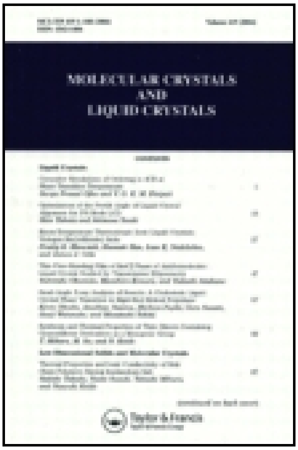

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Statistical Thermodynamic Calculation of Nematic-Isotropic Coexistence Lines in Binary Mixtures of Liquid Crystals: 4, 4′-di-n, n′-Alkoxyazoxybenzenes

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Version of record first published: 20 Apr 2011.

To cite this article: Sharon R. Lunt & Gerald R. Van Hecke (1984): Statistical Thermodynamic Calculation of Nematic-Isotropic Coexistence Lines in Binary Mixtures of Liquid Crystals: 4, 4′-di-n, n′-Alkoxyazoxybenzenes, Molecular Crystals and Liquid Crystals, 111:1-2, 1-29

To link to this article: http://dx.doi.org/10.1080/00268948408082173

Mol. Cryst. Liq. Cryst. 1984, Vol. 111, pp. 1-29
0026-8941/84/1112-0001/$18.50/0

Printed in the United States of America

STATISTICAL THERMODYNAMIC CALCULATION OF NEMATIC-ISOTROPIC COEXISTENCE LINES IN BINARY MIXTURES OF LIQUID CRYSTALS: 4,4′-di-n,n′-ALKOXYAZOXYBENZENES

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Recently Palffy-Muhoray, Dunmur, Miller, and Balzarini (PDMB) applied a modified Maier-Saupe mean field treatment to the calculation of properties of binary mixtures of nematogens. The theory of PDMB is here applied to some phase diagrams of 4,4′-di-n,n′-alkoxyazoxybenzenes that were previously quantitatively studied. The The PDMB equations were expanded using confluent hypergeometric functions for ease of calculation. Also predications for the slopes of the phase diagrams were calculated by recasting the statistical thermodynamic formulas for use in a new thermodynamic formulation called the equal G analysis. Reasonable agreement between theory and experiment was obtained.

INTRODUCTION

For some time the question of two-phase coexistence in liquid crystalline mixtures, particularly binary mixtures of nematic and/or

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smectic liquid crystals has been the subject of much theoretical discussion and experimental verification. There no longer seems to be any experimental doubt as to the reality of phase coexistence, though the composition-temperature region over which phases coexist is more often than not quite small. Theoretical approaches discussing the question have used lattice model, hard particle, and molecular field theories.(1) Most work, by whatever theory, has been directed towards systems of a mesogen with a non-mesogenic solute and then only over short composition ranges close to that of the pure mesogen.(2) Little work to date has addressed the problem of calculating the two phase coexistence lines, herein called the nematicus for N⟶ N + I and the liquidus for I⟶ N + I, for the entire composition region, mole fraction zero to one. A seminal work in this area is that of Humphries, James, and Luckhurst who did address the problem with a mean field theory for the nematicus over the entire composition region but did not calculate the liquidus.(3) A lattice model was used by Sivardiere in which he took the solid, nematic, isotropic phase equilibria to be analogous to a spin one and spin one-half lattice gas. With an Ising like Hamiltonian solved in a molecular field manner, he calculated many types of phase diagrams with the correct topologies for the experimentally observed nematic liquid diagrams.(4) In a different manner Phaovibul and Tang used the psuedo-potential suggested by Humphries, James, and Luckhurst in a Bethe-Peierls-Weiss cluster approach for the evaluation of the partition function.(5) Their treatment while matching the shape of the binary phase diagrams of some mixtures of symmetric alkoxyazoxybenzenes, nevertheless only accounted for the liquidus line. Also within a mean field treatment, Palffy-Muhoray, Dunmur, Miller and Balzarini (PDMB) have extended the simple Maier-Saupe treatment to a theory for mixtures that does successfully predict the nematicus and liquidus lines.(6) We have applied the theory of PDMB to the experimentally studied phase diagrams of 4,4′-di-n,n′-alkoxyazoxybenzenes (the same as those studied by Phaovibul and Tang) and have shown that these phase diagrams can be reasonably well accounted for by knowledge of just the pure component transition temperatures and molar volumes. Drawing on the work of Phaovibul and Tang, we show how the self-consistency integrals for the order parameters can be expanded in confluent hypergeometric series. In addition we have cast the statistical thermodynamic equations of PDMB for chemical potentials into the thermodynamic equal G analysis in order to better understand the meaning of the parameters derived from the PDMB analysis of the phase diagrams.

THEORY FOR BINARY MIXTURES

The treatment below is that of PDMB and the derivation will be only briefly sketched until the equations are expanded in the confluent hypergeometric functions when the origin of the final equations will be shown in detail.

The starting point in any statistical theory is the choice of the interaction potentials and following PDMB, the psuedopotential for a molecule 1 (component 1) in phase α is written as

$$\begin{aligned}\mathcal{E}_\alpha(\cos\theta_1) = \gamma_1^{\circ} &- u_{11}\rho_{1\alpha}S_{1\alpha}P_2(\cos\theta_1)\\ &- u_{22}\rho_{2\alpha}S_{2\alpha}P_2(\cos\theta_1)\\ &+ \tfrac{1}{2}u_{11}\rho_{1\alpha}S_{1\alpha}^2 + \tfrac{1}{2}u_{12}\rho_{2\alpha}S_{1\alpha}S_{2\alpha}\end{aligned} \qquad (1)$$

Here u_{11} and u_{22} are the anisotropic interaction energies between the like molecules 1 and 2 respectively while u_{12} is the anisotropic energy of 1 with 2; further it is assumed that $u_{12} = u_{21}$. The order parameter of i in phase α or β is given by the usual $S_{i\alpha,\beta} = \langle P_2(\cos\theta_i)\rangle_{\alpha,\beta}$ and $\rho_{i\alpha,\beta}$ is the number density of i in phase α or β. Further $\rho_{i\alpha,\beta} = N_{i\alpha,\beta}/V_{\alpha,\beta}$ where $N_{i\alpha,\beta}$ is the number of i in the volume of the α or β phase $V_{\alpha,\beta}$. Replacing 1 with 2, α with β, where appropriate will yield the psuedopotentials for 1 or 2 in the α or β phase. The extension to two components and two phases takes the form, then, of additional terms involving the u_{ij} and the cross products in the order parameters $S_{1\alpha,\beta}$ $S_{2\alpha,\beta}$.

In the four equations for the psuedopotentials it will be assumed that $\gamma_{1\alpha}^{0} = \gamma_{1\beta}^{0} = \gamma_{1}^{0}$ and $\gamma_{2\alpha}^{0} = \gamma_{2\beta}^{0} = \gamma_{2}^{0}$ which means that the isotropic energies of each molecule are equal in each phase.

The Helmholtz energy for the total system is $A = A_\alpha + A_\beta$ and is given by

(2)
$$A = -kT \ln Q_{1\alpha} Q_{2\alpha} - kT \ln Q_{1\beta} Q_{2\beta}$$

where

(3)
$$Q_{i\alpha,\beta} = \frac{\left(\int d\vec{r}^{3}\, d(\cos\theta)\, d\phi \exp\left[- \frac{\mathcal{E}(\cos\theta)}{kT} \right] \right)^{N_{i\alpha,\beta}}}{4\pi (N_{i\alpha,\beta})!}$$

The integration of the partition function is carried out over ϕ and when several substitutions and definitions are made, the result for A_α is

$$A = V_\alpha \left\{ \rho_{1\alpha} \gamma_1^{0} + \rho_{2\alpha} \gamma_2^{0} + \tfrac{1}{2} \sigma_\alpha^{2} \right.$$
$$- kT \rho_{1\alpha} \ln (I_{1\alpha} / \rho_{1\alpha})$$

(4)
$$\left. - kT \rho_{2\alpha} \ln (I_{2\alpha} / \rho_{2\alpha}) \right\}$$

where

(5)
$$I_{i\alpha,\beta} = \int d(\cos\theta) \exp\left[\frac{+u_{ii}\, \sigma_{\alpha,\beta} P_2(\cos\theta)}{kT} \right]$$

Similarly for A_β. Implicit in the above is the assumption $u_{12} = u_{21} = \sqrt{(u_{11}\, u_{22})}$, the geometric mean rule, and the total order parameters defined for each phase as

$$(6) \quad \sigma_{\alpha,\beta} = \sqrt{u_{11}}\, \rho_{1\alpha,\beta}\, S_{1\alpha,\beta} + \sqrt{u_{22}}\, \rho_{2\alpha,\beta}\, S_{2\alpha,\beta}$$

The individual component order parameters, e.g., $S_{i\alpha,\beta}$ are defined in the customary manner. Here we note that these total order parameters are density weighted averages of the order parameters of pure components.

Phase equilibrium is found by demanding that the derivatives of the Helmholtz energy with respect to the variables σ_α, σ_β, $N_{1\alpha}$, $N_{2\alpha}$ be equal to zero. The first two derivatives lead to self-consistency relationships for $\sigma_\alpha, \sigma_\beta$ while the second two derivatives lead to the chemical potentials. The results are

$$(7) \quad \sigma_\alpha = \frac{\rho_{1\alpha}\sqrt{u_{11}}\, I_{1\alpha}(P_2)}{I_{1\alpha}} + \frac{\rho_{2\alpha}\sqrt{u_{22}}\, I_{2\alpha}(P_2)}{I_{2\alpha}}$$

$$(8) \quad \begin{aligned} \mu_{1\alpha} = {} & \gamma_1^{\,0} + \tfrac{1}{2}\sigma_\alpha^{2} v_1 + kT \rho_{2\alpha}(v_2 - v_1) \\ & - kT \ln(I_{1\alpha}/\rho_{1\alpha}) \end{aligned}$$

$$\mu_{2\alpha} = \mu_2^0 + \tfrac{1}{2}\sigma_\alpha^2 v_2 + kT\rho_{1\alpha}(v_1 - v_2) - kT\ln(I_{2\alpha}/\rho_{2\alpha}) \qquad (9)$$

where replacing α with β gives the appropriate equations for β phase. Implicit in these equations is the assumption of volume additivity, that is, the total volume of either phase is the mole fraction weighted sum of the molecular volumes of each component in phase.

The equations are conveniently cast now in terms of volume fractions via $y_{1\alpha} = \rho_{1\alpha} v_1$, $y_{2\alpha} = \rho_{2\alpha} v_2$ where again changing α to β gives β phase results. If β phase is taken to be the isotropic phase than $\sigma_\beta = 0$ and the above equations in terms of volume fractions become, after equating $\mu_{1\alpha}$ to $\mu_{1\beta}$ and $\mu_{2\alpha}$ to $\mu_{2\beta}$,

$$(10) \quad \sigma_\alpha = \frac{y_{1\alpha}\sqrt{U_{11}}\, I_{1\alpha}(P_2)}{v_1 I_{1\alpha}} + \frac{y_{2\alpha}\sqrt{U_{22}}\, I_{2\alpha}(P_2)}{v_2 I_{2\alpha}}$$

(11)

$$\frac{\sigma_\alpha^2 v_1}{2kT} - \ln\left(\frac{I_{1\alpha}}{\rho_{1\alpha}}\right) + y_{2\alpha}\left(1-\frac{v_1}{v_2}\right) =$$

$$+\ln y_{1\beta} + y_{2\beta}\left(1-\frac{v_1}{v_2}\right)$$

(12)

$$\frac{\sigma_\alpha^2 v_2}{2kT} - \ln\left(\frac{I_{2\alpha}}{\rho_{2\alpha}}\right) + y_{1\alpha}\left(1-\frac{v_2}{v_1}\right) =$$

$$+\ln y_{2\beta} + y_{1\beta}\left(1-\frac{v_2}{v_1}\right)$$

Equations 10-12 are the results of PDMB. What we have done next is to express the integrals in the manner pointed out by Phaovibul and Tang, that is, in terms of confluent hypergeometric functions and then expanding the functions to the linear term. Our procedure is as follows. Since $P_2(\cos\theta) = (3\cos^2\theta - 1)/2$

$$I_i = \int_0^1 d(\cos\theta)\exp\left[\frac{\sqrt{u_{ii}}\,\sigma_\alpha(3\cos^2\theta-1)}{2kT}\right]$$

(13)

$$= \int_0^1 dx \exp\left[\frac{-A_i(3x^2-1)}{2kT}\right]$$

where $A_i = -\sqrt{u_{ii}}\,\sigma_\alpha/kT$ and $x = \cos\theta$. The error function in I_i can be expressed in terms of a confluent hypergeometric function ${}_1F_1$. Since

$$(14)\quad \int_0^a du \exp(-u^2) = a\,{}_1F_1\left(1/2, 3/2; -a^2\right)$$

then letting $u_{ii} = \sqrt{3\ A_i\ x/2}$, substituting into eqn 13, I_i becomes

$$(15)\quad I_i = \exp\left(\frac{A_i}{2}\right){}_1F_1\left(1/2, 3/2; \frac{-3A_i}{2}\right)$$

Further using the Kummer transformation

$$(16)\quad {}_1F_1(a, c; z) = \exp(z)\,{}_1F_1(c-a, c; -z)$$

the I_i of eqn 15 becomes

$$I_i = \exp\left(\frac{A_i}{2}\right)\exp\left(\frac{-3A_i}{2}\right){}_1F_1\left(1, 3/2; \frac{3A_i}{2}\right)$$

$$(17)\quad = \exp(-A_i)\,{}_1F_1\left(1, 3/2; \frac{3A_i}{2}\right)$$

Equation 7 contains the integral $I_i(P_2)$ which to the same level of approximation becomes

$$(18)\quad I_i(P_2) = \frac{I_i}{2}\left(\frac{1}{A_i} - 1\right) - \frac{\exp(-A_i)}{2A_i}$$

With these integrals now expressed in terms of the confluent hypergeometric functions, equations 10-12 become, on substituting I_i, $I_i(P_2)$, noting $y_{2\alpha} = 1 - y_{1\alpha}$, and collecting terms

$$\frac{\sigma_\alpha^2 v_1}{2kT} - A_1 + \ln\left(\frac{y_{1\alpha}}{y_{1\beta}}\right) - \ln\left[{}_1F_1\left(1, 3/2; -\frac{3A_1}{2}\right)\right] + (y_{1\beta} - y_{1\alpha})\left(1 - \frac{v_1}{v_2}\right) = 0 \tag{19}$$

$$\frac{\sigma_\alpha^2 v_2}{2kT} - A_2 + \ln\left(\frac{1 - y_{1\alpha}}{1 - y_{1\beta}}\right) - \ln\left[{}_1F_1\left(1, 3/2; -\frac{3A_2}{2}\right)\right] + (y_{1\alpha} - y_{1\beta})\left(1 - \frac{v_2}{v_1}\right) = 0 \tag{20}$$

$$\sigma_\alpha = \frac{y_{1\alpha}\sqrt{u_{11}}\,kT}{v_1\left[2\sqrt{u_{11}}\,\sigma_\alpha\,{}_1F_1\left(1, 3/2; -\frac{3A_1}{2}\right)\right]} - \frac{y_{1\alpha}\sqrt{u_{11}}}{2v_1} - \frac{kT\,y_{1\alpha}}{2v_1\sigma_\alpha} + \frac{(1 - y_{1\alpha})\sqrt{u_{22}}\,kT}{v_2\left[2\sqrt{u_{22}}\,\sigma_\alpha\,{}_1F_1\left(1, 3/2; -\frac{3A_2}{2}\right)\right]} - \frac{(1 - y_{1\alpha})\sqrt{u_{22}}}{2v_2} - \frac{(1 - y_{1\alpha})\,kT}{2v_2\,\sigma_\alpha} \tag{21}$$

At this point these equations could be solved for $y_{1\alpha}$, $y_{1\beta}$, and σ_α knowing T, v_1, v_2, estimating u_{ii} from the Maier-Saupe result $u_{ii} = 5\,k\,T_i\,v_i$ and evaluating the ${}_1F_1(1,3/2;z)$ functions to complete convergence. It might be will to remember here that these results assume the geometric mean rule, volume additivity and the same molecular volumes in each phase. Further we assume that the Helmholtz energy is approximately equal to the Gibbs energy and thus the equations are, to a good approximation, applicable to the constant pressure phase diagrams studied here.

The ${}_1F_1(a,c;z)$ functions expand in series as

$$ {}_1F_1(a,c;z) = 1 + \frac{a}{c}z + \frac{a(a+1)}{c(c+1)2!}z^2 + \cdots \tag{22}$$

Substituting this expansion up to the linear term into equations 19-21 gives

$$\left(\frac{v_1\sigma_\alpha^2 - 2\sqrt{u_{11}}\,\sigma_\alpha}{2kT}\right) + \ln\left(\frac{y_{1\alpha}}{y_{1\beta}}\right) - \ln(1+A_1) + (y_{1\beta}-y_{1\alpha})\left(1-\frac{v_1}{v_2}\right) = 0 \tag{23}$$

$$\left(\frac{v_2\sigma_\alpha^2 - 2\sqrt{u_{22}}\,\sigma_\alpha}{2kT}\right) + \ln\left(\frac{1-y_{1\alpha}}{1-y_{1\beta}}\right) - \ln(1+A_2) + (y_{1\alpha}-y_{1\beta})\left(1-\frac{v_2}{v_1}\right) = 0 \tag{24}$$

$$\frac{y_{1\alpha}}{2v_1}\left[\frac{kT}{\left(\sigma_\alpha - \frac{\sigma_\alpha^2\sqrt{u_{11}}}{kT}\right)} - \sqrt{u_{11}} - \frac{kT}{\sigma_\alpha}\right] - \sigma_\alpha + \frac{(1-y_{1\alpha})}{2v_2}\left[\frac{kT}{\left(\sigma_\alpha - \frac{\sigma_\alpha^2\sqrt{u_{22}}}{kT}\right)} - \sqrt{u_{22}} - \frac{kT}{\sigma_\alpha}\right] = 0 \tag{25}$$

It is this last set of equations which we have programmed to solve for the nematicus ($y_{1\alpha}$) and the liquidus ($y_{1\beta}$) lines as well as the total order parameter σ_α for the N⟶N + I transition temperatures and compositions.

Among the phase diagrams considered below are several which exhibit minima. From a thermodynamic point of view a minimum forming system is non-ideal which infers that the intermolecular forces of any arbitrary composition are not simply related to the intermolecular forces between molecules of pure components. This suggests that it is poor to invoke the geometric mean rule to treat non-ideal systems. However, it is not obvious from the study of eqns 10-12 what could be adjudged responsible for the minima, that is, the non-ideal behavior. In an attempt to understand the origin of such behavior the PDMB equations were cast in a different form.

Normally to establish the equations for phase equilibria, the chemical potentials of each component in each phase are set equal. Another approach, however, is to set the Helmholtz energies of each phase equal, which under the asumption that pV effects in condensed phases are unimportant, gives $A_\alpha = G_\alpha = G_\beta = A_\beta$ and thus the Gibbs energies are also set equal. This treatment, called the equal G analysis by Oonk, has the effect of reducing the composition variables from two to one the value of which must always lie between the true equilibrium compositions of each phase.(7)

From the discussion above we write for α phase

$$G_\alpha \approx A_\alpha = x\mu_{1\alpha} + (1-x)\mu_{2\alpha} \tag{26}$$

where again changing α to β gives G_β. Thus

$$A_\beta - A_\alpha = 0 = x(\mu_{1\beta}-\mu_{1\alpha}) + (1-x)(\mu_{2\beta}-\mu_{2\alpha}) \tag{27}$$

where x is mole fraction of the first component. From before using eqns 8-9

$$(\mu_{1\beta}-\mu_{1\alpha}) = kT\,(v_2-v_1)(\rho_{2\beta}-\rho_{2\alpha}) + kT \ln\left(\frac{Q_{1\alpha}}{Q_{1\beta}(0)}\right) - \frac{\sigma_\alpha^2 v_1}{2} \tag{28}$$

where $Q_{1\beta}(0)$ is the partition function for $\sigma_\beta = 0$. To obtain the parallel expressions for the second component exchange 1 and 2.

One of the key features of this analysis is that the composition variables $y_{1\alpha}$, $y_{1\beta}$, are replaced by just one composition which is the composition where G_α and G_β are equal. It can be shown that this composition must always be between the equilibrium values of $y_{1\alpha}$ and $y_{1\beta}$. Here in this case since the molar volumes of each component are assumed equal in each phase the equal G point infers $\rho_{1\alpha} = \rho_{1\beta}$ and $\rho_{2\alpha} = \rho_{2\beta}$. Thus the density terms drop out under these circumstances, and the chemical potential differences become

(29) $$(\mu_{1\beta} - \mu_{1\alpha}) = kT \ln I_1 - \frac{\sigma_\alpha^{2} v_1}{2}$$

(30) $$(\mu_{2\beta} - \mu_{2\alpha}) = kT \ln I_2 - \frac{\sigma_\alpha^{2} v_2}{2}$$

and the total difference in Gibbs energy (which equals zero) eqn 27 becomes

(31) $$x\left[kT \ln I_1 - \frac{\sigma_\alpha^{2} v_1}{2}\right] + (1-x)\left[kT \ln I_2 - \frac{\sigma_\alpha^{2} v_2}{2}\right] = 0$$

Equation 31, which is in effect a combination of eqns 24 and 25, describes the equal G phase diagram which is T, x graph where the composition x is always between the true coexisting phase compositions. If the two phase region is very narrow, then the equal G phase diagram is a very good estimate to the true phase diagram. Of course the solutions of eqn 31 depend on σ_α which must be found from a suitably modified eqn 23.

Rather than solving the coupled eqns "23" and

31, we studied the slope dT/dx of the equal G phase diagram for the practical reason that is easier, and, as it turns out, does shed some insight as to the terms responsible for non-ideality. (See below). To calculate dT/dx we first found dx/dT of the the total equal G eqn 31, and then took its inverse. Thus

(32)

$$\frac{dT}{dx} = \frac{\ln\left(\frac{I_1}{I_2}\right) + \frac{\sigma_\alpha^2(v_2 - v_1)}{2kT}}{-x\frac{d\ln I_1}{dT} - (1-x)\frac{d\ln I_2}{dT} - \frac{\sigma_\alpha^2}{2kT^2}\left[x v_1 + (1-x)v_2\right]}$$

where I_i has the same meaning as in eqn 13. If the integrals are expanded in terms of the confluent hypergeometric series up to the linear term and the Maier-Saupe result of $u_{ii} = 5\,k\,T_i\,v_i$ is used, the result for the slope at any T, x point is

$$\frac{dT}{dx} = \frac{N}{D}$$

(33) $$N = \frac{\sigma_\alpha(\sqrt{u_{11}} - \sqrt{u_{22}})}{kT} + \ln\left(\frac{kT - \sigma_\alpha\sqrt{u_{11}}}{kT - \sigma_\alpha u_{22}}\right) + \frac{\sigma_\alpha^2(v_2 - v_1)}{2kT}$$

$$D = \frac{x\,u_{11}\left(\frac{\sigma_\alpha}{kT}\right)^2}{2T\left(1-\frac{\sqrt{u_{11}\sigma_\alpha}}{kT}\right)} + \frac{(1-x)\,u_{22}\left(\frac{\sigma_\alpha}{kT}\right)^2}{2T\left(1-\frac{\sqrt{u_{22}\sigma_\alpha}}{kT}\right)} + \frac{\sigma_\alpha^2\left[x v_1+(1-x)v_2\right]}{2kT^2}$$

where in this case the total order parameter is given by

$$(34) \qquad \sigma_\alpha = \frac{\sqrt{u_{11}}\,x\,S_1 + \sqrt{u_{22}}\,(1-x)\,S_2}{x v_1 + (1-x)v_2}$$

The limiting slope behavior is easily obtained by setting x = 0 or 1 and $T = T_2$ or T_1 respectively. Use of these equations is illustrated below.

RESULTS AND DISCUSSION

Mixtures of homologus 4,4′-di-n,n′-alkoxy-azoxybenzenes have been well studied. We present here the results of applying PDMB theory and its equal G modification to several binary phase diagrams of these compounds that have been quantitatively studied.(10) The nematic-isotropic transition temperature and molar volume data for the pure components is presented in Table 1. The symmetric azoxybenzenes studied here had terminal alkyl chains whose length ranged from one to seven carbons and a specfic homolog will henceforth be abbreviated by the number of carbons in that terminal chain. Hence 2 will refer to 4,4′-di-n,n′-ethyloxyazoxybenzene.

Since estimates can be made for u_{11} and u_{22} while T and v are known experimentally, the final

TABLE 1

NEMATIC-ISOTROPIC TRANSITION TEMPERATURES AND MOLECULAR VOLUMES FOR 4,4′-di-n,n′-ALKOXY-AZOXYBENZENES

COMPOUND	TEMPERATURE(a)	VOLUME(b)
1, Methoxy	408.5	3.74
2, Ethoxy	440.7	4.40
3. Propoxy	396.8	4.96
4, Butoxy	409.9	5.63
5, Pentoxy	396.4	6.13
6, Hexoxy	402.3	6.76
7, Heptoxy	397.2	7.29

(a) Data from reference (8). Units: K
(b) Data from reference (9). Units: 10^{-22} cm^3 /molecule

equations of the theory, eqns 10-12 are three equations in the three unknowns $y_{1\alpha}$, $y_{1\beta}$, and σ_α. These equations were solved using a numerical analysis routine implementing Marquardt's method for finding roots of systems of equations.(11) This method, which is a modification of Newton's method, invokes an extra parameter to allow for functions with steep slopes, and those which are slow to converge.

In order to solve for the desired variables of σ_α and composition, the interaction parameters u_{11} and u_{22}, as mentioned above, must be estimated. Various estimates were tried. Initially the relationship suggested by Maier-Saupe where $u_{11}/u_{22} = K(T_1 v_1/T_2 v_2)$ and K = 1 was used. Desired agreement of theory and experiment was achieved only if the ratio u_{11}/u_{22} was very close or equal to one in all systems. Even a slight deviation from one for this ratio caused a large disparity between experiment with theory. Manipulation of the values of u_{11} and u_{22} while maintaining their ratio at one, resulted in only slight variations and/or smoothing of the theoretically derived phase diagrams. The effects on the phase diagram by changing the u_{ii} values were relatively minor. However, the effects on σ_α were quite large. The interaction parameters given in Table 2 were those that yield σ_α's such that the individual order parameters S_1 and S_2 were "close" to the traditional value of 0.4.

In the approximation of only a single term expansion for the integrals, the failure of the Maier-Saupe estimate for u_{ii} can readily be seen from the general slope equal G eqn 33. For eqn 33 to describe a minimum, dT/dx must equal zero which can only occur if $u_{11}\sigma_\alpha$, or $u_{22}\sigma_\alpha$ equal kT. Since the Maier-Saupe estimate sets $u_{ii} = 5\ k\ T_i\ v_i$ and given the definition of σ_α in eqn 34, neither condition can ever be met for reasonable values of σ_α and hence S_i. By the nature of the definition of σ_α, the magnitude of its actual numbers is not very informative, but the trends in σ_α with T and x for a given phase diagram are interesting. If the phase diagram exhibits a minimum so does σ_α when plotted vs composition. If the phase diagram is a simple spindle with positive or negative slope, σ_α also increases or decreases monotonically with composition. Such behavior certainly argues against the order parameter of a pure material being a universal constant, a fact which is immediately obvious from the results in Table 2.

TABLE 2

INTERACTION PARAMETERS AND PURE COMPONENT ORDER PARAMETERS FOR BINARY MIXTURES OF HOMOLOGUS 4,4′-di-n,n′-ALKOXYAZOXYBENZENES

SYSTEM		INTERACTION	ORDER PARAMETERS	
Component 1	Component 2	PARAMETER Uii(a)	Component 1	Component 2
2	1	6.76	0.40	0.32
3	1	3.45	0.81	0.59
4	1	7.76	0.42	0.26
7	1	5.83	0.69	0.35
3	2	6.76	0.39	0.38
4	2	6.76	0.46	0.38
5	2	8.83	0.36	0.29
6	2	8.83	0.41	0.29
5	3	8.18	0.42	0.31
5	4	7.76	0.42	0.39
6	4	8.83	0.41	0.35
6	5	8.83	0.44	0.39

(a) Units: 10^{-35} erg cm^3

In Table 3 are the limiting slope values calculated from the observed u_{ii} and σ_α values. The limiting slopes were calculated from the equations below which were obtained from eqn 33 by setting $u_{11} = u_{22}$, and $x = 0$ and $T = T_2$, or $x = 1$ and $T = T_1$. Thus

(35) $$\frac{dT}{dX} = \frac{T_2(v_2 - v_1)}{\dfrac{u_{22}}{kT_2 v_2 - u_{22} S_2} - 1}$$

(36) $$\frac{dT}{dX} = \frac{T_1(v_2 - v_1)}{\dfrac{u_{11}}{kT_1 v_1 - u_{11} S_1} - 1}$$

Several disconcerting features of the results in Tables 2 and 3 are evident with very little study. Any given S_i value, since it represents the order parameter for pure i, should be the same regardless of whether it is calculated for an ij or an ik mixture. This aspect of S_i is not evident in the results given in Table 2. Moreover, this inconsistency in the S_i values is not understood. The calculated limiting slope values presented in Table 3 match at least all signs of the observed slopes. Agreement in terms of magnitudes is only fair to poor, however. Since T , v , and S_i should all be the same for a given pure i, the limiting slope of pure component i in an ij or ik mixture is only a function of the interaction parameter u_{ii} for the ij or ik mixture. In fact since both S_i and u_{ii} vary in ij and ik mixtures (Table 2), the poor values for the calculated slopes most likely must be caused by the same effect that gives rise to the inconsistent S_L values.

TABLE 3

LIMITING SLOPES FOR PURE COMPONENTS CALCULATED BY THE EQUAL G ANALYSIS FOR BINARY PHASE DIAGRAMS OF 4,4′-di-n,n′-ALKOXYAZOXYBENZENES

SYSTEM		LIMITING SLOPES(a)	
Component 1	Component 2	Component 1	Component 2
2	1	0.6(17)	0.3(43)
3	1	-2.8(-42)	2.1(5)
4	1	-2.4(-36)	1.3(16)
7	1	-4.4(-137)	0.9(23)
3	2	-0.9(-52)	-0.6(-35)
4	2	-2.0(-52)	-1.0(-19)
5	2	-2.3(-69)	-2.2(-30)
6	2	-3.1(-87)	-2.1(-16)
5	3	-2.1(-13)	0.8(15)
5	4	-0.7(-14)	-0.9(-14)
6	4	-0.9(-6)	-1.0(-9)
6	5	0.4(2)	0.6(9)

(a) Units: K. Phase diagrams in text are plotted with mole fraction of component 1 increasing left to right. The limiting slope of component 1 should match the slope observed in the limit at the right hand side of the diagram. Observed values are given in parenthesis.

Some of the phase diagrams drawn using the methods discussed so far are shown in Figure

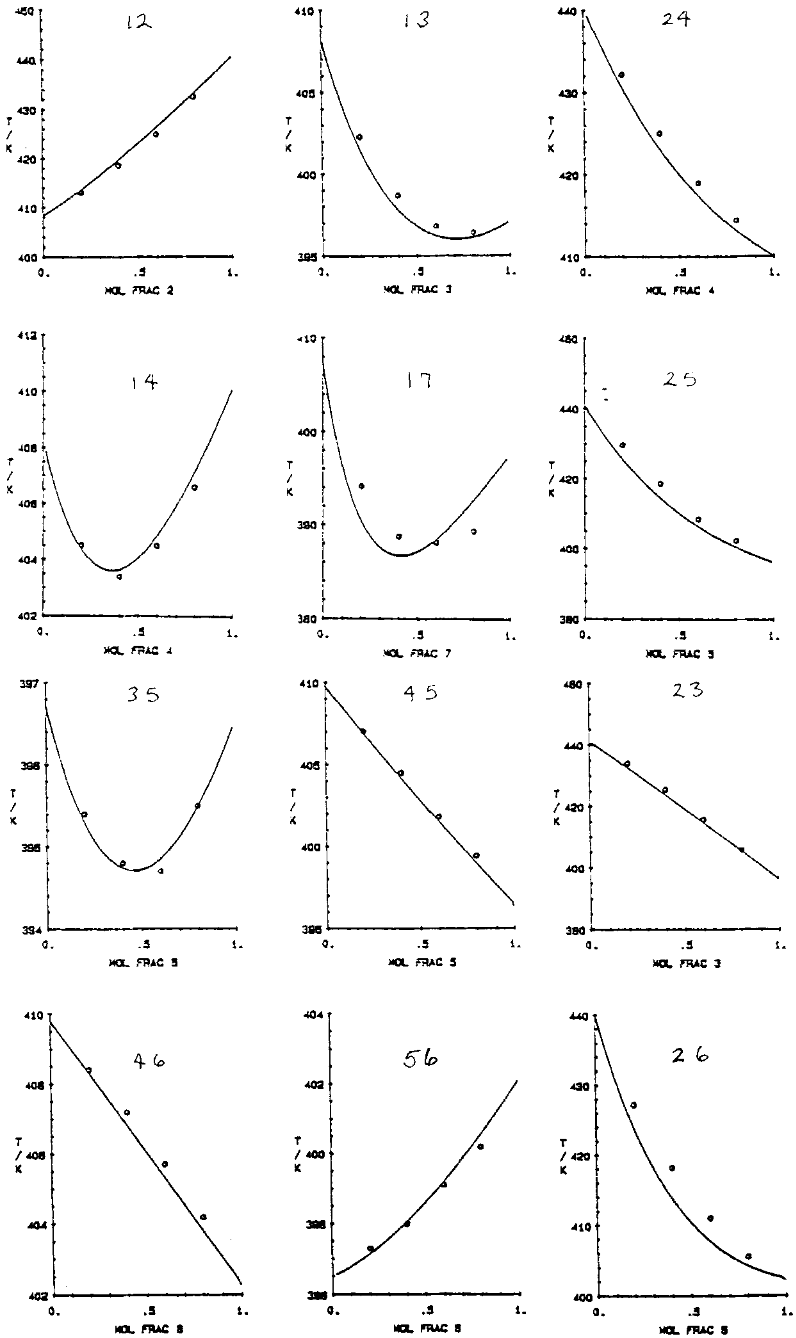
12
T / K
400
410
420
430
440
450
0.
.5
1.
MOL FRAC 2
13
T / K
395
400
405
410
0.
.5
1.
MOL FRAC 3
24
T / K
410
420
430
440
0.
.5
1.
MOL FRAC 4
14
T / K
402
404
406
408
410
412
0.
.5
1.
MOL FRAC 4
17
T / K
380
390
400
410
0.
.5
1.
MOL FRAC 7
25
T / K
380
400
420
440
460
0.
.5
1.
MOL FRAC 5
35
T / K
394
396
398
400
0.
.5
1.
MOL FRAC 5
45
T / K
395
400
405
410
0.
.5
1.
MOL FRAC 5
23
T / K
380
400
420
440
460
0.
.5
1.
MOL FRAC 3
46
T / K
402
404
406
408
410
0.
.5
1.
MOL FRAC 6
56
T / K
396
398
400
402
404
0.
.5
1.
MOL FRAC 6
26
T / K
400
410
420
430
440
0.
.5
1.
MOL FRAC 6

FIGURE 1. CALCULATED (-) AND EXPERIMENTAL (o) ISOBARIC PHASE DIAGRAMS FOR BINARY MIXTURES OF 4,4′-di-n,n′-ALKOXYAZOXYBENZENES. SYSTEMS ARE DESIGNATED BY THE NUMBER OF CARBONS IN THE TERMINAL ALKOXY CHAIN. THUS 12 MEANS A MIXTURE OF METHOXY- AND ETHOXY- HOMOLOGS. EXPERIMENTAL DATA WAS OBTAINED FROM REFERENCE 10 IN TEXT.

1.(12) The o′s are experimental points. The theoretical lines seem to give good agreement in a wide variety of systems. The systems exhibiting a pronounced minima are not as well described, however. While the minima diagrams look reasonable, they are misleading, since the nematicus and liquidus lines cross instead of coming tangent at the minimum point which is obviously incorrect behavior, but also not understood at this time. The system of equations does account for the whole phase diagram, with both nematicus and liquidus lines calculated. These lines are extremely close together both in theory and experiment. As an unexplored area for future work the fact that the lines are experimentally so narrow means that the equal G phase diagram obtained by solving eqn 31 should be an excellent approximation to the true phase diagram.

Several comments on these results in the way of conclusions are pertinent. First the empirical finding that the solution to the equations required $u_{11} = u_{22}$ does not make physical sense since clearly the intermolecular forces between two different molecules should be different. This finding appears to be saying an ij system is described by some average interaction parameter whose relationship to u_{ii} and u_{jj} is unknown. Empirically the result of u_{11} equaling u_{22} may be due to any one of several assumptions: use of the geometric mean rule; use of volume additivity; expansion of the confluent hypergeometric series only to the first term. The work of Phaovibul and Tang clearly showed that volume additivity does not hold for mixtures of these azoxybenzenes but the effect should not be of such a magnitude to account for the inconsistencies in these calculations. The most likely cause is the expansion to only the linear term. The equations could be solved rigorously by numerical evaulation of the integrals involved. This was not done here in the attempt to see if good calculations could be obtained with the simplifying expansion successfully used by Phaovibul and Tang (5) in their earlier work on these compounds. Expansion to the quadratic term looks to entail as much effort as simply numerically evaulating the integrals directly; thus while such an expansion might have yielded better results, it was not tried.

Regardless of the origin of the effects described by the equations the fact remains that the theory can calculate phase diagrams including non-ideal minima systems even if the agreement with experiment is not the best. Again the assumption of the geometric mean rule is associated with the concept of ideal behavior in terms of the intermolecular forces between different molecules. That the theory calculates the non-minimum diagrams with fair success should not be surprising since the deviation from ideality does not seem to be very great, but that it can calculate minima systems which are definitely non-ideal in terms of intermolecular forces is quite surprising.

ACKNOWLEDGEMENTS The authors wish to thank members of the Harvey Mudd College Mathematics

Department, especially Profs. R. Borrelli and J. Greever, and Messrs. N. Freed and K. Caroso for invaluable help and advice.

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