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# Role of steric factors in the mechanism of separation of structural isomers with nematic sorbents

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The model of a nematic binary mixture of rigid biaxial molecules is used to calculate the coefficients of selectivity enhancement $S_{m/p}$ (the ratio between the activity coefficients of *meta*- and *para*-substituted benzenes as sorbates at infinite dilution) in the nematogenic matrix of a nematic liquid-crystal sorbent and the parameters of orientation order of the components. It was found that in systems of particles in which interaction between the particles consists in steric repulsion, the $S_{m/p}$ coefficient is less than 1 and is practically constant in the isotropic phase, whereas in the nematic phase, $S_{m/p}$ is greater than 1 and increases in parallel with the order parameter.

**Key words:** nematic liquid-crystal sorbents, statistical thermodynamics of nematic liquid crystal—nonmesogen solutions, selectivity of nematic liquid crystals with respect to structural isomers.

The use of nematic liquid crystals (NLC) as sorbents for GLC is based on the fact that their selectivity with respect to organic structural isomers, specifically, *para*- and *meta*-substituted benzenes, increases as the sorbents pass from the isotropic (*I*) state to the nematic (*N*) state and as the temperature decreases.[1—5] The understanding of the retention mechanism is significant both for widening the analytical possibilities of liquid-crystal sorbents and for gaining information on thermodynamic properties of mixed anisotropic phases.

The limiting thermodynamic characteristics of nonmesomorphic solutes, first of all, activity coefficients, $\gamma_i^\infty$ ($\gamma_i \to 1$, $y_i \to 1$; $i$ is the index of a nonmesogen and $y_i$ is its mole fraction), serve as the criterion for the estimation of the selectivity of NLC as stationary phases. In fact, the

$$S_{B/A} = \gamma_B^\infty / \gamma_A^\infty$$

ratio (the coefficient of the selectivity enhancement) appears in the expression for the Herington separation coefficient ($\sigma_H$):[3,6,7]

$$\sigma_H = t'_A/t'_B = (\gamma_B^\infty/\gamma_A^\infty)(f_B^\circ/f_A^\circ),$$

where $t_A$ is the adjusted retention time and $f_i^\circ$ is the fugacity of the pure sorbate of kind $i$ ($i = A$, $B$). Since for *meta*- and *para*-derivatives of benzene, whose model analogs are considered below, the $f_m^\circ/f_p^\circ$ ratio varies only slightly over the temperature range usually studied by GLC,[3,6,7] the $S_{m/p}$ coefficient reflecting the interaction of molecules of the components being separated with the stationary phase is one of the main indicators of the *meta*- and *para*-selectivity of NLC.

Numerous experimental studies have been devoted to the study of temperature dependences of $\gamma_i^\infty$ in both phases of NLC;[1,6—10] an important target of these studies was to analyze the characteristic features of the intermolecular interactions in mixed systems. Based on the data on $\gamma_i^\infty(T)$ obtained by GLC for nonmesogens of various chemical classes (branched and nonbranched alkanes, alkenes, substituted benzenes, *etc.*), enthalpies and entropies of their dissolution and solvation in the *N* and *I* phases of NLC were calculated. A comparative analysis of these properties made it possible to identify the correlations between the thermodynamic functions of the sorption of nonmesogens in NLC and molecular parameters such as the size and the shape of particles, their polarity and polarizability, and the flexibility of separate fragments of the molecules. The *meta—para*-selectivity of a nematic sorbent has been studied in the framework of this approach by Martire *et al.*[7] Based on data on the enthalpy and entropy of solvation of structural isomers, they concluded that the enthalpy contribution to the $\sigma_H$ factor of the stationary phase (4,4′-di(hexyloxy)azoxybenzene (DHAB)) predominates. However, the author noted that even a qualitative discussion of the experimental data is complicated due to the existence of a relationship between the geometric and electronic characteristics of individual molecules (for example, *meta*- or *ortho*-substitution in a benzene ring results in the appearance of dipole moment). In addition, it was noted in this study[7] and in other studies dealing with the separation of substituted benzenes and polynuclear aromatic compounds[1,3,5,6,11] consisting of rigid planar molecules that the biaxiality of their molecular form must be taken into account in interpreting the data on the retention.

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This accounts for the interest in the statistical thermodynamic investigation of the steric correlations between the anisometric molecules of a sorbate and a sorbent in phases of various symmetries as one of the aspects of the problem of the mechanism of separation of structural isomers with nematic stationary phases. The statement of this problem is influenced mostly by modern concepts, according to which the orientational ordering of nematic systems is predetermined by the anisotropy of repulsive (steric) interactions of molecules,[12–14] the parameters of the $N$–$I$ transition depending substantially on the characteristics of their biaxiality.[15,16]

Modelling of the sorbate—sorbent systems based on molecular-statistic methods for describing mixed nematic phases began not long ago. Resorting to the previously developed lattice models of nematic solutions,[17,18] Martire[19] has analyzed the increase in the relative selectivity (SE) of nematic sorbents, caused by their orientation ordering, with respect to sorbates consisting of particles of various shapes, *viz.*, cubes, rigid "blocks" $r\times1\times1$ in size, plates, and partly flexible molecules. The molecules of NLC have rigid nuclei $r\times1\times1$ in size and partly flexible terminal radicals. According to Martire,[19]

$$\ln(\mathrm{SE}) = \ln[(\gamma_c^{\infty})^{(N)}/(\gamma_c^{\infty})^{(I)}] - \ln[(\gamma_s^{\infty})^{(N)}/(\gamma_s^{\infty})^{(I)}],$$

where the indices $c$ and $s$ refer to sorbates with cubic and anisometric particles having identical volumes. It was shown that the ability of NLC to separate sorbates increases with an increase in the parameter of the orientation order of the nematic sorbent; the SE value is maximum for rigid "blocks" of dimensions $r\times1\times1$.

The lattice approach has been developed further by Yan and Martire,[4] who calculated the constant of distribution of the sorbate between an anisotropic sorbent (a completely ordered laminated system) and an isotropic mobile phase in terms of the model system of rectangular prisms and established the relationship of this constant with the surface and the volume of a sorbate molecule and the effective surface area of its contact with molecules in both phases.

The present paper continues the statistical thermodynamic consideration to the role of steric factors in the mechanism of the retention of sorbates in nematic sorbents; attention is focused on the problem of the effect of biaxiality of sorbate molecules on the *meta—para*-selectivity of NLC, which has not been studied in terms of the existing models of nematic mixtures. For this purpose, we used the previously suggested[20] model of a nematic mixture of rigid biaxial molecules (rectangular parallelepiped), whose faces are parallel to the axes of a fixed system of coordinates. According to the lattice version of this model, developed by using the Flory—Di Marzio probability method[21] for calculating the number of configurations, the smaller the volume ($\Delta V$) of the lattice unit cell compared to the volume of a molecule, the better the properties of a molecular system can be described.[22,23] In the present work we used the continuous version of the corresponding lattice theory, in which the transition from a discrete distribution of the centers of mass of molecules to the continuous distribution has been accomplished with passage to the limit $\Delta V \to 0$.[20] This model has been used previously in studies of orientational ordering and the lines of coexistence of the nematic and isotropic phases in mixed nematic systems.[16]

The purpose of the present work is to analyze the dependences of the coefficient of the selectivity enhancement

$$S_{m/p} = \gamma_m^{\infty}/\gamma_p^{\infty}$$

on the relative temperature and on the characteristics of the orientational ordering of sorbates (model analogs of *meta-* and *para*-isomers) and a nematic sorbent. The volumes and linear sizes of molecules approximated by rectangular parallelepipeds are the input parameters of the model.

It should be noted that a mean-field model of a binary mixture of biaxial molecules with continuous distribution of orientations has been developed recently;[24] the model was used for determining the fields of stability of nematic phases of various symmetries. However, in the study mentioned above,[24] the parameters of the mean-field potential were not related in an explicit form to such characteristics of molecules as their size and shape, and, besides, the distribution of the centers of mass of particles surrounding any particle was supposed to be spherically symmetrical; this assumption finds no support in the theories[13,14] of nematic fluids of anisometric molecules.

**The statistical thermodynamic model.** A binary nematic system is simulated by an $\{N_l\} = N_1, N_2$ fluid of sterically interacting particles, *viz.*, parallelepipeds having volume $\upsilon_l$ and sizes $A^{(l)}_1 \geq A^{(l)}_2 \geq A^{(l)}_3$. The **n** axis of the predominant orientation of the mesophase coincides with the $Z$ axis of the fixed $XYZ$ system of coordinates; the $\mathbf{e}^{(l)}_i$ unit vectors ($i = x, y, z$) of the molecular system of coordinates are directed along the edges of a parallelepiped. The diagonal matrix elements are parameters of the orientation order of component $l$ [12]

$$S_{ii}^{(l)} = \frac{1}{2}\langle 3\cos^2(\widehat{\mathbf{n},\mathbf{e}_i^{(l)}}) - 1\rangle, \qquad (1)$$

$$i = x, y, z,$$

where angle brackets denote averaging over an ensemble of molecules.

Since

$$S^{(l)}_{xx} + S^{(l)}_{yy} + S^{(l)}_{zz} = 0,$$

then the orientation ordering of biaxial molecules of kind $l$ is described by two independent values: the $S^{(l)}_{zz} \equiv S^{(l)}$ parameter characterizing the average degree of orientation of an $\mathbf{e}^{(l)}_z$ vector with respect to $\mathbf{n}$ and the biaxiality parameter[23—26]

$$D^{(l)} = S^{(l)}_{yy} - S^{(l)}_{xx},$$

determining the average projection of the lateral axes of a molecule (the $\mathbf{e}^{(l)}_y$ and $\mathbf{e}^{(l)}_x$ vectors) onto the $\mathbf{n}$ axis. For a binary nematic mixture of biaxial molecules, four order parameters are required, *viz.*, $S^{(l)}$ and $D^{(l)}$ ($l$ = 1, 2); if a molecule of kind $l$ is uniaxial, $D^{(l)} = 0$.

The assumption that the axes of a molecular system of coordinates are parallel to the *X*, *Y*, *Z* axes makes it possible to obtain expressions for thermodynamic functions of a nematic fluid of parallelepipeds in an analytical form.[20] In the general case for a particle with the $D_{2h}$ symmetry ("biaxial"), six orientations are possible (Fig. 1). The distribution over the orientations is characterized by a $\{s_{\alpha l}\}$ ($s_{\alpha l} = N_{\alpha l}/N_l$) set of the fractions of particles of kind $l$ with orientation α. Since the nematic phase as a whole possesses an uniaxial symmetry,

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

then from definition (1), it follows that[20,23]

$$\begin{aligned} S^{(l)} &= 3s_{1l} - 1/2, \\ D^{(l)} &= 3(s_{3l} - s_{5l}). \end{aligned} \tag{3}$$

For particles with the $D_{4h}$ symmetry, the biaxiality parameter $D^{(l)}$ is 0. In the isotropic phase, $s_{\alpha l} = 1/6$ ($\alpha = 1,...,6$), $S^{(l)} = 0$, and $D^{(l)} = 0$ for each component of the system.

To analyze the $\mathbf{S}_{m/p}$ factor, it is necessary to identify the relationship between the thermodynamic properties of a NLC (component 1)—sorbate (component 2 infinitely diluted with respect to the NLC) system and the orientational order parameters and geometric characteristics of the molecules. According to the thermodynamic definition,

$$kT \ln \gamma_2^{\infty} = \lim_{y_2 \to 0} \left[\mu_2^M - kT \ln y_2\right] - \mu_2,$$

where $k$ is Boltzmann's constant and $\mu_2{}^M$ and $\mu_2$ are the chemical potentials of component 2 in the mixture and in a pure state at a given temperature and pressure.

The contributions to the $\gamma_2{}^{\infty}$ and $\mu_l$ functions caused by steric interactions of the molecules are derived from the expression reported previously[20] for the configurational constituent, $F_c(\{N_{\alpha l}\})$, of the free Helmholtz energy of an athermal nematic fluid, which is a mixture of parallelepipeds with continuous translation coordinates. The relationships for $\gamma_2{}^{\infty}$ and $\mu_l$ are the following:

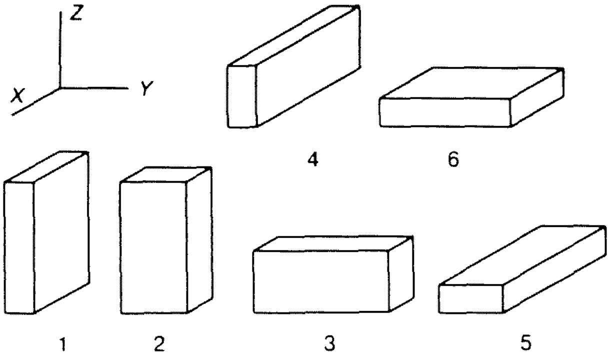

**Fig. 1.** Orientations ($\alpha$ = 1,...,6) of a rectangular parallelepiped $A_1 > A_2 > A_3$ with respect to an *XYZ* fixed system of coordinates. The direction of the $\mathbf{n}$ director of the mesophase coincides with the *Z* axis. The $\mathbf{e}_z$, $\mathbf{e}_y$, and $\mathbf{e}_x$ unit vectors of the molecular system of coordinates are directed along the $A_1$, $A_2$, and $A_3$ edges, respectively.

$$\begin{aligned} \ln \gamma_2^{\infty} = {} & \ln \frac{s_{\alpha 2}^{\infty}}{v_1(\bar{V}_1 - 1)} - 1 + \Phi_1 \frac{v_2}{v_1} + \\ & + \frac{1}{\bar{V}_1 - 1} \sum_{i=1}^{3} \left[ f_{\alpha 2}^{(i)} a_1^{(i)} + \frac{f_2}{f_{\alpha 2}^{(i)}} b_1^{(i)} \right] + \\ & + \frac{1}{(\bar{V}_1 - 1)^2} \prod_{i=1}^{3} a_1^{(i)} \cdot \sum_{i=1}^{3} \frac{f_2}{f_{\alpha 2}^{(i)}} \frac{1}{a_1^{(i)}} - \frac{\mu_2}{kT} \end{aligned} \tag{4}$$

$$\begin{aligned} \frac{\mu_l}{kT} = {} & \ln \frac{s_{\alpha l}^{\infty}}{v_l(\bar{V}_l - 1)} - 1 + \Phi_l + \\ & + \frac{1}{\bar{V}_l - 1} \sum_{i=1}^{3} \left[ f_{\alpha l}^{(i)} a_l^{(i)} + \frac{f_l}{f_{\alpha l}^{(i)}} b_l^{(i)} \right] + \\ & + \frac{1}{(\bar{V}_l - 1)^2} \prod_{i=1}^{3} a_l^{(i)} \cdot \sum_{i=1}^{3} \frac{f_l}{f_{\alpha l}^{(i)}} \frac{1}{a_l^{(i)}} \end{aligned} \tag{5}$$

Here $f_l = v_l/a^3$ ($v_l$ is the volume of a molecule and $a$ is the unit of length) and $f_{\alpha l}$ is the length of the edge of kind $l$ particles with orientation α along direction $i$,

$$\bar{V} = V/(N_l v_l) = 1/\eta_l$$

($V$ is the volume of the system and $\eta_l$ is the density of the pure fluid of kind $l$),

$$a_l^{(i)} \equiv \sum_{\alpha=1}^{6} s_{\alpha l}/f_{\alpha l}^{(i)}, \quad b_l^{(i)} \equiv \sum_{\alpha=1}^{6} s_{\alpha l} f_{\alpha l}^{(i)}/f_l,$$

$s^{\infty}{}_{\alpha 2}$ is the proportion of kind 2 particles with orientation α in a solution of NLC, infinitely diluted with respect to them. The chemical potential $\mu_l$ was normalized to the state of pure fluid $l$ with detached interactions and at unit density.

The equation of state (the $\Phi_l = Pv_l/kT$ function) of pure component $l$ is defined by the following expression:

$$\Phi_l = \frac{1}{\bar{V}_l - 1} + \frac{f_l}{(\bar{V}_l - 1)^2} \sum_{i=1}^{3} \left(a_l^{(i)} b_l^{(i)}\right) + \frac{2f_l}{(\bar{V}_l - 1)^3} \prod_{i=1}^{3} a_l^{(i)}. \tag{6}$$

It has been shown[20,23] that for the systems under consideration in which there is equilibrium distribution of particles over orientations, the following thermodynamic conditions are necessarily satisfied:

$$\mu^M{}_l = \mu^M{}_{\alpha l,}\ \alpha = 1,\ldots,6, \qquad (7)$$

where $\mu^M{}_{\alpha l} = (\partial F_c/\partial N_{\alpha l})_{T,V,N\beta l\,\neq\,N\alpha l}$ is the chemical potential per kind $l$ particle with orientation $\alpha$ in a mixture of particles of various kinds.

To calculate the $\gamma_2{}^\infty$ functions of sorbates from relationships (4)—(6) in order to analyze the $S_{m/p}$ factor, it is necessary to determine densities and order parameters of nematic sorbents at the point of the nematic-isotropic transition and on decreasing the temperature, and also to calculate the densities of pure sorbates under the same conditions. To characterize the ordering of sorbates dissolved in NLC, two independent values, $s^\infty{}_{1l}$ and $s^\infty{}_{3l}$, from the $\{s^\infty{}_{\alpha l}\}$ set are required.

The characteristics of the $N$—$I$ transition of pure fluids were calculated from the set of equations including the $\mu_l{}^{(N)} = \mu_l{}^{(I)}$ and $\Phi_l{}^{(N)} = \Phi_l{}^{(I)}$ equalities and the equations of set (7). Due to the fulfillment of conditions (2), for component $l$ consisting of particles with the $D_{2h}$ symmetry, two Eqs. (7), $\mu_{1l} = \mu_{3l}$, $\mu_{1l} = \mu_{5l}$, are required.

For athermal systems, the relative temperature

$$T^* = T/T_{NI} = (\Phi_l)_{NI}/\Phi_l = (Pv_l/kT)_{NI}/(Pv_l/kT),$$

where the values with the $NI$ subscript refer to the $N$—$I$ transition, is used.[17,18,22] The density and order parameters of a nematic at $T^* < 1$ were determined from the set of equations consisting of two Eqs. (7) and the relationship:

$$\Phi_1 = (\Phi_1)_{NI}/T^*.$$

The density of the isotropic component at $T^* > 1$ was calculated from the equation

$$\Phi_2 = (\Phi_2)_{NI}/T^*.$$

The $s^\infty{}_{\alpha 2}$ values ($\alpha = 1, 3$) characterizing the orientational order of the sorbates in the NLC at the infinite dilution were calculated directly from Eq. (4) using the normalization constraints:

$$2(s^\infty{}_{12} + s^\infty{}_{32} + s^\infty{}_{52}) = 1.$$

The order parameters were calculated according to definition (3).

## Results and Discussion

**Table 1.** Volumes and axial ratios of the molecules of model analogs of the compounds studied

| Model | $v_0$/nm$^3$ | $\Gamma_1$ | $\Gamma_2$ |
|---|---|---|---|
| I | 0.2324 | 2.76 | 1.82 |
| IIA | 0.2664 | 3.17 | 1.82 |
| IIB | 0.2664 | 3.63 | 1.24 |
| III | 0.3004 | 3.57 | 1.82 |
| IV | 0.3344 | 3.97 | 1.82 |
| V | 0.4028 | 4.79 | 1.82 |
| VI | 0.2677 | 2.80 | 1.88 |
| VII | 0.3017 | 3.18 | 1.88 |
| *Ap* | 0.1174 | 2.41 | 1.69 |
| *Am* | 0.1174 | 1.81 | 1.96 |
| *Bp* | 0.1403 | 2.88 | 1.69 |
| *Bm* | 0.1403 | 2.16 | 1.96 |
| *Cp* | 0.1461 | 3.00 | 1.69 |
| *Cm* | 0.1461 | 2.25 | 1.96 |

The data on the volumes and the axial ratios ($\Gamma_1{}^{(k)} = A_1{}^{(k)}/A_2{}^{(k)}$, $\Gamma_2{}^{(k)} = A_2{}^{(k)}/A_3{}^{(k)}$) of the particles approximating the nematic (I—VII) and nonmesomorphic (*A*, *B*, *C*) components are presented in Table 1. The geometric characteristics of particles of kinds I and VI were brought near to the shapes of the molecules of *para*-azoxyanisole (PAA) and 4-methoxybenzylidene-4′-butylaniline (MBBA), respectively. The volumes $v_l$ were calculated using the Bondi Tables.[27] The size of a particle in the direction of the *para*-axis was specified as the distance between the terminal carbon atoms of the side chains with allowance for the fact that the dihedral angles between the phenylene rings in PAA and MBBA are 4° and 40°, respectively.[1] The $A_2{}^{(1)}$ value was set equal to twice the distance from the longitudinal axis to the carbon atom most distant from it. The thickness of particles was calculated as $A_3{}^{(1)} = v_1/(A^{(1)}{}_1 \times A^{(1)}{}_2)$.

The volume of each subsequent particle in series I—V and VI—VII increases by an increment that corresponds to two methylene groups; simultaneously, the longitudinal size of particles increases (except for IIB), with the lateral sizes being fixed.

Thus, the tendency of the variation of the size of the molecules in the series of 4,4′-dialkoxyazoxybenzenes (II—V are analogs of *para*-azoxyphenetole (PAP) and 4,4′-dipropyloxy-, 4,4′-dibutyloxy-, and 4,4′-di(hexyloxy)azoxybenzene (in the *trans*-conformation), respectively) and Schiff's bases (VII is the analog of 4-ethoxybenzylidene-4′-butylaniline (EBBA)) is reproduced in a simplified form.

Since no model of the NLC molecule can be unambiguously chosen, in addition to fluid IIA, fluid IIB was considered as a geometric analog of PAP; its sizes were determined according to the same scheme as those of component I. As this was done, it was taken into account that the C—C bond of the $-OCH_2-CH_3$ group in the PAP molecule is directed along the long axis of the central fragment.

The particles of components *A*, *B*, and *C* approximate the planar molecules of *meta*- and *para*-disubstituted benzenes, *viz.*, xylenes (*Am*, *Ap*), divinylbenzenes (*Bm*, *Bp*), and ethylvinylbenzenes (*Cm*, *Cp*). The size of $A_3{}^{(2)}$ is taken to be 0.257 nm, which corresponds to the thickness of the benzene ring.[4] In the case of *meta*-isomers, the longitudinal axis of the particles was drawn through the center of gravity of the molecule, parallel to

**Table 2.** Characteristics of the *N—I* transition of model NLC

| NLC | Φ | $\bar{\rho}$ | $\Delta\rho/\bar{\rho} \cdot 10^2$ | $S_1$ | $D_1$ | $\Sigma_{NI}/k$ |
|---|---|---|---|---|---|---|
| I | 1.9244 | 0.3261 | 1.4 | 0.3564 | 0.1746 | 0.0825 |
| IIA | 1.4375 | 0.2902 | 2.3 | 0.4290 | 0.1717 | 0.1164 |
| IIB | 1.9030 | 0.3312 | 4.5 | 0.6719 | 0.0640 | 0.2591 |
| 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 |
| VI | 1.7475 | 0.3130 | 1.3 | 0.3371 | 0.1749 | 0.0750 |
| VII | 1.3462 | 0.2798 | 2.2 | 0.4056 | 0.1750 | 0.1056 |

the segment connecting the centers of the substituents. The $\Gamma_1^{(2)}$ parameter was set equal to the ratio of the length of this segment to twice the distance from the center of one of the substituents to the chosen axis.

Characteristics of the *N—I* phase transition (PT) (Φ, the average density $\bar{\eta} = (\eta_{(N)} + \eta_{(I)})/2$, the density jump $\Delta\eta/\bar{\eta} = (\eta_{(N)} - \eta_{(I)})/\bar{\eta}$, and the adjusted entropy $\Sigma_{NI}/k$) for model NLC are presented in Table 2. The $S^{(1)}$ and $\Sigma_{NI}/k$ order parameters lie in the intervals normal for typical NLC.[12] However, the $\bar{\eta}$ values are too low and the density jumps are too high, which results from both the athermal character of the model and the approximations made to take into account the collective effects of the interaction of the molecules. In all cases, the biaxiality parameter $D^{(2)} \neq 0$; $D^{(2)}$ decreases with an increase in the longitudinal sizes of particles, with the lateral sizes being constant. The *N—I* PT characteristics for fluid IIB are higher than those for fluid IIA, because its particles are more prolate.

It should be noted that systems of rigid biaxial molecules approximating the sorbates under study can also exhibit mesogenic properties. However, in the

$$0.8 \leq T/T^{(1)}_{NI} \leq 1,$$

temperature range, which is of interest for investigating the selectivity of nematic sorbents, the model nonmesogens under consideration are isotropic. In fact, their relative pressures at the *N—I* PT point are the following:

| Component | *Ap* | *Am* | *Bp* | *Bm* | *Cp* | *Cm* |
|---|---|---|---|---|---|---|
| $\Phi_2$ | 3.0236 | 4.3618 | 2.0586 | 2.9498 | 1.8328 | 2.8137 |

Since in an athermal system at a constant *P*, the $T_1/T_2 = (\Phi_2/\Phi_1)\times(\upsilon_1/\upsilon_2)$ condition holds for the PT temperatures of components 1 and 2, from a comparison of $\Phi_1$ (Table 2) and $\Phi_2$, it follows that

$$T_2^{(NI)}/T_1^{(NI)} \leq 0.3.$$

This inequality indicates that under the conditions being considered, the isotropic phase of the model sorbates is stable.

The values of $\gamma_2^{\infty}$ and the order parameters of nonmesogens (model *para-* and *meta*-xylenes) dissolved in the coexisting phases of NLC are presented in Table 3.

**Table 3.** 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-* Xylene | | | |
|---|---|---|---|---|
| | $(I)\gamma^{\infty}$ | $(N)\gamma^{\infty}$ | $S_{\infty}^{(2)}$ | $D_{\infty}^{(2)}$ |
| I | 0.9435<br>0.9328 | 0.9947<br>0.9895 | 0.2145<br>0.1684 | 0.1221<br>0.1595 |
| IIA | 0.9195<br>0.9079 | 0.9980<br>0.9935 | 0.2157<br>0.1689 | 0.1215<br>0.1589 |
| IIB | 0.9254<br>0.9146 | 1.1059<br>1.1121 | 0.3705<br>0.2892 | 0.1713<br>0.2355 |
| III | 0.8933<br>0.8813 | 0.9952<br>0.9892 | 0.2084<br>0.1638 | 0.1179<br>0.1579 |
| IV | 0.8676<br>0.8552 | 0.9881<br>0.9804 | 0.1988<br>0.1558 | 0.1134<br>0.1477 |
| V | 0.8266<br>0.8147 | 0.9740<br>0.9640 | 0.1784<br>0.1399 | 0.1039<br>0.1347 |
| VI | 0.9243<br>0.9129 | 0.9700<br>0.9637 | 0.1828<br>0.1435 | 0.1071<br>0.1388 |
| VII | 0.9115<br>0.8989 | 0.9824<br>0.9750 | 0.1865<br>0.1463 | 0.1078<br>0.1402 |

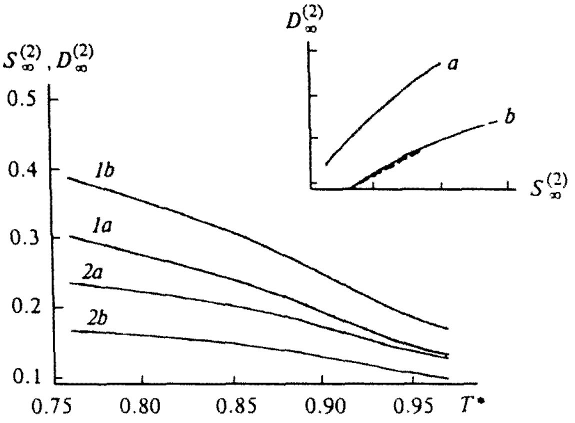

**Fig. 2.** Order parameters $S_{\infty}^{(2)}$ (*1*) and $D_{\infty}^{(2)}$ (*2*) of *meta*-xylene (*a*) and *para*-xylene (*b*) in EBBA. The solid lines are the results of the calculation and the dotted lines correspond to experimental data obtained in Ref. 26.

The $S_{\infty}^{(2)}$ and $D_{\infty}^{(2)}$ values belong to the same interval, as has been observed for solutions of *para*-xylene in EBBA[26] (Fig. 2) and in other NLC[28] as well as for aromatic nonmesogens, whose molecules have the shape of planar biaxial plates.[29,30] An increase in the longitudinal sizes of the molecules of model sorbates occurring on the *para*-substitution, their thickness remaining the same, is accompanied by an increase in $S_{\infty}^{(2)}$ and a decrease in $D_{\infty}^{(2)}$. Note that the increase in $S_{\infty}^{(2)}$ upon elongation of the molecule (for substances of the same chemical nature) has been observed experimentally for many dyes dissolved in nematic matrices.[31]

According to calculations, elongation of molecules of nematic solvents leads to a slight decrease in the $S_\infty^{(2)}$ and $D_\infty^{(2)}$ values of nonmesogens. In real solutions of nonmesogens in lower homologs of NLC, the odd—even alteration of $S_\infty^{(2)}$ and $D_\infty^{(2)}$ is exhibited, with a tendency to a slight decrease in these values with an increase in the number of the odd and even homologs.[28]

The data of Table 3 indicates further that $\gamma_m^\infty < 1$ and $\gamma_p^\infty < 1$ in the isotropic phases of all systems. These properties are exhibited by athermal molecular fluids containing rigid nonspherical particles of various sizes and shapes.[32] In nematic phases, except for fluid IIB, the deviations from the ideal behavior are also negative. As regards real systems, in the case of disubstituted benzenes, $\gamma_2^\infty > 1$ in both phases of NLC; the major positive contribution to $\gamma_2^\infty$ is made by the endothermal effect of mixing NLC and a nonmesogen.[7,8]

At the *N—I* PT of a nematic sorbent in a model system, $\gamma_m^\infty < \gamma_p^\infty$ and, consequently, $\mathbf{S}_{m/p} < 1$. On the orientational ordering of NLC, the $\mathbf{S}_{m/p}$ factor increases (Fig. 3). At the same time, according to experimental data, $\gamma_m^\infty > \gamma_p^\infty$ in a broad temperature range in which the *N* phase is stable; for example, for disubstituted benzene derivatives in the nematic phase of DHAB ($T_{NI}$ = 128 °C), $\gamma_m^\infty > \gamma_p^\infty$ in the 83—113 °C temperature range. The $\Delta\gamma^\infty = \gamma_m^\infty - \gamma_p^\infty$ difference increases; however, as the PT point of the NLC is approached, *i.e.*, at 83 and 113 °C, $\Delta\gamma^\infty$ amounts to 0.156 and 0.079, respectively, and, thus, the tendency to the attenuation of the $\gamma_m^\infty > \gamma_p^\infty$ inequality is manifested. The difference between the experimental characteristics of *meta*- and *para*-isomers has been explained[5,7,8] by the more clear-cut correlation between the long axes of the NLC molecules and the *para*-isomer, which leads to a more intense dispersion interaction compared to that in the case of *meta*-isomer; simultaneously, with the decrease in the correlation between the NLC molecules and *meta*-xylene, the contribution of the dipole constituent to the intermolecular attraction decreases.[7]

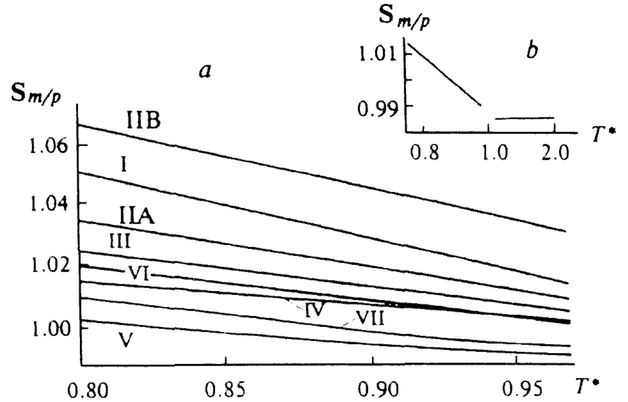

**Fig. 3.** *a*. Temperature dependences of the $\mathbf{S}_{m/p}$ factor of mesogens (the designations are given in Table 1) with respect to *meta*- and *para*-xylenes. *b*. $\mathbf{S}_{m/p}$ in the nematic and isotropic phases of fluid I.

According to the data of calculations, a decrease in the relative temperature $T^*$ is accompanied by an increase in the $S_\infty^{(2)}$ and $D_\infty^{(2)}$ parameters (Fig. 2), which has also been confirmed by spectroscopic[26,28,29] studies of the orientational ordering of biaxial molecules in nematic solutions. It can also be seen from Fig. 2 that the $|dS_\infty^{(2)}/dT^*|$ derivative for the *para*-isomer is greater than that for the *meta*-isomer, whereas the $|D_\infty^{(2)}/dT^*|$ derivative for the *para*-isomer is smaller. Thus, the enhancement of the correlation between the long axes of the molecules of NLC and the *para*-isomer with a decrease in $T^*$ is more pronounced than that in the case of *meta*-isomer, and, consequently, the entropy constituent of the activity coefficient caused by the translation motion of the sorbate molecules in the nematic matrix increases to a larger degree. Hence, $\gamma_p^\infty$ becomes smaller than $\gamma_m^\infty$, the $\gamma_m^\infty - \gamma_p^\infty$ increasing with a decrease in $T^*$; the $\mathbf{S}_{m/p}$ coefficient increases, compared to its magnitude at the *N—I* PT point, and becomes greater than unity (Fig. 3). According to the data presented in Fig. 3, the $\mathbf{S}_{m/p} > 1$ inequality is reinforced with a decrease in $T^*$. This result is in agreement with the data of numerous experimental studies[1—3,6,7] that imply that the $\mathbf{S}_{m/p}$ coefficient increases with a decrease in the temperature, accompanied by an increase in the orientational order of a nematic sorbent.

The $\mathbf{S}_{m/p}(T^*)$ plots for model NLC are shown in Fig. 3. From these data, it follows that the $\mathbf{S}_{m/p}$ factor decreases in the I, IIA, III—V and VI, VII series as the longitudinal size of the NLC molecules increases (with the lateral size being constant). Thus, the results of the calculation correspond to the experimental trend of variation of $\sigma_H(T)$ with the elongation of the NLC molecules, when the number of a homolog with the same parity increases.[2] Note as well that the $\mathbf{S}_{m/p}$ factor in a solution of model sorbent IIB is higher than that in a solution of I, whereas in the case of sorbents IIA and I, an opposite relationship is observed (Fig. 3). This regularity for the model results from the more pronounced anisometricity of the IIB molecules compared to those of IIA. As regards the properties of PAA and PAP, the higher *meta—para*-selectivity of PAP may be due to higher anisotropy of the polarizability of the PAP molecule, which is consistently associated with the increase in the longitudinal size of the molecule due to the addition of the second methylene group to the alkyl radical. This variation of the geometric anisotropy of the molecule was reflected in a simplified form in the modelling of the IIB particle.

In addition to the data on the selectivity of NLC with respect to isomeric xylenes, the $\mathbf{S}_{m/p}$ factors were also calculated for nematic systems containing isomers of divinylbenzene and ethylvinylbenzene. In Fig. 4, the experimental $\mathbf{S}_{m/p}(T^*)$ plots for DHAB as the sorbent[33] are compared to the values of this factor calculated for the corresponding model objects: fluid VII and nonmesogens *Bm*, *Bp* and *Cm*, *Cp*. Although the experimental values are greater than the calculated ones, it can

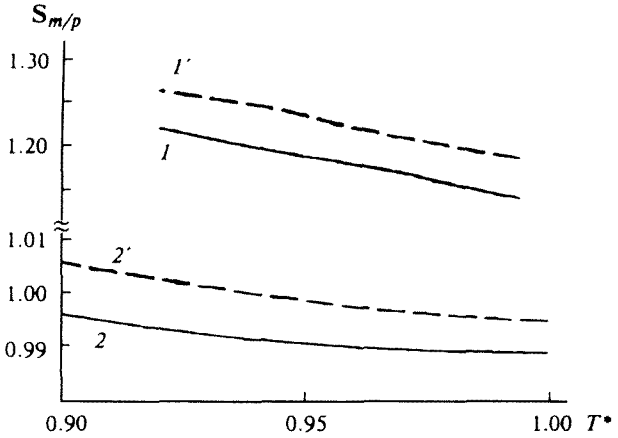

**Fig. 4.** Temperature dependences of the $S_{m/p}$ factor of DHAB and its model analog with respect to *meta*- and *para*-isomers of ethylvinylbenzene (*1′*, *2′*) and divinylbenzene (*1*, *2*). The *1* and *1′* dependences correspond to experimental data[33] and the *2* and *2′* dependences are calculated plots.

be seen that the allowance for the differences in the volumes and linear sizes of molecules of various isomers of the sorbates under consideration (Table 1) makes it possible to predict the temperature dependence of the $S_{m/p}$ factor and also the increase in $S_{m/p}$ (for a particular $T^*$) on going from divinylbenzenes to ethylvinylbenzenes.

The results of the calculations indicate that steric interactions between biaxial molecules play a significant role in the mechanism of separation of structural organic isomers on nematic stationary phases. A nematic fluid of an athermal mixture of anisometric molecules may be used as a reference model for taking into account intermolecular attraction in order to carry out further studies of the Herington factor of nematic sorbents. In addition, the development of the views of mixed nematic phases is of interest regarding the prospects of establishing the correlation between the data on the orientation order parameters of the components and the thermodynamic characteristics of the systems obtained using various experimental methods.

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