

action distance. The D values can be obtained by NMR methods. The Q values should be directly related to the equilibrium thermodynamics of the system. It clearly takes a very large amount of good data to attempt such a fit. We are pursuing this approach on some well-characterized systems.

At the same time, we have examined a large number of systems using data on aqueous amines, alcohols, and ethers from our own and other laboratories. In every case, $(\alpha/f^2 - B)$ approaches linearity with $f^{1/2}$ if the data cover a wide enough frequency range and go to a relatively low frequency (≤ 5 M Hz). We feel that this is strong evidence for the fluctuation approach.

One of the main conceptual problems with the fluctuation approach is that it does not provide a simple "chemical" kinetic process like $A + B \rightarrow C$ for the audience. Instead, we obtain parameters purported to describe a thermodynamic fluctuation. It is useful to consider how such a fluctuation could arise. We note that the amplitude of the sound absorption phenomenon in such systems is governed by the ratio of hydrophobic to hydrophilic area on the molecule. That is, as we go from MeOH to t -BuOH, the effect goes up in amplitude dramatically. If we go from EtOH to ethylene glycol, the effect is diminished. So our fluctuation is related to the response of the water to the introduction of a hydrophobic moiety, and the thermodynamic properties of the water in the vicinity of the hydrophobic moiety are different from bulk water. In effect, we are seeing a dynamic version of the well-known propensity of such organic molecules to form clathrate hydrates. t -BuNH₂ is well-known²¹ to form such a hydrate. It is probably not coincidental that the hydrate formula (t -BuNH₂·9.75H₂O) is not far removed from the "peak sound

absorption concentration". It, thus, seems at least possible to conceive of a hybrid theory which has the virtues of a "chemical" model and still has the quantitative advantages of the fluctuations approach.

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References and Notes

- (1) Department of Chemistry, Al-Azhar University, Cairo, Egypt.
- (2) Department of Physics, National Defense Academy, Yokosuka, Japan.
- (3) M. J. Blandamer and D. Waddington, *Adv. Mol. Relaxation Processes*, **2**, 1 (1970).
- (4) M. J. Blandamer, In "Water—A Comprehensive Treatise", Vol. 2, F. Franks, Ed., Plenum Press, New York, 1973.
- (5) J. H. Andreae et al., *Acustica*, **15**, 74 (1965).
- (6) V. P. Romanov and V. A. Solov'ev, *Sov. Phys.-Acoust. (Engl. Transl.)*, **11**, 68 (1965).
- (7) M. M. Emara, G. Atkinson, and E. Baumgartner, *J. Phys. Chem.*, **76**, 334 (1972).
- (8) M. Eigen, G. Maass, and G. Schwarz, *Z. Phys. Chem.*, **74**, 319 (1971).
- (9) R. S. Brundage and K. Kustin, *J. Phys. Chem.*, **74**, 672 (1970).
- (10) S. Niskikawa et al., *Bull. Chem. Soc. Jpn.*, **46**, 1098 (1973).
- (11) S. Niskikawa et al., *Bull. Chem. Soc. Jpn.*, **52**, 655 (1979).
- (12) R. E. Verrell, personal communication.
- (13) M. J. Blandamer et al., *Trans. Faraday Soc.*, **63**, 66 (1967).
- (14) K. Applegate, L. J. Slutsky, and R. C. Parker, *J. Am. Chem. Soc.*, **90**, 6909 (1968).
- (15) P. Kruus, *Can. J. Chem.*, **42**, 1712 (1964).
- (16) M. J. Blandamer, N. J. Hadden, and M. C. R. Symons, *Trans. Faraday Soc.*, **66**, 316 (1970).
- (17) "Stability Constants of Metal-Ion Complexes", 2nd ed., The Chemical Society, London, 1964.
- (18) K. Tamura, M. Maekawa, and T. Yasunaga, *J. Phys. Chem.*, **81**, 2122 (1977).
- (19) R. Garnsey and D. W. Ebdon, *J. Am. Chem. Soc.*, **91**, 50 (1969).
- (20) R. Garnsey, R. J. Boe, R. Mahoney, and T. A. Litovitz, *J. Chem. Phys.*, **50**, 5222 (1969).
- (21) R. K. McMullan, G. A. Jeffrey, and T. H. Jordan, *J. Chem. Phys.*, **47**, 1229 (1967).

Use of Regular Solution Theory for Calculating Binary Mesogenic Phase Diagrams Exhibiting Azeotrope-Like Behavior. 2. Maxima Forming Systems¹

G. R. Van Hecke,* T. S. Cantu,

Department of Chemistry, Harvey Mudd College, Claremont, California 91711

M. Domon, and J. Billard

Laboratoire de Dynamique des Cristaux Moleculaires, Université des Sciences et Techniques de Lille, B.P. 36, 59650 Villeneuve D'Ascq, France (Received July 12, 1979)

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Many binary phase diagrams of mesomorphic components exhibit maxima azeotrope-like phase behavior. Regular solution theory is successfully applied to calculate four such diagrams arising from binary mixtures of three cholesterol esters and a tolane with enantiomeric p -nitrobenzalamino cinnamic acid 2-methylhexyl ester.

Introduction

While more and more phase diagrams of binary mixtures of crystalline materials are appearing in the literature, little work calculating such diagrams by some thermodynamic means has appeared.²⁻⁴ Regular solution theory has been successfully applied to calculating the fluid two phase region between the nematic and isotropic phases exhibited in binary mixtures of homologous symmetric azoxybenzenes.⁵ We report here the results of applying the regular solution approximation to relatively complex phase diagrams, which, in some cases, exhibit three phases in

equilibrium, for example, smectic A, cholesteric, and a crystal, or smectic A, nematic, and isotropic. The method does indeed appear to be a successful means for calculating even complex phase diagrams.

Experimental Section

The four phase diagrams discussed here were obtained for combinations of three cholesterol esters and one tolane with a common reference compound, enantiomeric p -nitrobenzalamino cinnamic acid 2-methylhexyl ester (I).⁶ The cholesterol esters were nonanoate (pelargonate, II),

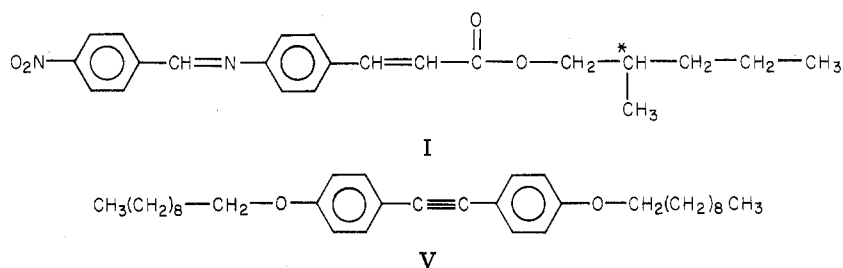


TABLE I: Temperatures (T , K) and Enthalpies ($\Delta H_{\alpha\beta}$, kJ mol⁻¹) of the Various Phase Transitions for the Pure Compounds *p*-Nitrobenzalamino-2-methylhexyl Ester (I), Cholesterol Nonanoate (II), Cholesterol Tetradecanoate (III), Cholesterol Octadecanoate (IV), and 4,4'-Bis(decyloxy)tolane (V)^a

compd	phase α	phase β : T ; $\Delta H_{\alpha\beta}$			
		S_C	S_A	nematic	I
I ^c	K ^b		[369.8; 26.78]	[367.8; 28.04]	365.7; 30.96
	S_A			(330; 1.255)	341.86; 4.184
	N_g				(347.2; 2.929)
II ^d	K		[352.8; 25.83]	352.8; 26.36	358.7; 1.269
	S_A			349.3; 0.548	
	N_g				363.9; 0.736
III ^d	K		344.0; 47.94		
	S_A			352.2; 1.293	
	N_g				357.3; 0.728
IV ^e	K		[355.4; 67.03]	[355.1; 68.66]	355.0; 70.29
	S_A			(342; 1.632)	
	N^*				(346.6; 1.632)
V ^c	K	359.7; 52.30	[359.8; 55.23]		
	S_C		362.2; 2.929		
	S_A			368.7; 3.557	[371.3; 6.862]
	N				374.2; 3.306

^a Parentheses denote a monotropic phase transition and square brackets a calculated virtual phase transition. ^b K denotes crystal, S_A , S_C smectic A, C, respectively, I isotropic. Several types of nematic phases are referred to here. Compounds I, II, III are N_g , levorotatory twisted nematics (cholesterics): ref 9 (I), 10 (II and III). Compound V is N, an untwisted nematic and the sense of rotation for compound IV, N^* , is unknown. ^c Data courtesy of Laboratoire de Chimie des Hormones, Collège de France, private communication. ^d Data courtesy of D. Demus, private communications. ^e Davis et al. (ref 11).

obtained from K and K Chemicals, tetradecanoate (myristate, III), obtained from Eastman Chemicals, and octadecanoate (stearate, IV), obtained from Van Schuppen Chemicals.⁷ The tolane was a symmetric alkoxy derivative, 4,4'-bis(decyloxy)tolane (V).^{2b} The phase diagrams were obtained by the contact method.⁸ From such studies transition temperatures and the phases in equilibrium are known, and in some cases suggested compositions can be obtained. The transition temperatures and enthalpies for the pure compounds were obtained from various literature sources and are presented in Table I. In some cases the data presented in Table I have more significant figures than warranted by the original data. This was done, however, to permit calculation of the required virtual transition temperatures and enthalpies that were very close in magnitude (vide infra).

Theory

As shown previously, phase diagrams exhibiting nonidealities, which the presence of any minimum or maxima (azeotrope-like behavior) would immediately indicate, can be calculated within the framework of regular solution theory.⁵ The chemical potential for component 1 in phase α is written as

$$\mu_{1\alpha} = \mu_{1\alpha}^0 + RT \ln x_{1\alpha} + A_{\alpha} x_{2\alpha}^2 \quad (1)$$

where the last term on the right-hand side of eq 1 accounts for the nonidealities. The parameter A_{α} for phase α is taken to be independent of temperature and composition. This manner of treating nonidealities leads to the following pair of equations, the solutions to which describe the

coexistence, that is temperature-composition lines, for two phases α and β in equilibrium.

$$\ln(x_{1\beta}/x_{1\alpha}) + (A_{\beta}x_{2\beta}^2 - A_{\alpha}x_{2\alpha}^2)/RT = H_1 \quad (2a)$$

$$\ln(x_{2\beta}/x_{2\alpha}) + (A_{\beta}x_{1\beta}^2 - A_{\alpha}x_{1\alpha}^2)/RT = H_2 \quad (2b)$$

$$H_i = \Delta H_{i\alpha\beta}^0(T - T_i)/RTT_i \quad (3)$$

A regular solution parameter A is used for each phase. The transition enthalpies have been assumed independent of temperature. Iterative solution of (2) is possible for $x_{1\alpha}$ and $x_{1\beta}$ once given T , the properties of the pure components, and some estimates for A_{α} and A_{β} . In principle the A parameters can be related to enthalpies of vaporization, but in these systems, enthalpies of vaporization do not provide a practical means of estimating the parameters. As pointed out earlier, however, the presence of a maxima or minimum in the phase diagram affords an estimate of the difference in the parameters. Since at the "azeotrope" point $T = T_m$, $x_{1\alpha} = x_{1\beta} = x_{1m}$ and $x_{2\alpha} = x_{2\beta} = x_{2m}$, eq 2a and 2b simplify a great deal to yield

$$(A_{\beta} - A_{\alpha})x_{2m}^2 = RT_m H_1 \quad (4a)$$

$$(A_{\beta} - A_{\alpha})x_{1m}^2 = RT_m H_2 \quad (4b)$$

Further it can be shown that

$$x_{1m} = [1 + (H_1/H_2)^{1/2}]^{-1} \quad (5)$$

$$(A_{\beta} - A_{\alpha}) = RT_m H_2 [1 + (H_1/H_2)^{1/2}]^2 \quad (6)$$

Therefore only the pure component transition temperatures and enthalpies and knowledge of T_m are required to

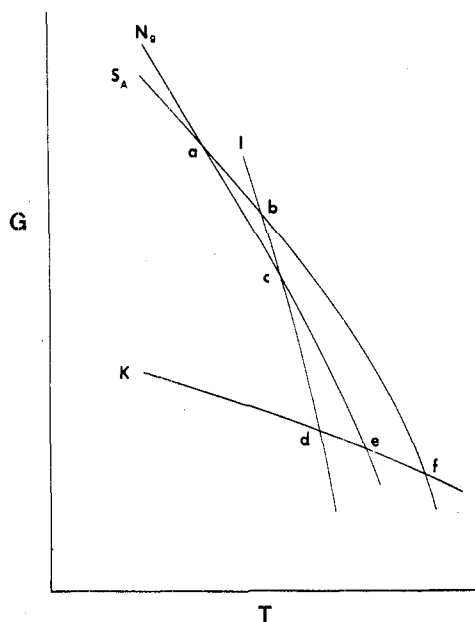


Figure 1. Idealized, qualitative isobaric free energy vs. temperature diagram for *p*-nitrobenzalaminoctinnamic acid 2-methylhexyl ester. The intersection points, for example a, mark the positions of phase equilibria. Point a is the monotropic transition temperature for the S_A - N_g phase equilibrium, while point e, moreover, indicates the virtual K - N_g phase transition temperature. Note: assuming the enthalpies independent of temperature would require the lines in the figure to be straight rather than curved. However, no loss in principle is obtained drawing the lines curved.

calculate the composition of the azeotrope point and the regular solution parameters, which, in turn, allow estimation of the phase diagram. It is convenient that so much can be accomplished with only knowledge of T_m , since the contact method used only provides temperature information.

In the case that one of the phases can be treated as ideal, for example, the equilibrium between a solid and liquid where the solid is taken to be ideal, then one of the parameters can be equated to zero and eq 2a and 2b become

$$\ln x_{1\beta} + A_\beta(1 - x_{1\beta})^2/RT = H_1 \quad (7)$$

where the α phase has been taken as an ideal pure solid for which, then $A_\alpha = 0$, $x_{1\alpha} = 1$, and $x_{2\alpha} = 0$. Equation 7 still requires solution by iteration and was used for calculating all coexistence lines between liquid phases and solid phases (vide infra).

In many cases transition temperature and enthalpies for the pure components had to be calculated for the experimentally unobservable virtual transitions. For the reference compound, the 2-methylhexyl ester, the observed phase transitions are denoted by the points a, c, and d in the idealized chemical potential vs. temperature diagram presented in Figure 1. Point b represents the virtual smectic A (S_A) to isotropic (I) transition, and point e represents the virtual crystal (K) to cholesteric (N_g) transition. The temperature and enthalpy for the K to S_A transition are required, for instance, in order to calculate the coexistence line between the K and S_A phases observed in Figures 2-4, as well as for the eutectic observed in those phase diagrams. Following a method previously described,^{2c} for the K to S_A transition

$$\Delta H_{KI} = \Delta H_{S_{AN}} + \Delta H_{NI} + \Delta H_{KSA} \quad (8)$$

and further by using the entropy relationship $\Delta H/T = \Delta S$

$$\frac{\Delta H_{KI}}{T_{KI}} = \frac{\Delta H_{S_{AN}}}{T_{S_{AN}}} + \frac{\Delta H_{NI}}{T_{NI}} + \frac{\Delta H_{KSA}}{T_{KSA}} \quad (9)$$

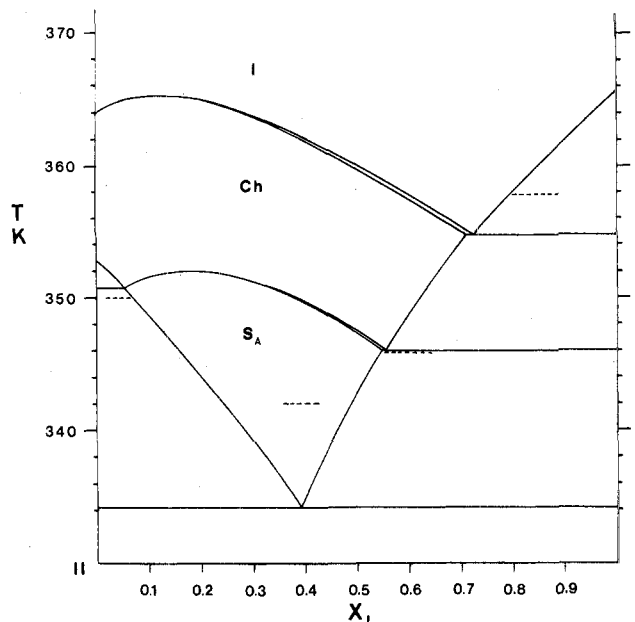


Figure 2. Isobaric binary temperature-composition phase diagram for *p*-nitrobenzalaminoctinnamic acid 2-methylhexyl ester (I) and cholesterol nonanoate (II). The solid lines are the calculated results and the horizontal dashed lines are the experimentally observed temperatures for the various three phase equilibria.

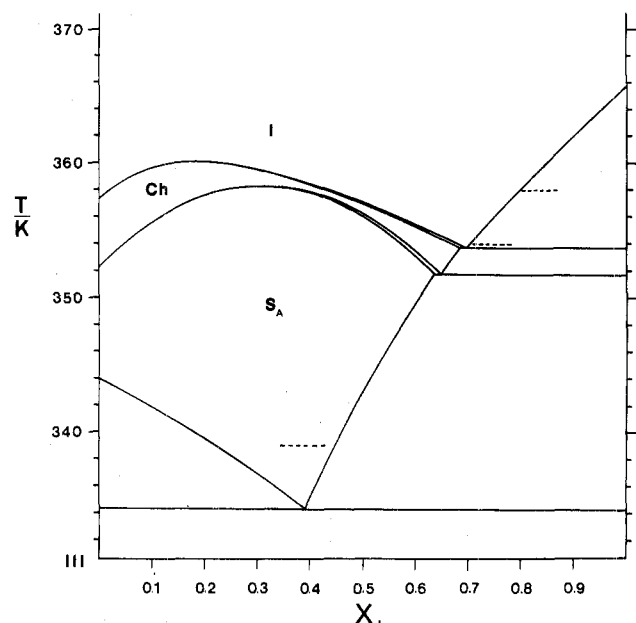


Figure 3. Isobaric binary temperature-composition phase diagram for *p*-nitrobenzalaminoctinnamic acid 2-methylhexyl ester (I) and cholesterol tetradecanoate (III). The solid lines are the calculated results and the horizontal dashed lines are the experimentally observed temperatures for the various three phase equilibria.

Equation 8 allows calculation of ΔH_{KSA} and, since all other enthalpies are known, eq 9 then allows calculation of T_{KSA} . Other required data for the virtual transitions were calculated by using similar thermodynamic cycles, and such data are presented in Table I in square brackets.

In calculating the phase diagrams, often an invariant temperature for the equilibria between three coexisting phases was required. This temperature was taken to be that obtained by graphical intersection of the appropriate two phase coexistence curves. In principle some complex iterative procedure could be devised to calculate such temperatures but the graphical procedure seems quicker and appears to be as accurate a solution as the basic data warrant.

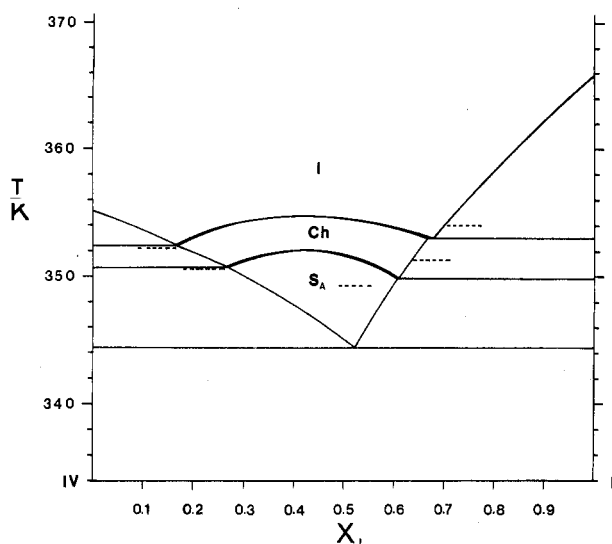


Figure 4. Isobaric binary temperature-composition phase diagram for *p*-nitrobenzalamincinnamic acid 2-methylhexyl ester (I) and cholesterol octadecanoate (IV). The solid lines are the calculated results and the horizontal dashed lines are the experimentally observed temperatures for the various three phase equilibria.

To calculate each phase diagram, three A parameters are required, one each for the isotropic, cholesteric (Ch), and smectic A phases. The maximum observed between the I and Ch phases gives via eq 6, the difference $A_I - A_{Ch}$, while the maximum between the Ch and S_A phases gives the difference $A_{Ch} - A_{S_A}$. Further we know that $A_a > 0$ for any phase, and that for the phases here, $A_I > A_{Ch} > A_{S_A}$. A third independent equation has been chosen arbitrarily to give values for each A by writing

$$A_{Ch} = 1.5(A_{Ch} - A_{S_A}) \quad (10a)$$

$$A_{S_A} = 0.5(A_{Ch} - A_{S_A}) \quad (10b)$$

then

$$A_I = A_{Ch} + (A_I - A_{Ch}) \quad (11)$$

No justification for this procedure is offered except its convenience. However, as long as the difference between the parameters for two phases in equilibrium is held constant, variation in the magnitude of the individual parameters only has the effect of shifting the degree of convexity on either side of the maximum or azeotrope point.

Results

Phase Diagram for *p*-Nitrobenzalamincinnamic Acid 2-Methylhexyl Ester and Cholesterol Nonanoate. The calculated diagram shown in Figure 2 maps the observed phase diagram exactly in a qualitative sense. The observed temperatures are shown in the diagram by dashed lines. It should be mentioned that the phase indicated as cholesteric arises from the mixture of what has been historically called the cholesteric phase of cholesterol nonanoate and the chiral nematic phase of the methylhexyl ester. Quantitatively, calculated temperatures agree very well with the observed as can be seen by comparing the dashed line experimental temperatures in Figure 2. The greatest disagreement is for the eutectic temperature but that might be expected, since that temperature depends very much on the location of the virtual K to S_A transition and its enthalpy. However, given estimates for the accuracy of the experimentally observed temperatures and enthalpies, the calculated diagram is in excellent agreement with the observed. For example, assuming errors of 10%

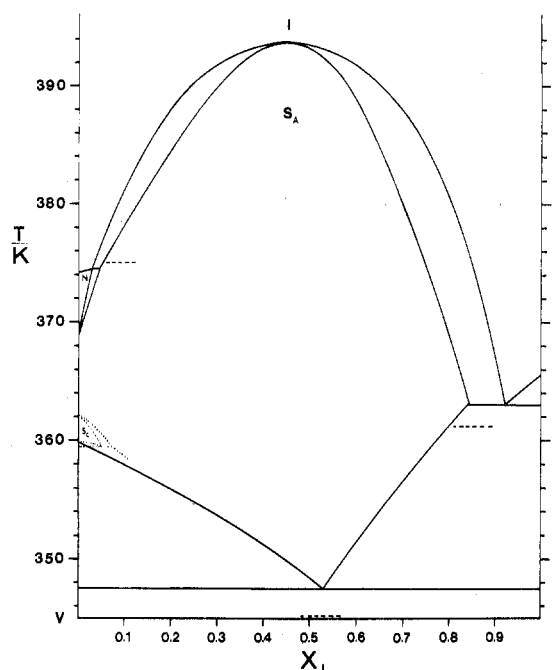


Figure 5. Isobaric binary temperature-composition phase diagram for *p*-nitrobenzalamincinnamic acid 2-methylhexyl ester (I) and 4,4'-bis(decyloxy)tolane (V). The solid lines are the calculated results and the horizontal dashed lines are the experimentally observed temperatures for the various three phase equilibria.

in the enthalpies of transition generally affects the invariant temperatures 3 or 4 deg. Again it should be pointed out that no composition data are available at this time to check the accuracy of the location of the maxima on the composition axis, the three phase equilibria points, or the eutectic.

Phase Diagram for *p*-Nitrobenzalamincinnamic Acid 2-Methylhexyl Ester and Cholesterol Tetradecanoate (Figure 3). The same comments as previous can be made about this calculation. It seems unlikely that the temperature range of the cholesteric phase around 0.4 mole fraction hexyl ester is in fact so small, implying that some temperature or enthalpy data are suspect.

Phase Diagram for *p*-Nitrobenzalamincinnamic Acid 2-Methylhexyl Ester and Cholesterol Octadecanoate (Figure 4). The appropriate calculated and observed temperatures agree very closely. However, the contact method observed diagram implies that the maximum in the Ch-I coexistence phase lines appears inside the isotropic methylhexyl ester crystal two phase region, that is, a metastable maximum in disagreement with the calculated diagram. The maximum composition value depends only on the transition temperatures and enthalpies not on the A parameters. Thus, the disagreement between the calculated and observed Ch-I maximum is probably the result of some discrepancy in the temperature and enthalpy data.

Phase Diagram for *p*-Nitrobenzalamincinnamic Acid 2-Methylhexyl Ester and 4,4'-Bis(decyloxy)tolane (Figure 5). The calculated diagram agrees with the experiment qualitatively and quantitatively very well. This is the only system where three liquid phase equilibria were observed and the equilibrium temperatures shown are those taken from the intersection of the appropriate two phase coexistence lines as discussed earlier. Several extrapolations had to be made, however, in order to obtain the necessary A parameters. In order to obtain the $A_I - A_N$ parameter difference the observed I-N coexistence curve was extrapolated to choose a maximum temperature at 375.4 K. This maximum temperature along with the observed tem-

TABLE II: Regular Solution Parameters Derived from the Phase Diagrams Observed for Binary Mixtures of *p*-Nitrobenzalaminoacetic Acid 2-Methylhexyl Ester (I) with Cholesterol Nonanoate (II), Cholesterol Tetradecanoate (III), Cholesterol Octadecanoate (IV), and 4,4'-Bis(Decyloxy)tolane (V)

phase diagram	$(A_I/R)/K$	$(A_{Ng}/R)/K$	$(A_{SA}/R)/K$
I-II (Figure 2)	46.359	22.652	7.551
I-III (Figure 3)	60.941	41.172	3.724
I-IV (Figure 4)	67.506	44.840	14.547
I-V (Figure 5)	374.073	322.104	124.691

perature for the I-S_A maximum, allowed calculation of the A_I , A_N , and A_{SA} parameters. The temperature of the metastable N-S_A maximum calculates to be 422.5 K and would probably never be observed. The N phase that occurs in the diagram should be noted is not apparently chiral or cholesteric, since it occurs only close to the pure tolane which exhibits only a normal nematic phase. The large temperature region of the I-S_A phase region should be noted. Experimentally for fixed compositions of approximately 70% methylhexyl ester, the coexistence of the two phases should be easily discernable over a 6–8 deg temperature range, a very large range, especially compared to the tenths or less range calculated for previous diagrams.

While it has been mentioned that the calculated results for this diagram agree well with experiment, a caution should be raised. The tolane exhibits a S_C phase and the experimental phase diagram is correctly drawn when the dotted line area around 360 K and almost pure tolane is included. In order to calculate a two phase spindle by either ideal or nonideal methods, thermodynamic properties of the two coexisting phases for each pure material must be known, or estimatable via the procedures mentioned earlier. No way exists to estimate the data required for the methylhexyl ester; some hint of a S_C to some other phase transition would be required. However, curiously, the presence of the S_C-S_A two-phase spindle demands that the pure methylhexyl ester exhibit a highly metastable, virtual S_C phase that can never be reached in the pure compound but is stabilized in the presence of the tolane's S_C phase, at least over a small composition range.

In Table II are presented the parameters used to calculate the phase diagrams. In contrast to the trend observed in the parameters obtained for a homologous series of mesogens, where the parameters varied linearly with molecular volume, no such simple, at least linear, trend is observed here. The parameters for a given phase do increase with molecular weight, but, as mentioned, not in a linear manner. A simple correlation with the magnitude of the parameters with some physical property of the molecular component is not obvious at this time. In the absence of some fundamental model that would allow estimation of the parameters, further speculation on their meaning is not particularly productive.

Summary

Binary phase diagrams exhibiting reasonably complex behavior, including smectic phase temperature enhancement, maxima formation, can be successfully calculated by using the thermodynamic regular solution approximation. The parameters derived by using the method require further work to understand their fundamental origin before some correlation between the observed magnitudes and molecular properties or structure can be proposed.

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References and Notes

- (1) Presented at the VII International Liquid Crystal Conference, Bordeaux, France, July 1978.
- (2) (a) Malthete, J.; Leclercq, M.; Gabard, J.; Billard, J.; Jacques, J. C. *R. Acad. Sci., Ser. C* **1971**, 273, 265. (b) Malthete, J.; Leclercq, M.; Dvolaitzky, M.; Gabard, J.; Billard, J.; Pontikis, V.; Jacques, J. *Mol. Cryst.* **1973**, 23, 233. (c) Domon, M.; Billard, J. *Pramana Suppl.* **1975**, No. 1, 131.
- (3) Demus, D.; Fietkau, C. H.; Schubert, R.; Kehlen, H. *Mol. Cryst. Liq. Cryst.* **1974**, 25, 215.
- (4) Cox, R. J.; Johnson, J. F. *IBM J. Res. Develop.* **1978**, 22, 51.
- (5) Van Hecke, G. R. J. *Phys. Chem.* **1979**, 83, 2344.
- (6) Leclercq, M.; Billard, J.; Jacques, J. *Mol. Cryst.* **1969**, 8, 369.
- (7) Arnold H.; and Broediger, P. *Z. Phys. Chem.* **1968**, 239, 23.
- (8) Domon, M.; Billard, J. J. *Phys. C3* **1979**, 40, 413.
- (9) Unpublished experiments, B. Soulestin using method described by Billard, J. C. *R. Acad. Sci.* **1972**, 274, 333.
- (10) Friedel, G. *Ann Phys.* **1922**, 18, 273.
- (11) Davis, G. J.; Porter, R. S.; Barrall, E. M. *Mol. Cryst. Liq. Cryst.* **1970**, 10, 1.