Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

A quasichemical lattice model for a binary mixture of hard rectangular parallelepipeds Application to systems composed of nematic and non-mesogenic molecules

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To cite this Article Sokolova, E. P. and Vlasov, A. Yu.(1990) 'A quasichemical lattice model for a binary mixture of hard rectangular parallelepipeds Application to systems composed of nematic and non-mesogenic molecules', Liquid Crystals, 8: 1, 47 — 61

To link to this Article: DOI: 10.1080/02678299008047329
URL: http://dx.doi.org/10.1080/02678299008047329

LIQUID CRYSTALS, 1990, VOL. 8, NO. 1, 47–61

A quasichemical lattice model for a binary mixture of hard rectangular parallelepipeds

Application to systems composed of nematic and non-mesogenic molecules

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(*Received 9 October 1989; accepted 28 December 1989*)

The hole lattice model of rectangular parallelepipeds is presented to describe the structural and excess thermodynamic properties of nematic–non-mesogenic mixtures. The molecular attractions are taken into account within the quasi-chemical approximation. A procedure for evaluating model parameters from data on the thermodynamic characteristics of pure components and the activity coefficients of the non-mesogen at infinite dilution at the nematic–isotropic transition temperature of the mesomorphic component is proposed. The mixing functions (enthalpy and volume), activity coefficient of the non-mesogen and the order parameters of the components are calculated at a molecular level for systems composed of 4-methoxybenzylidene-4′-propylaniline and a non-mesogen (tetrachlormethane, benzene and *n*-heptane). The calculated results are in quite good agreement with experiment in the temperature range from 319·2 to 335·4 K.

1. Introduction

In recent years mixtures of nematogens and non-mesogens have been actively studied in connection with their considerable practical importance since small amounts of non-mesogens are frequently added to nematogentic mixtures used in liquid crystal displays. It is of interest to investigate the concentration dependence of mesomorphic mixture properties not only from the viewpoint of their applications but also from that of fundamental studies in the field of molecular interactions.

Due to the complexity of condensed anisotropic systems a statistical mechanical treatment of realistic models for nematic mixtures is not feasible. It is possible to investigate the orientational properties of these systems using a variety of idealized statistical approaches [1]. Among these models the generalized van der Waals approach would seem to treat both anisotropic hard core repulsions and angle dependent attractions in the most explicit manner [2, 3]. The weakness of the van der Waals theory, as presently formulated, is the neglect of multiple centres of attraction and the flexibility of the terminal molecular chains. Using a translational and orientational continuum model it is difficult to account for the lower than cylindrical symmetry of the molecules and the short range order due to attractive interparticle interactions.

These difficulties can be overcome in the lattice model offering a plausible frame within which some of these effects may be examined in a crude but simple way. Most of the existing models utilize Flory–Di Marzio statistics. To date it is known that the lattice approach for rigid rod-like particles appeared to be of little use when considering the properties at the nematic–isotropic transition in single component systems [4].

The lattice models are shown, however, to be useful for the investigation of solutions with non-mesomorphic and nematic solutes. These studies have been extended to mixtures of hard rods [4, 5], and of hard rods and cubes [6], to rods with hard cores and semiflexible tails [7].

During the past 15 years the effect of molecular biaxiality has been intensively discussed (see, e.g., [8] and references therein). In the framework of the Flory–Di Marzio counting procedure Shih and Alben have examined the configurational statistics of plate-like molecules with dimensions $r \times w \times 1$ on a simple cubic lattice in an effort to gain insight into the influence of molecular shape upon the stability of both uniaxial and biaxial phases in nematic liquid crystals [9]. As we show in the Appendix, however, the counting method of Shih and Alben results in an equation of state, which is accurate only up to the second virial coefficient.

The lattice approach was extended later to multicomponent athermal mixtures of hard rectangular parallelepipeds with dimensions $A_{1k} \times A_{2k} \times A_{3k}$ (here k denotes the index of component). The configurational partition function of such a system was evaluated by Mitra and Allnatt [10], who utilized the approach of Mayer full stars, and alternatively by Tumanjan and Sokolova in the framework of the Flory–Di Marzio probability methods [11, 12]. As shown in [12], the corresponding translational continuum model provided a description of the isotropic phase equation of state up to the third virial coefficient. The model developed in [11, 12] explained some experimental trends in binary mesogen–non-mesogen systems with respect to the dependence on the shape and size of the solute particles [13, 14] of: (1) the reduced transition temperature depression, (2) the order parameters and (3) the solute activity coefficients in both phases. In addition, this approach proved to be successful in studying the influence of molecular biaxiality on the phase equilibria in binary liquid crystal mixtures [15].

In the present paper the lattice approach is applied to a binary nematic mixture of hard rectangular parallelepipeds with attractive interactions treated in the quasi-chemical Bethe–Guggenheim–Barker approximation. This treatment was extended in earlier work only to systems of hard uniaxial rods with dimensions $r \times 1 \times 1$ [5, 16, 17], the numerical results obtained in [17] relating to two component systems of chemically homogeneous particles. The present work generalizes the analysis in so far as we discuss binary systems of rigid parallelepipeds with nematic order. Moreover, we treat numerically systems of energetically inhomogeneous particles. The mixture volumes are also accountable inasmuch as the presence of vacant sites on a lattice is assumed. The lattice approach, however, is relevant for the estimation of the excess thermodynamic functions rather than their nematic–isotropic transitional properties. The information on the mixing functions can essentially extend the possibilities of testing statistical mechanic considerations of molecular interactions in anisotropic solutions. To date there have been no reports on the predictions of thermodynamic mixing functions in binary systems with nematic liquid-crystalline components. The paper contains a comparison of such predictions with experimental data for three binary solutions composed of 4-methoxybenzylidene-4′-propylaniline (MBPA) and a non-mesogen (benzene, tetrachlormethane or n-heptane). The model is presented in §2. In §3 the counting scheme and the procedure used to select the model parameters are discussed. In §4 the results of model calculations are compared with the experimental data on the nematic–isotropic transition temperatures of the solutions, heats of mixing and the activity coefficients of the non-mesomorphic solutes.

2. The model

In the present study a simple cubic lattice model with attractive forces is extended to binary nematic mixtures composed of hard biaxial particles. M is the total number of lattice cells, each having a volume Δv equal to y^3. The system consists of $\{\mathcal{N}_l\}$ ($l = 1, 2$) molecules each with the symmetry of a rectangular parallelepiped, the principal axes of particles being directed along axes x, y, z of the quasilattice frame. A particle of the lth sort has dimensions $A_{1l} \times A_{2l} \times A_{3l}$, the limits $A_{1l} > A_{2l} = A_{3l}$ and $A_{1l} < A_{2l} = A_{3l}$ correspond to rod and plate, respectively. Each particle occupies $L_l = A_{1l} \times A_{2l} \times A_{3l}$ sites on the lattice, and so its molecular volume is $v_l = L_l \cdot \Delta v$. $\mathcal{N}_0$ cells of the lattice are vacant, i.e.

$$M = \mathcal{N}_0 + \sum_{l=1}^{2} L_l \mathcal{N}_l .$$

In the general case $A_{1l} \neq A_{2l} \neq A_{3l}$, i.e. the particles do not have axial symmetry. In the lattice under consideration each particle can adopt six distinct orientations [18]; N_α is the number of particles with orientation α. This index is assigned values from 1 to 6 for the particles of the first sort and from 7 to 12 for the second sort;

$$\sum_{\alpha=1}^{6} N_\alpha = \mathcal{N}_1 \quad \text{and} \quad \sum_{\alpha=7}^{12} N_\alpha = \mathcal{N}_2 .$$

The set of unit vectors $\mathbf{e}_{1l}$, $\mathbf{e}_{2l}$, $\mathbf{e}_{3l}$ lay along the edges A_{1l}, A_{2l}, A_{3l} of the particle and the direction of the preferred orientation $\mathbf{n}$ be parallel to the z axis. Then a convenient procedure of labelling orientations can be adopted so that

$$\alpha = \begin{cases} 2i - 1, \quad 2i & (l = 1), \\ 2i + 5, \quad 2i + 6 & (l = 2), \end{cases} \qquad i = 1, 2, 3,$$

if $|\mathbf{n} \cdot \mathbf{e}_{il}| = 1$. Then for an axially symmetry nematic phase: $s_\lambda = s_{\lambda - 1}$, $\lambda = 2\alpha$, $\alpha = 1, \ldots, 6$, where $s_\alpha = N_\alpha / \mathcal{N}_l$. For a discrete orientational distribution of particles the long range order parameters [19] for each component should be defined as

$$\left.\begin{aligned} S_1^{(l)} &= 3s_{6l-5} - 1/2, \\ S_2^{(l)} &= 3s_{6l-3} - 1/2, \\ S_3^{(l)} &= -S_1^{(l)} - S_2^{(l)}. \end{aligned}\right\} \tag{1}$$

The configurational properties of the system are of primary interest in the study of the relative stabilities of phases and the excess thermodynamic functions of binary mixtures. The configurational partition function $Q_{\{N_\alpha\}}$ for a system of $\{N_\alpha\}$ particles distributed on a lattice of M sites is given by

$$Q_{\{N_\alpha\}} = \frac{(\Delta v)^N}{6^N \prod_{\alpha=1}^{12} N_\alpha!} \sum_{\{U_N\}} g(\{N_\alpha\}, M) \exp(-U_N/kT), \tag{2}$$

where the summation is carried out over all values of the configurational energy with the most probable distribution $\{N_\alpha\}$. The quantity $g(\{N_\alpha\}, M)$ in the number of configurations having equal energy; and $\Sigma_\alpha N_\alpha = N$.

If the interactions between molecules are determined only by steric repulsions, the term $g(\{N_\alpha\}, M)$ equals the number of ways to arrange $\{N_\alpha\}$ indistinguishable particles on a lattice. For the latter we use [10, 11]

$$\left.\begin{aligned} g(\{N_\alpha\}, M) &= \frac{\prod_{i=1}^{3} (\mathcal{N}_0 + B_i)!(\mathcal{N}_0 + B_{123})!}{\mathcal{N}_0! \prod\prod_{i<j} (\mathcal{N}_0 + B_{ij})! \prod_{\alpha=1}^{12} N_\alpha!}, \\ B_i &= \sum_\alpha N_\alpha \left(\prod_{i=1}^{3} r_\alpha^{(i)} \right) \Big/ r_\alpha^{(i)}, \quad B_{ij} = \sum_\alpha N_\alpha r_\alpha^{(k)} (r_\alpha^{(i)} + r_\alpha^{(j)} - 1), \\ &\quad (k \neq i \neq j), \\ B_{123} &= \sum_\alpha N_\alpha \left[\prod_{i=1}^{3} r_\alpha^{(i)} - \prod_{i=1}^{3} (r_\alpha^{(i)} - 1) \right], \end{aligned}\right\} \tag{3}$$

where $r_\alpha^{(i)}$ is the number of lattice cells within an edge constrained along the direction i ($i = x, y, z$) for a particle with orientation α. For the adopted way of labelling α it follows that: $r_1^{(1)} = A_{11}$, $r_1^{(2)} = A_{21}$, $r_1^{(3)} = A_{31}$, $r_7^{(4)} = A_{12}$, $r_7^{(2)} = A_{22}$, $r_7^{(3)} = A_{32}$. The other elements of the array $\{r_\alpha^{(i)}\}$ are determined likewise.

In accord with earlier studies [3, 5, 18, 20] particles in each of the allowed orientations may be considered formally as different species. The repulsive contributions to the pressure and to the chemical potential of the particles having orientation α, are derived straightforwardly from (3)

$$\begin{aligned} P_{\text{rep}} \Delta v / kT &= (\partial \ln g / \partial M)_{T, \{N_\alpha\}} = \ln\left(1 - \rho \sum_{l=1}^{2} d_l \varphi_l\right) - \ln(1 - \rho) \\ &\quad + \sum_i \ln[1 - \rho(1 - a_i)] - \sum\sum_{i<j} \ln[1 - \rho(a_i + a_j - b_k)], \end{aligned} \tag{4}$$

$$\begin{aligned} \mu_\alpha^{\text{rep}} / kT &= -(\partial \ln g / \partial N_\alpha)_{T, M, N_{\beta \neq \alpha}} = -\sum_{i=1}^{3} L_l (1/r_\alpha^{(i)} - 1) \ln[1 - \rho(1 - a_i)] \\ &\quad + \prod_{i=1}^{3} (r_\alpha^{(i)} - 1) \ln\left(1 - \rho \sum_l d_l \varphi_l\right) - L_l \ln(1 - \rho) + \ln(s_\alpha \varphi_l \rho / L_l) \\ &\quad - \sum\sum_{i<j} [L_l - r_\alpha^{(k)} (r_\alpha^{(i)} + r_\alpha^{(j)} - 1)] \ln[1 - \rho(a_i + a_j - b_k)], \end{aligned} \tag{5}$$

where

$$a_i = \sum_{l=1}^{2} \varphi_l \sum_{\alpha=6l-5}^{6l} s_\alpha / r_\alpha^{(i)}, \quad b_i = \sum_{l=1}^{2} \varphi_l \sum_{\alpha=6l-5}^{6l} s_\alpha \left(\prod_{i=1}^{3} r_\alpha^{(i)} \right) \Big/ r_\alpha^{(i)},$$

$$d_l = \prod_{i=1}^{3} (r_{6l-5}^{(i)} - 1) / L_l,$$

here $\rho = \Sigma_l L_l \mathcal{N}_l / M$ and $\varphi_l = L_l \mathcal{N}_l / \Sigma_l L_l \mathcal{N}_l$; they are the density and volume fraction of the lth kind of component, respectively.

The first order approximation dealing with intermolecular attractions is the quasichemical or Bethe–Guggenheim–Barker approximation. In this framework the surface of each molecule is divided into contact sites, each of them having an area y^2. In general a molecule is supposed to be energetically inhomogeneous, i.e. the contact sites have different energetic characteristics. The sites with the same characteristics form one class. Henceforth m denotes the class of contact sites. The area of all of the contact sites orthogonal to a direction i is given by

$$Q_i = 2y^2\left(\mathcal{N}_0 + \sum_{\alpha=1}^{12} N_\alpha r_\alpha^{(j)} r_\alpha^{(k)}\right), \quad i \neq j \neq k.$$

ϑ_m is the surface fraction of contact sites belonging to the class m and located on the particle with orientation α. (For vacancies it holds, formally, that $\vartheta_0 = 1$.) There are different contacts between sites of neighbouring particles along the direction i, namely $m_\alpha m_\alpha$, $m_\alpha m_\beta$, $m_\alpha m_\beta$, $m_\alpha l_\alpha$, 00, $0m_\alpha$. For a number of contacts, $N^{(i)}_{m_\alpha l_\beta}$, laying along direction i the constraint equations

$$2N_\alpha r_\alpha^{(j)} r_\alpha^{(k)} \vartheta_m = 2N^{(i)}_{m_\alpha m_\alpha} + \sum_{l_\beta \neq m_\alpha} N^{(i)}_{m_\alpha l_\beta}. \tag{6}$$

have to be obeyed. The left hand side of this equation is the number of contact sites of the mth class located on particles with orientation α orthogonally to an axis i. The configurational energy of the system is taken to equal the sum of contributions from the nearest neighbour pairs of the contact sites

$$U_N = \sum_i \sum_{\{m_\alpha\}} \left(u_{m_\alpha m_\alpha} N^{(i)}_{m_\alpha m_\alpha} + \frac{1}{2} \sum_{l_\beta \neq m_\alpha} u_{m_\alpha l_\beta} N^{(i)}_{m_\alpha l_\beta}\right), \tag{7}$$

where $u_{m_\alpha l_\beta}$ is the energy of interaction between the contact sites of the mth and lth classes belonging to particles with orientations α and β, respectively.

The quasichemical equilibrium of contact pairs is supposed to take place for each set of configurations with a given orientational distributions $\{N_\alpha\}$. Thus for the sum on the right hand side of equation (2) it holds that

$$Q'_N = \sum_{\{N^{(i)}_{m_\alpha l_\beta}\}} g(\{N_\alpha\}, \{N^{(i)}_{m_\alpha l_\beta}\}) \exp(-U_N/kT), \tag{8}$$

where $g(\{N_\alpha\}, \{N^{(i)}_{m_\alpha l_\beta}\})$ is the number of configurations with an equal energy for the given sets of $\{N_\alpha\}$ and $\{N^{(i)}_{m_\alpha l_\beta}\}$. The value of $g(\{N_\alpha\}, \{N^{(i)}_{m_\alpha l_\beta}\})$ is estimated by use of equation (3) and by introducing the factors h_i according to

$$g_{\max}(\{N_\alpha\}, \{N^{(i)}_{m_\alpha l_\beta}\}) \approx g^{\text{ath}} \prod_{i=1}^{3} h_i, \tag{9}$$

where

$$h_i = \frac{{}^*N^{(i)}_{00}!}{N^{(i)}_{00}!} \prod_{m_\alpha} \left[\frac{{}^*N_{m_\alpha m_\alpha}!}{N_{m_\alpha m_\alpha}!} \frac{({}^*N^{(i)}_{0m_\alpha}/2)!^2}{(N^{(i)}_{0m_\alpha}/2)!^2} \prod_{l_\beta \neq m_\alpha} \frac{({}^*N^{(i)}_{m_\alpha l_\beta}/2)!}{(N_{m_\alpha l_\beta}/2)!}\right];$$

the starred variables correspond to the equilibrium distribution of contact pairs in the athermal system, i.e. that with a random distribution of pairs. After use of equation (9) the maximum term approximation gives the estimate for the partition function in equation (8)

$$Q'_N \approx g^{\text{ath}} \prod_{i=1}^{3} h_i \exp(-U_N/kT), \tag{10}$$

where with respect to the conditions in equation (6) it holds that

$$(N^{(i)}_{m_\alpha l_\beta})^2 = 4N^{(i)}_{m_\alpha m_\alpha} N^{(i)}_{l_\beta l_\beta} \exp(-2w_{m_\alpha l_\beta}/kT). \tag{11}$$

Here the variables $w_{m_\alpha l_\beta} = u_{m_\alpha l_\beta} - (u_{m_\alpha m_\alpha} + u_{l_\beta l_\beta})/2$ are the effective interchange energies for a contact pair involving sites of the designated classes. It holds also that

$w_{0m_\alpha} = -u_{m_\alpha m_\alpha}/2$. The values $w_{m_\alpha l_\beta}$, $u_{m_\alpha m_\alpha}$ describe the interactions averaged over the ensemble of particles. These quantities should be evaluated from the thermodynamic data on the systems under investigation.

In order to simplify the system of constraint equations (6) it is convenient to introduce the set of variables $\chi^{(i)}_{m_\alpha}$

$$N^{(i)}_{m_\alpha m_\alpha} = (\chi^{(i)}_{m_\alpha} P^{(i)}_{m_\alpha})^2 Q_i/2, \tag{12}$$

where

$$P^{(i)}_{m_\alpha} = 2y^2 r^{(j)}_\alpha r^{(k)}_\alpha s_\alpha \mathcal{N}_l \vartheta_m / Q_i$$

is the fraction of the total surface Q_i of the particles orthogonal to direction i, occupied by the contact sites of the mth class, the sites being located on the particles having orientation α.

We proceed now with the implicit assumption that the repulsive forces are the principal factor of nematic stability [3]. This assumption permits us to neglect the dependence of the variables $u_{m_\alpha m_\beta}$ and $w_{m_\alpha l_\beta}$ upon the mutual orientations or particles. Then it holds that $u_{m_\alpha m_\alpha} = u_{mm}$, $w_{m_\alpha l_\beta} = w_{ml}$ and

$$\chi^{(i)}_{m_\lambda} = \cdots = \chi^{(i)}_{m_{\lambda+5}}, \tag{13}$$

where

$$\lambda = 6l - 5, \quad l = 1, 2$$

Equations (11) and (13) taking into account the constraint equations (6) in terms of variables $\chi^{(i)}_{m_\lambda}$ give

$$\chi^{(i)}_{m_\lambda} \sum_{\lambda} \sum_{n \geqslant 0} A^{(i)}_{n_\lambda} \chi^{(i)}_{n_\lambda} \eta_{mn} = 1, \quad m \geqslant 0, \quad \lambda = 6l - 5, \tag{14}$$

where

$$\eta_{mn} = \exp(-w_{mn}/kT), \quad A^{(i)}_{n_\lambda} = P^{(i)}_{n_\lambda} \sum_{\alpha=\lambda}^{\lambda+5} s_\alpha r^{(i)}_\lambda / s_\lambda r^{(i)}_\alpha .$$

In a phase with long range orientational ordering the quasichemical equations (14) have to be solved simultaneously with the condition of the equilibrium orientational arrangement of the molecules, the latter for a discrete set of orientations is given by

$$M_l = \mu_{6(l-1)+\lambda}, \quad l = 1, 2, \quad \lambda = 1, \ldots, 6, \tag{15}$$

where

$$M_l/kT = -(\partial \ln Q_N / \partial \mathcal{N}_l)_{T,M,\{\mathcal{N}_{l'}\}_{l' \neq l}}$$

is the chemical potential of the molecular species of the lth type. Thus, for an axially symmetric nematic phase formed from a binary mixture of particles with lower than axial symmetry system of four equations

$$\left.\begin{aligned} \mu_\alpha &= \mu_{\alpha+2} \\ \mu_\alpha &= \mu_{\alpha+4}, \quad \alpha = 6l - 5, \quad l = 1, 2 \end{aligned}\right\} \tag{16}$$

has to be obeyed. The compositions and densities of the nematic (ρ_{N}) and isotropic (ρ_{I}) phases in a mixture can be located by simultaneous solution of equations (16) with

$$\left.\begin{aligned} M^{\mathrm{I}}_l &= M^{\mathrm{N}}_l \\ P^{\mathrm{I}} &= P^{\mathrm{N}} \end{aligned}\right\} \tag{17}$$

and the quasichemical equations (14) for each phase. The number of equations (14) is equal to the total number of classes of contact sites, including that of vacancies.

As to an axially symmetric nematic phase the quantity of such equations is doubled. The expressions for the chemical potential and for the pressure are given by

$$\mu_\alpha/kT = \mu_\alpha^{\mathrm{rep}}/kT - L_l \sum_{i=1}^{3} \left[2 \ln \chi_0^{(i)} - (1/r_\alpha^{(i)}) \sum_{m \geqslant 1} \vartheta_m (2 \ln \psi_m^{(i)} - u_{mm}/kT) \right],$$

$$\alpha = 6l - 5 \tag{18}$$

$$P \Delta v/kT = P^{\mathrm{rep}} \Delta v/kT - 2 \sum_{l=1}^{3} \ln \chi_0^{(i)}, \tag{19}$$

where $\mu_\alpha^{\mathrm{rep}}$ and P^{rep} are taken from equations (4) and (5). The summation over the index m includes only those classes of contact sites which belong to a molecule of the lth sort.

In so far as the lattice contains holes it is possible to define the volume of mixing of solution as

$$V^M = N_{\mathrm{A}} \Delta v \sum_{l \geqslant 1} L_l x_l (\rho^{-1} - \rho_l^{-1}), \tag{20}$$

where ρ_l is the density of the lth sort of component and x_l is its mole fraction.

Applying expressions (11)–(13) the molar configurational internal energy in equation (7), averaged over the ensemble of particles, reduces to

$$U_N = - \sum_{l} x_l C_l \sum_{m \geqslant 1} \vartheta_m u_{mm}$$

$$+ 2 \sum_{i=1}^{3} \left\{ x_l L_l \left[(1/\rho - 1) + \sum_{\beta=\lambda}^{\lambda+5} s_\beta / r_\beta^{(i)} \right] \sum_{m,n \geqslant 0}\sum \chi_{m_\lambda}^{(i)} \chi_{n_\lambda}^{(i)} A_{m_\lambda}^{(i)} A_{n_\lambda}^{(i)} \eta_{mn} w_{mn} \right\}, \tag{21}$$

where C_l is the whole number of sites on the surface of the lth sort of molecule, $\lambda = 6l - 5$. Expression (21) and the other thermodynamic quantities are obtained with the assumption that the effective interactions $\{u_{mm}\}$ are independent of temperature. The activity coefficient of the non-mesogen and the molar mixing enthalpy may be obtained from

$$\ln \gamma_2 = (M_2 - M_2^0)/kT - \ln x_2, \tag{22}$$

$$H^M = U^M + PV^M, \tag{23}$$

$$U^M = U_N - \Sigma\, x_l u_l, \tag{24}$$

where u_l is the configurational internal energy of the pure substance of the lth sort.

The validity of the model is now tested in the next sections by comparing the present theoretical results with experiment.

3. Evaluation of the parameters for the model

3.1. *Experimental*

The adjusting procedure described in §3.2 uses values of activity coefficients of non-mesogens, densities of the pure components and thermodynamic characteristics of the nematic–isotropic transition in MBPA. The information on the concentration dependence of the activity coefficient for the non-mesogenic component for the systems, listed in the introduction, was obtained by Peterson and Martire by means of a gravimetric technique [21]. The enthalpies of mixing were determined using a Calvet calorimeter [22], three temperatures for the study having been chosen from the range of those discussed in [21]. Two of them correspond to the stability of the nematic phase of pure MBPA ($T = 319{\cdot}5$ and $326{\cdot}4$ K) and the third ($T = 335{\cdot}3$ K) to that of the isotropic phase. The transition characteristics, namely the temperature (T_{NI}) and entropy ($\Delta\Sigma_{NI}/R$), were obtained using DSC. Their values are $T_{NI} = 333{\cdot}4$ K, $\Delta\Sigma_{NI}/R = 0{\cdot}1465$. The temperature dependence of the density for MBPA in the vicinity of transition ($T_{NI} \pm 15$ K) was determined with a bicapillary picnometer. The value of $S_1^{(1)}$ at the transition was evaluated in an indirect way from comparison of plots of $S_1^{(1)}$ and ρ_N for the homologues series of Schiffs' bases [23] and anizlidene-*p*-aminophenylalcanoates [24] which gave $S_1^{(1)} = 0{\cdot}375$.

3.2. *Calculations*

The first stage of the calculations concerns adjusting the parameters describing interactions in pure MBPA (component 1). The distinct set of the contact sites classes for each molecular species implies a definite model of interactions between constituent fragments of the molecules. However, the model of attractions is ambiguous due to the complicated structure of the molecule. The present work deals with two assumptions relating to the MBPA molecular structure. The first reflects a certain trend of MBPA towards correlation of the neighbouring dipole moments perpendicular to the molecular para axis. This assertion for Schiffs' bases was made by Dunmur and Miller via estimate of the Kirkwood *g* factor components in terms of the extended Fröhlich theory [25]. Because the MBPA molecule contains a system of conjugated bonds, the formal subdivision of the molecule into two classes of contact sites with equal surface fractions seems to be the simplest way to account for the dipole correlation. Thus, as a first assumption we have $\vartheta_1 = \vartheta_2 = 0{\cdot}5$. The other approach treats the surface of the molecule as composed of two classes of contact sites, namely, those belonging to the conjugated aromatic fragment (labelled as class 1) and those corresponding to the terminal alkyl chains (class 2). Their surface fractions evaluated from Bondi's table [26] are $\vartheta_1 = 0{\cdot}61$ and $\vartheta_2 = 0{\cdot}39$.

Thus, the set of model parameters for pure MBPA can be presented at fixed $T = T_{NI}$ as the molecular volume v_1, the axial ratios $\lambda_1^{(1)} = A_{11}/\sqrt{(A_{21}A_{31})}$, $\lambda_2^{(1)} = A_{21}/A_{31}$, the effective attraction parameters u_{11}, u_{22}, w_{12} and the volume of the lattice cell Δv. The values v_1 and $\lambda_1^{(1)}$ are chosen to be the estimated volume and axial ratio of a MBPA molecule, namely $0{\cdot}253\,\mathrm{nm}^3$ and $2{\cdot}5$ [26]. If the volume Δv is kept fixed, then the other model parameters are estimated from solution of equations (16) and (17) with the set of quasichemical variables given by equations (14). These parameters were determined such that the experimental data on ρ_1, $S_1^{(1)}$ and the entropy $\Delta\Sigma_{NI}$ at the nematic–isotropic transition were reproduced. The value of Δv was $3{\cdot}75 \times 10^{-3}\,\mathrm{nm}^3$ in all of the calculations. It is to be noted, however, that there are uncertainties in the choice of Δv as an input parameter. The chosen Δv led to $p\Delta v/kT_{NI}$, which was the least in the series of calculations made with other values of Δv (the difference between the values of Δv was $0{\cdot}25 \times 10^{-3}\,\mathrm{nm}^3$). From table 1 we see, however, that in both approximations the reduced pressure and the density change $\Delta\rho = \rho_N - \rho_1$ are overestimated to a great extent; the experimental values of $P\Delta v/kT_{NI}$ and $\Delta\rho/\bar{\rho}$ are 0·004 and 0·002, respectively. This shows the intrinsic shortcomings of the lattice approximation.

The second stage of the calculation deals with the estimation of the effective shapes of the non-mesogens molecules ($\lambda_1^{(2)} = A_{12}/\sqrt{(A_{22}A_{32})}$, $\lambda_2^{(2)} = A_{22}/A_{32}$) and the effective attractive parameters for molecules of the same sort and of MBPA and the non-mesogens. The shape of particles in terms with their chemical structure is ascribed

Table 1. Model and transitional parameters of MBPA for different assumptions concerning the intermolecular attractions. $\vartheta_1 = \vartheta_2 = 0{\cdot}5$ (A), $\vartheta_1 = 0{\cdot}61$, $\vartheta_2 = 0{\cdot}39$ (B). $\tilde{u}_{ii} = u_{ii}/kT_{\mathrm{NI}}$, $\tilde{w}_{12} = w_{12}/kT_{\mathrm{NI}}$. The experimental value of ρ_1 is 0·6176. $\Delta\Sigma_{\mathrm{NI}}/R = 0{\cdot}1364$ in assumption B. The other transitional parameters are in the text.

	$-\tilde{u}_{11}$	$-\tilde{u}_{22}$	$\tilde{w}_{12} \times 10^3$	$-S_2^{(1)}$	$\frac{\Delta\rho}{\bar{\rho}} \times 10^2$	$\frac{P\Delta v}{kT_{\mathrm{NI}}} \times 10^2$
A	0·1676	0·0599	1·41	0·274	1·6	4·88
B	0·1682	0·0772	−1·35	0·279	1·3	4·80

Table 2. Model parameters for the non-mesogen and the characteristics of attraction between the non-mesogen and MBPA. For CCl_4 the values in brackets correspond to approximation B; v_2^* were obtained from Bondi's table [26].

Quantity	CCl_4	n-C_7H_{16}	C_6H_6
$\lambda_1^{(2)}$	1 (1)	3·18	0·70
$-\tilde{u}_{33} \times 10^2$	13·01 (17·89)	9·36	15·71
$\tilde{w}_{13} \times 10^2$	3·62 (5·18)	7·2	1·75
$\tilde{w}_{23} \times 10^2$	2·43 (5·07)	3·34	1·39
$v_2 \times 10^3/\mathrm{nm}^3$	89·1 (71·6)	131·6	91·0
$v_2^* \times 10^3/\mathrm{nm}^3$	82·7	130·9	80·2

a priori. It means, that the molecules of benzene, n-heptane and tetrachlormethane are approximated by plates, rods and cubes respectively, i.e. in all the cases $\lambda_2^{(2)} = 1$. Molecules of the non-mesogen are assumed to be energetically homogeneous, the class of their contact sites in each binary system having the number 3, i.e. $\vartheta_3 = 1$. Thus, the set of adjustable parameters contains u_{33}, w_{13}, w_{23} and $\lambda_1^{(2)}$. The values of the energetic characteristics for each binary system were estimated from the data on the densities of the pure non-mesogens [27] and their activity coefficients at infinite dilution in the coexisting phases of MBPA at $T = T_{\mathrm{NI}}$ [21]. The calculated parameters are summarized in table 2, where the results for the system MBPA–CCl_4 obtained with approximation B are also given.

The proposed evaluation procedure ensures also the correct reproduction of the values for

$$\beta_{2,\infty}^{(j)} = -\lim_{x_2 \to 0} (d(T/T_{\mathrm{NI}})/dx)^{(j)}, \quad (j = \mathrm{I}, \mathrm{N}),$$

which are the limiting slopes of the lines $(T, x_2)^{\mathrm{N}}$ and $(T, x_2)^{\mathrm{I}}$ bounding single phase regions in the phase diagram. This is the consequence of the thermodynamic relation

$$\beta_{2,\infty}^{(j)} = (R/\Delta\Sigma_{\mathrm{NI}})[\gamma_{2,\infty}^{\mathrm{N}}(T_{\mathrm{NI}}) - \gamma_{2,\infty}^{\mathrm{I}}(T_{\mathrm{NI}})]/\gamma_{2,\infty}^{(i)}(T_{\mathrm{NI}}), \quad (i \neq j,\ i, j = \mathrm{I}, \mathrm{N}),$$

where

$$\gamma_{2,\infty}^{(i)} = \exp[\lim_{x_2 \to 0} (M_2/kT - \ln x_2) - M_2^0/kT].$$

4. Numerical predictions

The adjusted model parameters were used to calculate H^M, V^M, γ_2, $S_1^{(l)}$, $S_2^{(l)}$ ($l = 1, 2$) as functions of composition at $T = 319{\cdot}5$, $326{\cdot}1$ and $335{\cdot}3$ K. Those quantities were calculated from equations (1), (20) and (22)–(24) via equations (14) and conditions (16). No additional fitting parameters were used to those obtained from the data on the pure components and infinitely dilute solutions.

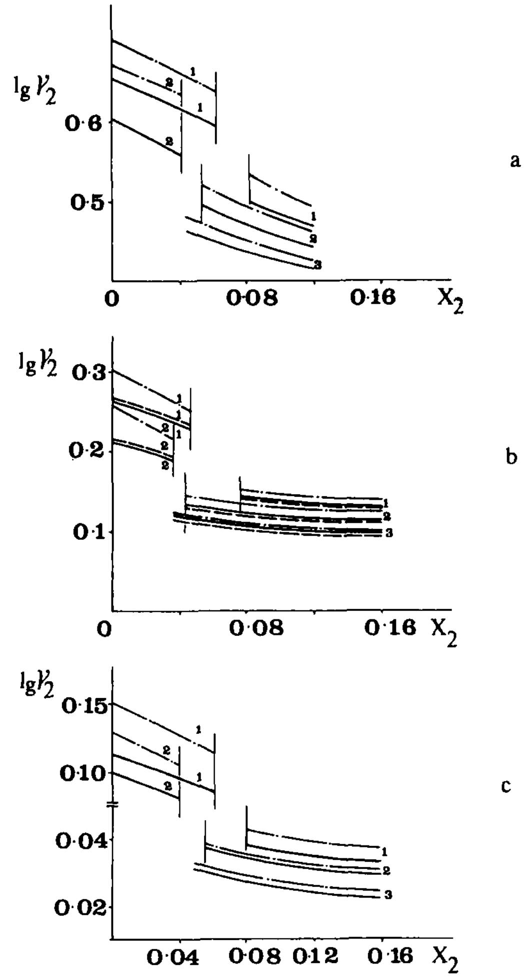

Figure 1. Activity coefficients of *n*-heptane (*a*), carbon tetrachloride (*b*) and benzene (*c*) as functions of the non-mesogen mole fraction in binary mixtures with MBPA at $T = 319{\cdot}5$ K (1), 326·1 K (2) and 335·3 K (3). The full lines are the results of the calculations with approximation A, the dashed lines refer to approximation B, the dash-dot curves present the experimental results [21]. The vertical lines are the boundaries of the nematic–isotropic equilibria.

The calculated and experimental results for $\lg \gamma_2$ versus x_2 are shown in figure 1, for three fixed temperatures. We note that the temperature trend of γ_2 and the calculated discontinuities $\lg \gamma_2^N - \lg \gamma_2^I$ at the phase boundaries fit the experimental data satisfactorily. It is to be noted estimate of the difference $\lg \gamma_2^N - \lg \gamma_2^I$ carried out in the athermal systems composed of linear *r*-mers [4] lead to essential discrepancies with experiment.

We find good agreement between the mixing enthalpies calculated theoretically and the experiment for mixtures of MBPA with *n*-heptane and carbon tetrachloride (see figures 2 and 3), including the temperature trend of H^M. The predictions for the system MBPA–benzene are worse (see figure 4), which may be ascribed to a weak association of benzene molecules. In all of the systems the model was unable to reproduce a weak change of curvature of H^M in the nematic region. The overestimate

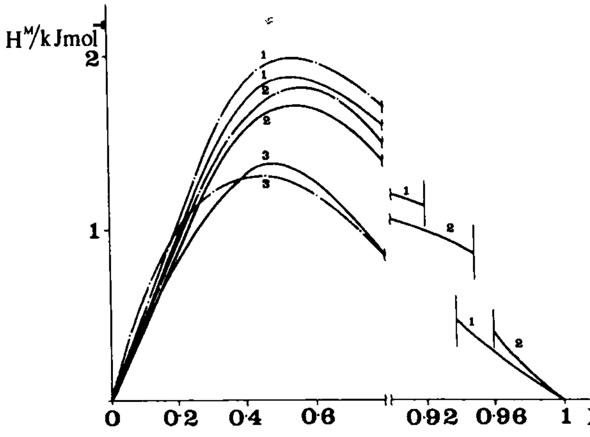

Figure 2. The mixing enthalpies versus the mole fraction x_l in the binary system MBPA–*n*-heptane. The other notation is the same as in figure 1. The experiment is that of [22].

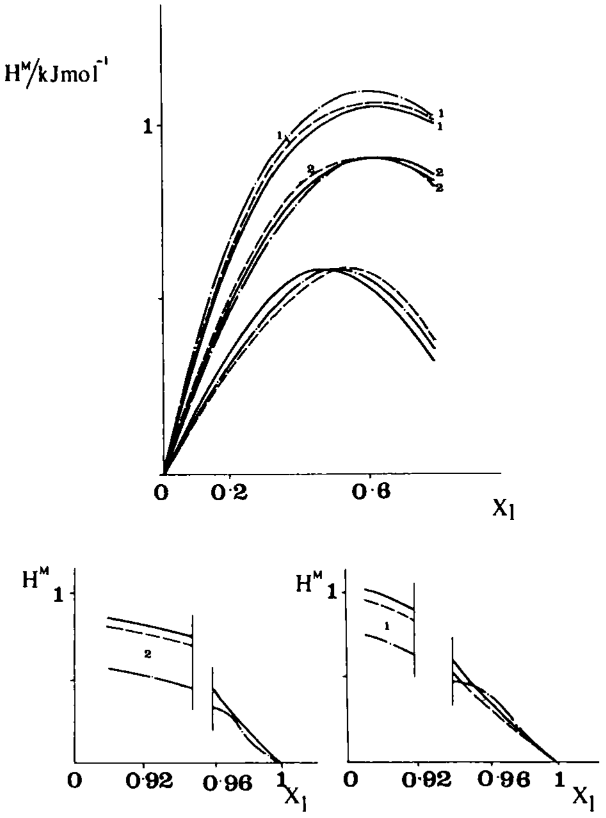

Figure 3. The mixing enthalpies as functions of x_l in the system MBPA–CCl_4. The notation is that from figure 1.

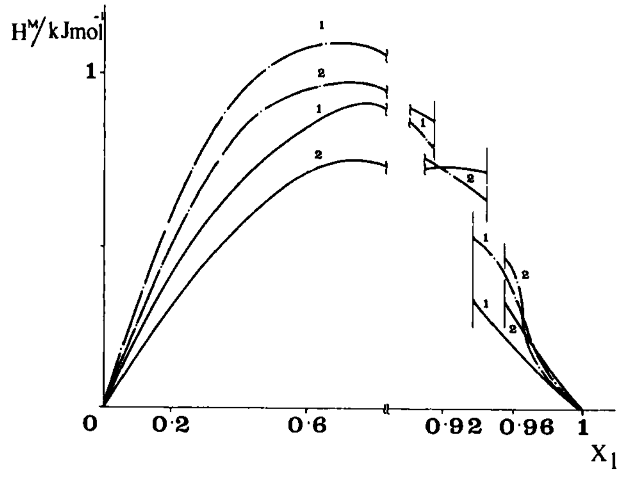

Figure 4. The mixing enthalpies versus the mole fraction x_1 in the system MBPA–benzene. The notation is that of figure 1.

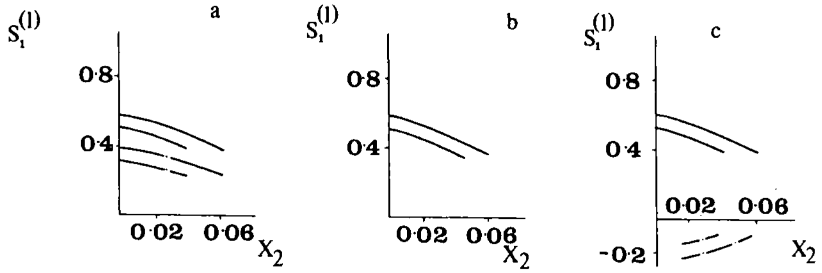

Figure 5. The calculated order parameters of the components as a function of the non-mesogen mole fraction in the mixtures composed of MBPA and *n*-heptane (*a*), carbon tetrachloride (*b*) and benzene (*c*) at $T = 319{\cdot}5$ K (1) and $326{\cdot}1$ K (2). The full lines correspond to MBPA and the dash–dot lines refer to the non-mesogen. All of the results were obtained with approximation A.

of the difference between H^M at the boundary points of the biphasic region is presumably connected with the overestimate of the density change at the nematic–isotropic transition in the pure nematic.

The calculated order parameters for MBPA and the non-mesogen are plotted in figure 5. The value of $S_1^{(1)}$ for MBPA is found to be constant on the line (T, x^{N}), where the isotropic phase first appears on heating. Experimentally this behaviour of $S_1^{(1)}$ is observed in a number of nematic mixtures composed of 4-methoxybenzyliden-4′-*n*-butylaniline and non-mesomorphic compounds [28]. Functions of $S_1^{(2)}$ and $S_2^{(2)}$ versus $T = T/T_{\mathrm{N}}(x_2)$ for benzene are shown in figure 6 together with the experimental values of those for *p*-difluorobenzene dissolved in 4-ethoxybenzyliden-4′-*n*-butylaniline [29]. In this mixture $S_2^{(2)} \neq S_1^{(2)}/2$ which is due to the lower than axial symmetry of $C_6H_4F_2$. The results of the present work as well as the experimental data of [29] suggest a universal character for the dependence of $S_i^{(2)}(T^*)$ on temperature for non-polar non-mesogens in Schiffs' bases.

There are no experimental data for V^M in the systems under investigation, but we can point out that under the condition $T < T_{\mathrm{NI}}$ it holds that $V^M > 0$ and $(dV^M/dT)_x < 0$. These inequalities are also found experimentally for the mixture MBBA–CCl_4 [30].

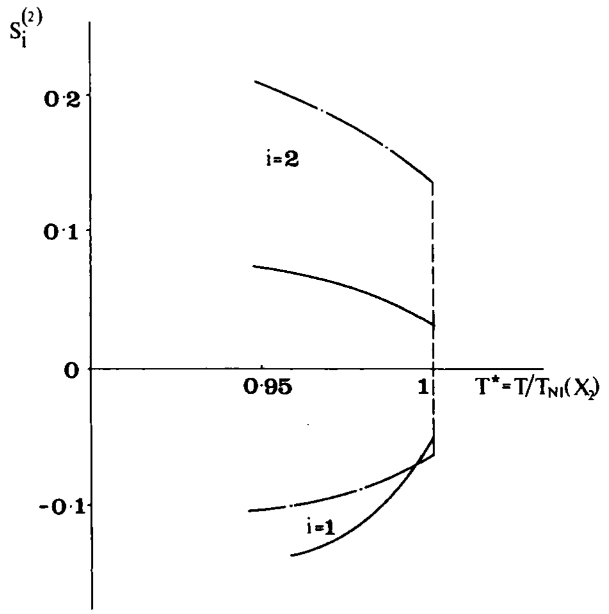

Figure 6. The order parameters of the non-mesogens as functions of the reduced temperature. The full lines correspond to the system MBPA within approximation A. The dash-dot curves present experimental data for the system EBBA–difluorobenzene [29].

The results of the calculation for the mixture MBPA–CCl_4 reveal also that the model parameters depend on an assumption concerning the contact sites for MBPA. Nevertheless the thermodynamic quantities are rather insensitive with respect to the choice of such an assumption. This seems to be a consequence of the crude account taken of the effective intermolecular attractions and repulsions, when the balance between them can be found by the proper choice of fitting parameters.

In conclusion we should emphasize that the concentration dependence of the order parameters and excess thermodynamic properties were calculated with limited information on the characteristics of the pure components and the activity coefficients of the non-mesogens at infinite dilution. In the proposed version the quasichemical model of rectangular parallelepipeds permits us to describe the thermodynamic properties of nematic and isotropic phases for mixtures of nematic–non-mesogenic molecules in a physically reasonable way.

The authors wish to thank Professor A. G. Morachevsky for many stimulating discussions and Dr. Tumanjan for help with equation (A 4) of the Appendix.

Appendix

The model system consists of N square particles $r \times r$ on a square lattice of M sites and of volume $V = M\Delta v$. Using the Alben counting scheme [9], the number of ways $v(x + 1)$ of adding the $(x + 1)$th particle to a lattice containing x such particles is

$$v(x + 1) = N_0 P_1^{(r-1)} P_2^{(r-1)} P_{12}^{(r-1)^2}, \qquad \text{(A 1)}$$

where

$$N_0 = M - r^2 X, \quad P_i = N_0/(N_0 + B_i), \quad B_1 = B_2 = rX,$$

$$P_{12} = N_0/(N_0 + B_{12}), \quad B_{12} = X.$$

The expression for the number of distinct ways of adding N particles is

$$g(N) = \frac{1}{N!}\prod_{x=0}^{N-1} \nu(x+1) = \frac{\{[M - r(r-1)N]!\}^{2/r}\cdot\{[M-(r^2-1)N]!\}^{(r-1)/(r+1)}}{(M!)^{2/(r^2+r)}N!(M-r^2N)!}. \tag{A 2}$$

By straightforward manipulation from expressions (2), where in this case $\alpha = 2$, and equation (A 2) we obtain the pressure of the lattice system as

$$P\Delta v/kT = \ln\frac{1-\rho+\rho/r^2}{1-\rho} + \frac{2}{r}\ln\frac{1-\rho+\rho/r}{1-\rho+\rho/r^2} + \frac{2}{r^2+r}\ln\left(1-\rho+\frac{\rho}{r^2}\right), \tag{A 3}$$

where

$$\rho = Nr^2/M.$$

The continuum translation model can be obtained by taking the limit $\Delta v \to 0$ in equation (A 3) and holding ρ constant. Thus the continuum limit gives

$$PV/NkT = \frac{2}{\rho}\ln(1-\rho) + \frac{3}{1-\rho} = 1 + 2\rho + \tfrac{2}{3}\rho^2 + \dots . \tag{A 4}$$

After the comparison of the virial coefficient in this $P(\rho)$ series with their exact values ($B_2 = 2$, $B_3 = 3$ [31]) we can see that the Alben approach provides an accurate equation of state up to the second virial coefficient B_2.

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