a can conveniently be performed so as to hold [14,22,24] $\mathrm{a} = 2i-1$; $2i$ $(i=1,2,3)$, if $|(\vec{n},\vec{e}_i^{(l)})|=1$.

The distribution of particles over orientations can be described by a set of values $\{s_{\mathrm{a}l}\}$ $(s_{\mathrm{a}l} = N_{\mathrm{a}l}/N_l)$, fractions of particles of sort l having orientation a, where in the general case of biaxial particles a =1,..,6 $(\sum_{\mathrm{a}=1}^{6} s_{\mathrm{a}l} = 1)$.

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

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

In the case of a descrete-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 [14,20,23,24]:

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

referred to as the order parameter and the parameter of biaxiallity $D^{(l)}$, the latter being linked with the difference of the average projections of the transverse molecular axes onto the director.

For each of the components in an isotropic phase one has

$s_{\mathrm{a}l} = 1/6$, $S^{(l)} = 0$, $D^{(l)} = 0$.

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 :

$$\frac{Pa^3}{kT} = \sum_{l=1}^{2} \frac{\mathrm{j}_l}{f_l(\bar{V}-1)} + \sum_{i=1}^{3} \frac{a_i b_i}{(\bar{V}-1)^2} + \frac{2}{(\bar{V}-1)^3} \prod_{i=1}^{3} a_i \tag{3}$$

where V is the volume of a system, $\bar{V} \equiv V / \sum_{l=1}^{2} N_l v_l = 1/\mathrm{h}$, h is the density (the packing fraction), $a_i = \sum_{l=1}^{2} \mathrm{j}_l \sum_{\mathrm{a}=1}^{6} s_{\mathrm{a}l} / f_{\mathrm{a}l}^{(i)}$, $b_i = \sum_{l=1}^{2} \mathrm{j}_l \sum_{\mathrm{a}=1}^{6} s_{\mathrm{a}l} f_{\mathrm{a}l}^{(i)} / f_l$, x_l and $\mathrm{j}_l = x_l v_l / \sum_{k=1}^{2} x_k v_k$ 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:

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

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

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

$$\ln\gamma_2^\infty = \ln\left(\frac{s_{\alpha 2}^\infty v_2}{s_{\alpha 2}^0 v_1}\right) + \Phi_1 \frac{v_2}{v_1} - \Phi_2 + \sum_{i=1}^{2} h_l \left\{ \frac{1}{\bar{V}_l - 1} \times \right.$$

$$\left. \times \sum_{i=1}^{3} \left[f_{\alpha 2}^{(i)} a_i^{(l)} + \frac{f_2}{f_{\alpha 2}^{(i)}} b_i^{(l)} \right] + \frac{1}{(\bar{V} - 1)^2} \sum_{i=1}^{3} \prod_{i=1}^{3} a_i^{(l)} \cdot \sum_{i=1}^{3} \frac{f_2}{f_{\alpha 2}^{(i)} a_i^{(l)}} \right\} \tag{5}$$

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

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

ρ_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]:

$$T^* = kT / Pv_l \tag{7}$$

the relationships being independent of the separate variables P and T. Using expr. (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:

$$t^* \equiv T^* / (T^*_{NI})_1 = (\Phi_{NI})_1 / \Phi_1 \quad , \tag{8}$$

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

To check the consistency of the present model with other well-known descriptions of hard-particle fluids, we compare the results for γ_2^∞ for a mixture of parallel cubes having volumes $v_1 = L^3$, $v_2 = (qL)^3$ and for a solution composed of hard spheres having a ratio of their diameters $q = d_2 / d_1$, the latter case having been treated in the frame of the model by Lebowitz and Rowlinson [25].

The values of $ln\gamma_2^\infty$ for mixtures of particles having the ratio of molecular volumes 1:4 are displayed in Table 1. The data show, that although the present model is that of restricted orientations, it provides a reasonable description of the trends in the behavior of smaller particles in the media of larger ones and *v.v.* for various packing fractions of components.

3. Computational procedure.

It could be seen from the eq.(5), that the thermodynamic behavior of an

athermal nematic mixture at an infinite solute dilution is governed by the density, orientational properties of the pure solvent and the solvent-solute repulsion parameters specified by the ratio v_2 / v_1 and by the linear dimensions. In the present study the input model parameters are volumes of particles and their axial ratios, which are defined as $\Gamma_1^{(l)} = A_1^{(l)} / A_2^{(l)}$, $\Gamma_2^{(l)} = A_2^{(l)} / A_3^{(l)}$ (henceforth, we ascribe $l = 1,2$ for *NLC* and nonmesogen, correspondingly).

The comparison of model particles with real molecules of 4,4'-alkyloxyazoxybenzenes (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, *e.g.*, as follows (Table 2). The molecular volumes of *NLC* as well as of solutes were estimated on the base of the Bondi Tables [26]. The thickness of *meta*- and *para*-xylenes (labelled by acronyms m and p) and anthracene (denoted by a) was attributed the value of 0.257 nm, which was believed to adequately rate the thickness of the benzene ring [5]. In the case of *meta*-xylene the longitudinal axis of the particle was drawn through the mass centre of a molecule parallel to the stretch linking the centres of substituents. Then the quantity $G_1^{(2)}$ was set equal to the ratio of this stretch to double the radius of its revolution around the longitudinal axis. 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 from each other carbon atoms of the opposite terminal chains accounting for the dihedral angles between the phenylene rings in the the aromatic conjugated core (around 4^0) 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, $A_3^{(1)} = v_1 / (A_2^{(1)} \cdot A_1^{(1)})$. The models of homologous substances following *para*-azoxyanisole (PAA) in the series of 4,4'-alkyloxyazoxybenzenes 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 $A_2^{(1)}$ constant. It should be noted that thermodynamic properties of real conventional rod-like nematogens are subjected to molecular symmetry as well as to the odd or even carbon number of terminal chains, the even-odd alternation of macroscopic

properties with respect to the carbon number being observed. This results from the alternation of anisotropy of polarizability combined with alternation of axial ratios, both phenomenon 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).

To calculate the characteristics of the *NI* transition in the pure-component fluids, one needs to solve the equation set, including the phase equilibrium conditions $\mu_l^{(N)} = \mu_l^{(I)}$, $F_l^{(N)} = F_l^{(I)}$, and equations of the set (4); if the conditions (1) are obeyed, two equations (4) are needed for each component l having symmetry D_{2h} .

4. Results and discussion.

Table 3 gives thermodynamic characteristics of the *NI* transition in the pure nematic fluids of the model substances I-V, *viz.*, average density, $\bar{\rho} = (\rho^N + \rho^I)/2$, density discontinuity $\Delta\rho/\bar{\rho} = (\rho^N - \rho^I)/\bar{\rho}$, reduced entropy, S_{NI}/kT, the order parameter $S^{(1)}$ and the biaxiallity parameter $D^{(1)}$. Skipping involved details concerning the limitations of the descrete-orientation model which are presented in ref. [22] we draw attention to the comparison of model fluids of uniaxial particles, *viz.*, parallelepipeds and ellipsoids of revolution. It has shown that the present model provides a reasonable description of trends in the *NI* transition parameters following the variation of the molecular shape from the elongated to plate-like; the ellipsoid-of- revolution fluid was continuous in orientational distribution. The estimated parameters $S^{(1)}$, $\Delta\rho/\bar{\rho}$ and S_{NI}/kT span the intervals of values typical for real *NLC* [1]. The reduction of the degree of the first-order character of the *NI* transition compared to the values appropriate to models of uniaxial-symmetry particles is due to lowering of the particle symmetry, which is of significance for

the description of real mesogenic compounds. The parameter $D^{(1)}$, which accounts for particle biaxiallity, increases with a decrease in the axial ratio ξ_1.

It is also noteworthy that the ratio of the reduced densities of pure solute components η_p/η_m for about 80K below their boiling temperature has a constant value 0.996, which practically coincides with a prediction of the correlation method [27].

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 *NLC* are presented in Table4. It is seen that in both coexisting phases of all the *NLC* studied: $\gamma_p^\infty < 1$, $\gamma_m^\infty < 1$. The negative deviations from the ideal behavior are manifested by other athermal isotropic fluids built of rigid low-than-spherical particles having various sizes and shapes [28].

It is also seen in Table 4 that for all the solutes at the *NI* transition

$$\gamma_2^{\infty,N} / \gamma_2^{\infty,I} > 1 \ . \qquad (9)$$

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 [6,29,30]. Earlier the statistical thermodynamic interpretation of this result has been carried out in the frame of lattice models of nematic mixtures, which are built of particles having rigid core with linear sizes $r^{(l)} \times 1 \times 1$ and flexible terminal chains [12,13].

Consider now the estimation of γ_2^∞ given by the present model. 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 [31] , 4,4'-dialkyloxyazoxybenzenes [29] and other *NLC* [30].

In addition, it is 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 lowering of $D_{\infty}^{(2)}$. The similar regularity on $S_{\infty}^{(2)}$ has been observed experimentally for many dyes dissolved in *NLC* media [32].

Now we turn to specific features of the dependencies $g_{p}^{\infty}(t^{*})$ and $g_{m}^{\infty}(t^{*})$ in connection with structural properties of real solutions of *meta*- and *para*- xylenes. These characteristics are of significance for analyzing the factor $S_{m/p} = g_{m}^{\infty} / g_{p}^{\infty}$, coefficient of selectivity of the nematic stationary phase [4,5,31].

It is seen in Table 4, that in all the model systems studied the inequality $g_{m}^{\infty} < g_{p}^{\infty}$ $(S_{m/p} < 1)$ holds in the point of the *NI* transition of the nematic solvent. If t^{*} is lowered causing an increase of the orientational ordering of *NLC*, the coefficient $S_{m/p}$ grows surpassing the unity value. In the isotropic solutions, the value of $S_{m/p}$ is practically independent of t^{*}. 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 turn to be 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.1 the absolute value of the derivative $|dS_{\infty}^{(2)}/dt^{*}|$ for *para*-isomer is greater than for *meta*-isomer, whereas in the case of $|dD_{\infty}^{(2)}/dt^{*}|$ the situation is reverse. Hence, the correlation between the long molecular axes of *NLC* and the

para-isomer solute may enhance with a decrease in t^* faster compared to the *meta*-isomer in a nematic matrix. Employing the main ideas of Onsager theory of nematic ordering in hard-body fluids [33], 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 *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^*. Hereof the coefficient $S_{m/p}$ increases in comparison with its value at the clarification point and turns out to be greater than unity, the inequality $S_{m/p} > 1$ strengthening with a decrease in t^*. The latter agrees with numerous experimental data on solvents of various nature, *viz.*, azoxyethers, azines, azo-derivatives, esters [4,6,29-31].

Fig. 2 presents the dependency $S_{m/p}(t^*)$, which reflects the behavior of model xylenes in nematic fluids I-V. As is seen the coefficient $S_{m/p}$ for fixed t^* decreases, whereas the inequality $d(\mu_m^\infty - \mu_p^\infty)/dt^* < 0$ strengthens, with a growth in elongation of model particles. These trends agree with experimental observations. We cite the values of $S_{m/p}$ 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 - 1.69 (375.2/411.3). One of the basic reasons for this phenomenon is likely in manifestation of anisotropy of steric interactions in solutions of *NLC* belonging to one homologous series and characterized with the same transverse sizes but different elongation. It is actually seen in Fig.1 that the orientational behavior of model xylenes dissolved in fluids I and III are subject to a depression of t^* to a

different extent: for a given isomer of xylene under constant t^* with passage from *NLC* I to III the parameter $D^{(2)}$ changes insignificantly whence the order parameter $S^{(2)}$ observably diminishes. This fact seeming unusual may be explained by lowering of density in the model *NLC* resulting from the elongation of molecules (see Table 3). Hereof, the propensity for parallel alignment of long axes of the solvent and solute may weaken. Hence, a gain in the translational entropy of solutes stemming from this alignment could be in the case of less dense medium a minor contribution to the volume of space, where the solute molecules can move about. This effect seems to be especially pronounced for *para*-xelene and eventually explains strengthening of the inequality $d(\mu_m^\infty - \mu_p^\infty)/dt^* < 0$ concurrent with an elongation of *NLC* molecules.

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 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]. E.g., 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, correspondingly (the coefficient of correlation $\geq$ 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. Further, while more accurate molecular models with a continuous orientational distribution function are necessitated, the basic features concerning the effect of biaxiallity of particles on the excess thermodynamic properties and order parameters appear to be understood in mean features.

However, the present model is restricted with the case, when the molecules of both the solvent and solute are rigid. This is far from realistic description of concrete nematogens, which typically have flexible terminal and side chains and can undergo conformational and torsion transitions in the central core fragment. 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.

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Table 1. Infinite dilution activity coefficients in mixtures of hard spheres [25] and parallel cubes ($v_1 / v_2 = 1/4$).

η_1	spheres			cubes		
	η_2	g_1^∞	g_2^∞	η_2	g_1^∞	g_2^∞
0.3	0.4595	0.8271	0.7495	0.4676	0.8459	0.7820
0.4	0.5534	0.8128	0.7233	0.5612	0.8344	0.7621
0.5	0.6396	0.8015	0.7065	0.6461	0.8250	0.7501

Table 2. Volumes and axial ratios of model analogues of the compounds studied.

Substance	v , nm^3	Γ_1	Γ_2
I	0.2324	2.76	1.82
II	0.2664	3.17	1.82
III	0.3004	3.57	1.82
IV	0.3344	3.97	1.82
V	0.4028	4.79	1.82
p	0.1174	2.41	1.69
m	0.1174	1.81	1.96
a	0.1651	1.73	2.37

Table 3. Characteristics of the $N-I$ transition in the pure model *NLC*.

NLC	Φ	$\bar{\eta}$	$(\Delta\eta/\bar{\eta})\cdot 10^2$	$S^{(1)}$	$D^{(1)}$	S_{NI}/k
I	1.9244	0.3261	1.4	0.3564	0.1746	0.0825
II	1.4375	0.2902	2.3	0.4290	0.1717	0.1164
III	1.1337	0.2591	3.3	0.4808	0.1650	0.1444
IV	0.9290	0.2351	4.3	0.5202	0.1578	0.1683
V	0.6690	0.1977	6.1	0.5781	0.1447	0.2081

Table 4. 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				
	$g_2^{\infty,I}$	$g_2^{\infty,N}$	$S_\infty^{(2)}$	$D_\infty^{(2)}$	$g_2^{\infty,N}/g_2^{\infty,I}$
I	0.9435 (0.9328)	0.9947 (0.9895)	0.2145 (0.1684)	0.1221 (0.1595)	1.0543 (1.0608)
II	0.9195 (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)

Figure legends

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

Fig.2. The factor $S_{m/p}$ vs. t^{*} for infinitely diluted solutions of model *meta*- and *para*-xylenes in *NLC* I-V.