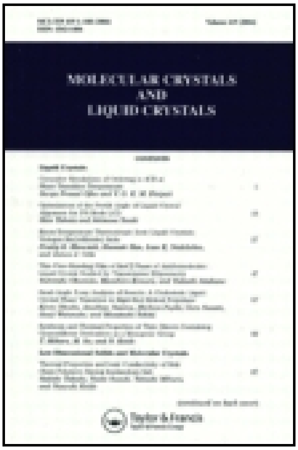

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

An Estimation of the Latent Liquid Crystal-Isotropic Liquid Transition Temperature of a Non-Liquid Crystalline Compound by Equal G Analysis

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Version of record first published: 24 Sep 2006.

To cite this article: K. Araya (1991): An Estimation of the Latent Liquid Crystal-Isotropic Liquid Transition Temperature of a Non-Liquid Crystalline Compound by Equal G Analysis, Molecular Crystals and Liquid Crystals, 201:1, 23-28

To link to this article: http://dx.doi.org/10.1080/00268949108038634

Mol. Cryst. Liq. Cryst., 1991, Vol. 201, pp. 23–28
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Printed in the United States of America

An Estimation of the Latent Liquid Crystal-Isotropic Liquid Transition Temperature of a Non-Liquid Crystalline Compound by Equal G Analysis

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(Received October 5, 1990; in final form January 11, 1991)

A calculation of nematic liquid crystal-isotropic liquid transition temperature-composition curves of binary phase diagrams, in which one of the components is a non-liquid crystalline compound, has been examined by means of equal G analysis, one of the thermodynamic treatments reported by Van Hecke. Five liquid crystals, azoxybenzene derivatives, are used for the calculation and one of them is assumed to be a non-liquid crystalline compound. As a result, if the latent transition entropy of a non-liquid crystalline compound can be expected in advance, the latent nematic liquid crystal-isotropic liquid transition temperature can be obtained more precisely than by the extrapolation method used so far. Even if the latent transition entropy cannot be expected in advance, a comparison between calculations of the two binary systems in which a non-liquid crystalline compound is common, can give the precise latent transition temperatures and the transition entropies.

INTRODUCTION

Recently, Van Hecke succeeded in quantifying liquid crystal-isotropic liquid transition temperature-composition curves of the binary phase diagrams in which both of the component compounds give a mesomorphic phase by means of a thermodynamic treatment.[1] The approach is called equal G analysis and is based on equalizing the total Gibbs energies of the two phases in equilibrium.

This technique seems to be useful in analyzing a number of the binary phase diagrams reported so far. Equal G analysis was applied to the binary system in which one of the components is a non-liquid crystalline compound. However, we deal with non-liquid crystalline compounds which can be considered to be potentially mesomorphic.[2,3] In these compounds, the liquid crystal-isotropic liquid transition cannot be observed because the melting point is much higher than the transition. The main purpose is to obtain the precise latent liquid crystal-isotropic liquid transition temperature. Up to date, these latent transition temperatures are obtained using the extrapolation method of the transition temperature-composition curves.[2–5] However, this method is limited to straight transition curves. On the contrary, the equal G analysis is very effective even when the transition curve is not straight. Moreover, it is found that the latent transition entropy can also be estimated.

In the present series of papers, the binary system, in which both components are non-liquid crystalline compounds,[3] will be analyzed using these latent transition temperatures. In this report, only the calculation method to estimate the latent transition temperatures is presented.

THEORETICAL

A liquid crystal-isotropic liquid transition temperature-composition curve, T-x, for nonideal system is given as follows by Van Hecke.[1]

$$T = \frac{(1 - x)\,\Delta S_1 T_1 + x\Delta S_2 T_2 + \Delta A x\,(1 - x)}{(1 - x)\,\Delta S_1 + x\Delta S_2} \tag{1}$$

where ΔS_1 is a constant transition entropy at the liquid crystal-isotropic liquid transition temperature T_1 of component 1 and ΔS_2 is a constant transition entropy at the liquid crystal-isotropic liquid transition temperature T_2 of component 2. Here ΔA is the difference between the regular solution parameters in isotropic liquid phase and in nematic liquid crystal phase, namely it is A(iso)-A(nem).[6,7] This value is related to molecular interactions which comprise both steric and electronic interactions. If ΔA equals zero, the T-x curve corresponds to that of the ideal system.

In the present calculation, T_1 and ΔS_1 are the transition temperature and transition entropy of a standard liquid crystalline compound. T_2 and ΔS_2 are a latent transition temperature and latent transition entropy of a non-liquid crystalline compound. Hereafter, T_2 and ΔS_2 are referred to as T_L and ΔS_L, respectively. For simplifying the calculation, Equation 1 is written as follows:

$$T = \frac{(1 - x)\,T_1 + xST_L + Ax\,(1 - x)}{(1 - x) + Sx} \tag{2}$$

where S is the entropy ratio $\Delta S_L/\Delta S_1$, and A is the excess parameter $\Delta A/\Delta S_1$ with units of degree. The best set of S, A, and T_L values can be obtained by solving Equation 2 by a nonlinear least squares method. However, a least squares linear method is used in the actual calculation assuming that the S term is a constant. Since the transition entropy of one compound is not much different from another, in general it is thought that S is in the vicinity of 1.0.[8] The calculations are performed with S ranging from 0.1 to 10.[9]

RESULTS AND DISCUSSION

Five azoxybenzene derivatives are used in the present calculation. These compounds have been studied by many researchers and one of them, p-azoxyanisole, is well known as a standard liquid crystalline compounds.[10-13] Thermodynamic data

TABLE I

Temperatures and entropies for the nematic liquid crystal-isotropic transition of azoxybenzene derivatives[a]

Compound	Symbol	T_{NI}/ °C	ΔS/J K^{-1} mol^{-1}
p-Azoxyanisole	PAA	135.35	1.4
p-Azoxyphenetole	PAP	167.5	3.1
p,p'-n-Dipropoxyazoxybenzene	DPRA	123.6	1.7
p,p'-n-Dibutoxyazoxybenzene	DBUA	136.7	2.5
p,p'-n-Dipentyloxyazoxybenzene	DPEA	123.2	1.8

[a] Data from Arnold, Reference 10.

TABLE II

The reference and calculated sets of entropy ratios, excess parameters, and latent transition temperatures in the binary mixtures of azoxybenzene derivatives

	Reference sets			Calculated sets					
Systems				method 1			method 2		
	S	A/K	T_L/K	S	A/K	T_L/K	S	A/K	T_L/K
PAA-DPEA	1.3	-49.9	123.2	5.9	1.2	115.0	1.3	-50.4	123.3
PAP-DPEA	0.6	-36.6	123.2	0.8	-30.8	122.8	0.6	-39.2	124.2
DPRA-DPEA	1.1	-2.4	123.2	0.6	-3.3	123.9	1.1	-3.4	123.4
DBUA-DPEA	0.7	-1.7	123.2	>10.0	122.0	123.1	0.7	-0.8	122.4

of these compounds are summarized in Table I. Hereafter, the compounds are presented by their symbols. Even-odd effects are seen in T_{NI} and ΔS. All these compounds exhibit a nematic liquid crystal phase. However, for the purpose of this paper, namely, to check the accuracy of the calculation to estimate the latent transition temperature, it is assumed here that one of the azoxybenzene derivatives, DPEA, is a non-liquid crystalline compound. The phase diagrams of all possible combinations of the derivatives are given by Demus et al.[11] Among them, the phase diagrams of the PAA-DPEA, PAP-DPEA, DPRA-DPEA, DBUA-DPEA systems, are used. The *T-x* curve is concave in the former two cases and almost straight in the latter two cases.

Firstly, the calculations have been performed using only the least squares method (method 1). The experimental data used are up to 80 mol% of DPEA, namely 69.7 mol%, for PAA, 77.3 mol% for PAP, 75.3 mol% for DPRA, and 79.0 mol% for DBUA, where it is assumed that DPEA is a non-liquid crystalline component. The reference sets of S, A, and T_L that are calculated using all the experimental points are shown in Table II. It is shown here that the S value ranges from 0.6 to 1.3. The most fitting sets of calculated S, A, and T_L are summarized in Table II.

In the PAA-DPEA system, neither S, A or T_L are in accord with the reference data. Especially, the calculated latent transition temperature is 115°C, 7°C lower than the real one. The extrapolation method may also give the temperature of 115°C. The S and A values of the other three combinations do not reflect the reference data either. But the latent transition temperatures are in accord with the real ones. In the DBUA-DPEA system, the least squares method does not converge. This is because the T-x curve is straight and the S term has a tendency to compensate the A term. In this system, the calculated latent transition temperatures give the same value of 123°C against each of the S terms used. The extrapolation method for this system may give the temperature of 123°C. From these results, it is concluded that the latent transition temperatures can be estimated from only the least squares method but the transition entropies and excess parameters cannot be estimated. This conclusion is not in all cases, however.

Consequently, the second calculation has been performed assuming that the S term can be expected in advance (method 2). This method is possible when the latent transition entropy can be expected in comparison with the molecular structure, for example, a terminal substituent group, a central linkage group or using the even-odd effect described above. In the case of azoxybenzene derivatives, the transition entropy of DPEA can be expected to be nearly equal to that of PAA or DPRA using the even-odd effect. The most fitting sets of S, A, and T_L in this method are summarized in Table II. All systems give a good latent transition temperature within one degree. Additionally, the A terms also correspond well with the experimental values. The calculated T-x curves as well as the observed points for the four systems are shown in Figure 1. From this figure, it is found that the equal G analysis is very effective even when the T-x curves are concave. Furthermore, the fact that the latent transition temperature can be estimated from the combination with the liquid crystalline components having different transition entropies gives us a unique calculation. Namely, even if the latent transition entropy cannot be expected in advance, the comparison between the calculations of two binary systems in which non-liquid crystalline compounds are common gives a precise estimation of the latent transition temperature and the transition entropy.

Lastly, such a case is considered (method 3). DPEA is also assumed as a non-liquid crystalline compound, and PAA and DPRA are used as standard liquid crystalline compounds. At first, the most suitable latent transition temperature against each S value for the PAA-DPEA system is calculated. The T-S curve is shown in Figure 2(a). The same calculation is performed for the DPRA-DPEA system. However, a direct comparison cannot be carried out because the S terms are different. The S term for the PAA-DPEA system is $\Delta S_L/\Delta S_1$, where ΔS_L and ΔS_1 are the transition entropies of DPEA and PAA, respectively. On the other hand, the S term for the DPRA-DPEA system is $\Delta S_L/\Delta S_3$, where ΔS_3 is the transition entropy of DPRA. Hereafter, the S-terms for the PAA-DPEA and the DPRA-DPEA systems are referred to as S_1 and S_3, respectively. Then $S_3 = \Delta S_L/\Delta S_3 = (\Delta S_1/\Delta S_3)(\Delta S_L/\Delta S_1) = (\Delta S_1/\Delta S_3)S_1$. Since ΔS_1 and ΔS_3 are known values, S_3 can be replaced as $0.82S_1$. Using this relationship, the T-S curve for the DPRA-DPEA system is normalized to a curve for the PAA-DPEA system. The resultant T-S curve is shown in Figure 2(b). Two curves intersect at $T = 123.2$°C, $S_1 = 1.26$

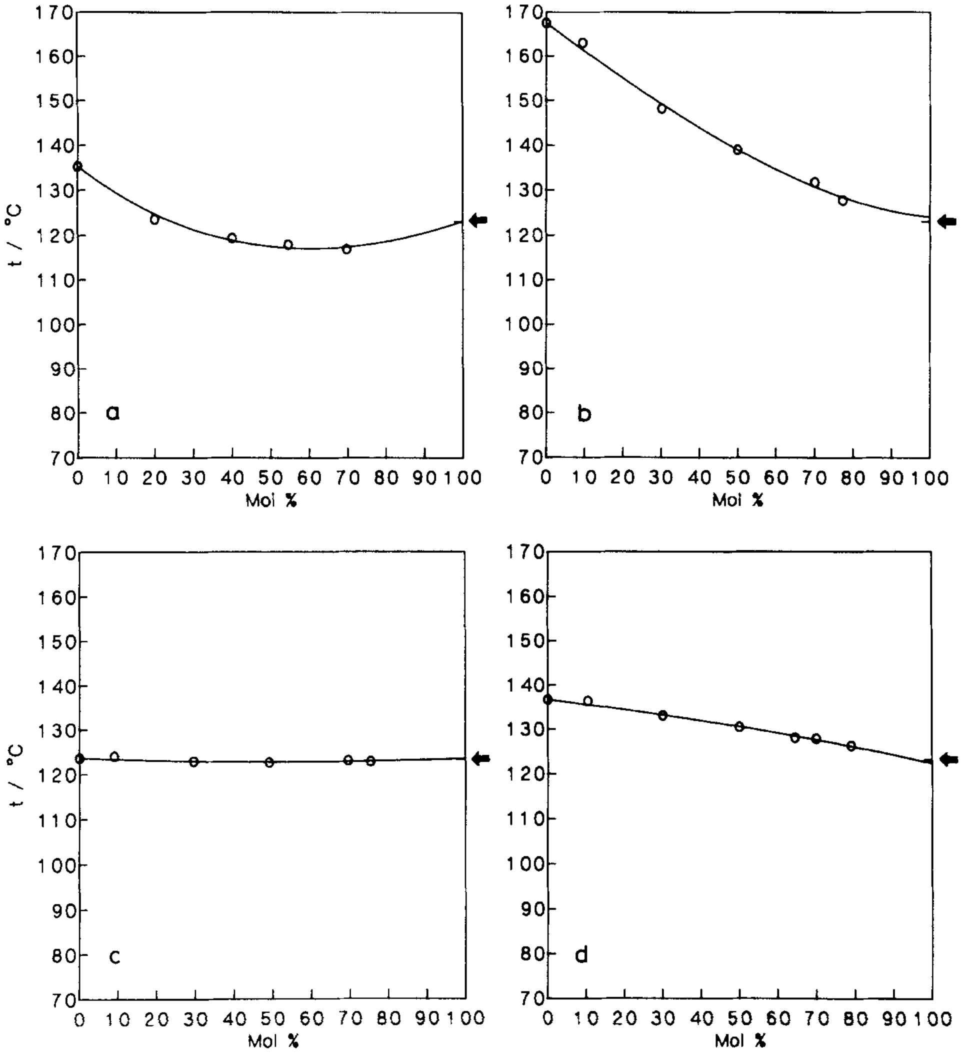

FIGURE 1 Phase diagrams of the systems of DPEA with (a), PAA, (b) PAP, (c) DPRA, (d) DBUA. The composition is for DPEA. The solid lines are the calculated nematic liquid crystal-isotropic liquid transition temperature-composition curves. The open circles are the experimental points redrawn from Reference 11. Arrows indicate the real nematic liquid crystal-isotropic liquid transition temperature of DPEA.

(S_3 = 1.03). This value corresponds well with the real values. Accordingly, it is concluded that the latent nematic liquid crystal-isotropic liquid transition temperature and the transition entropy can be estimated precisely even when the transition entropies of the non-liquid crystalline compounds are not expected in advance. The same results are obtained for three other combinations, the PAA-DPEA and DBUA-DPEA system, the PAP-DPEA and DPRA-DPEA system, and the PAP-DPEA and DBUA-DPEA system. The last method needs many more experimental tasks than the extrapolation method. However, it is strongly emphasized that the

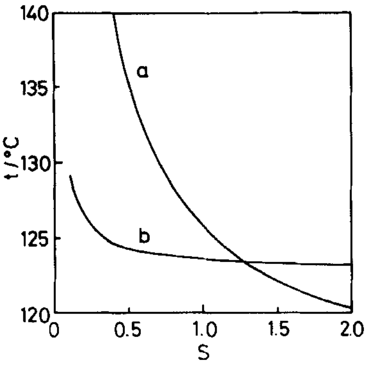

FIGURE 2 Latent transition temperatures calculated against each *S* term for (a) the PAA-DPEA and (b) DPRA-DPEA systems.

last method can present not only the latent transition temperature but also the transition entropy.

CONCLUSION

Latent nematic liquid crystal-isotropic liquid transition temperature of non-liquid crystalline compound has been calculated by means of equal G analysis. As a result, the latent transition temperature can be obtained more precisely than by the extrapolation method used so far. Moreover, it is found that the present method can give not only the precise latent transition temperatures but also the transition entropies.

Acknowledgment

The author would like to thank Mr. Naoki Tanaka of Hitachi Advanced Research Laboratory for helpful advice on the calculations.

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