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Thermodynamic Interpretation of the Terminal Group Effect on the Thermal Stability of a Mesophase

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Nematic liquid crystal-isotropic liquid transition temperature-composition curves were calculated for the four binary systems between *p*-azoxyanisole and Schiff bases. The calculation was done by means of equal G analysis, which is one of the thermodynamic treatments reported by Van Hecke. Two Schiff bases with nitro group were chosen as examples of convex upwards transition temperature-composition curves. Two Schiff bases with dimethylamino group were chosen as examples of concave upwards transition temperature-composition curves. As a result, deviations from linearity, which have been interpreted so far as due to the interaction between the component compounds, were attributed to the differences between the nematic liquid crystal-isotropic liquid transition entropies of *p*-azoxyanisole and a schiff base.

Keywords: p-azoxyanisole, binary system, Schiff bases, thermodynamics, transition curve, transition entropy, virtual transition temperature

INTRODUCTION

Recently, Van Hecke succeeded in estimating the liquid crystal-isotropic liquid transition temperature-composition curves of binary phase diagrams in which both of the component compounds give a mesomorphic phase.[1–3] 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 for analyzing a number of the binary phase diagrams reported so far. In fact, this method has been applied to binary systems in which one of the components is a non-liquid crystalline compound. This was done with the aim of obtaining the virtual liquid crystal-isotropic liquid transition temperature by Araya[4] and Masuda *et al.*[5]

In this paper, equal G analysis was used to examine the effect of terminal groups on the thermal stability of a mesophase. From a number of the binary phase diagrams between *p*-azoxyanisole (PAA) and Schiff bases investigated so far,[6–10] it was found that the liquid crystal-isotropic liquid transition temperature-composition curves were generally straight lines. However, in some binary systems the transition temperature-composition curves exhibit a deviation from linearity. For example, a Schiff base containing a nitro group as terminal one makes a mesophase

stable and the liquid crystal-isotropic liquid transition temperature-composition curves are convex upwards. On the contrary, a Schiff base containing a dimethylamino group makes the transition temperature-composition curves concave upwards. This influence of the terminal group on the thermal stability of a mesophase has been interpreted as the interaction between PAA and a Schiff base.[7,8,10] Equal G analysis was used for these abnormal binary systems to investigate the liquid crystal-isotropic liquid transition temperature-composition curves. As a result, it was found that the interaction between PAA and a Schiff base is negligibly small, thus, deviation from straight line transition temperature-composition curves was attributed to the difference between liquid crystal-isotropic liquid transition entropies of PAA and Schiff bases.

EXPERIMENTAL

The benzylideneanilines (Schiff bases) were prepared by a condensation reaction between a p-X derivative of benzaldehyde and a p-Y derivative of aniline, and were purified by repeated recrystallization from ethanol. Hereafter, the compounds are represented by their terminal groups (X, Y). Binary mixtures in known proportions were melted in small test tubes, shaken well to insure homogeneity, and then rapidly cooled.

The calorimetric curves were recorded on a Perkin-Elmer DSC-7 differential scanning calorimeter during the processes of heating and cooling. The heating rate in this work was 5°C/min. The temperature and heat capacity were calibrated with indium.

RESULTS AND DISCUSSION

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

$$T = [(1 - x)\Delta S_1 T_1 + x\Delta S_2 T_2 + x(1 - x)\Delta A]/[(1 - x)\Delta S_1 + x\Delta S_2] \quad (1)$$

where ΔS_1 is the transition entropy at the liquid crystal-isotropic liquid transition temperature T_1 of component 1, and ΔS_2 is the transition entropy at the liquid crystal-isotropic liquid transition temperature T_2 of component 2. Here, ΔA is the excess Gibbs energy parameter with units of free energy. 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 the transition entropy of PAA, while T_2 and ΔS_2 are the transition temperature and the transition entropy of a Schiff base. To simplify the calculation, Equation (1) is written as follows:

$$T = [(1 - x)T_1 + xST_2 + x(1 - x)A]/(1 - x + Sx) \quad (2)$$

where S is the entropy ratio $\Delta S_2/\Delta S_1$, and A is $\Delta A/\Delta S_1$ with units of degree. The best fitting A-value can be obtained by solving Equation (2) by a least squares linear method.

(a) PAA-(nitro, butoxy) System

As seen in Table I, (nitro, butoxy) is a monotropic liquid crystal and its liquid crystal-isotropic liquid transition entropy is very small compared with PAA. The entropy ratio, S, of this system becomes 0.3. The liquid crystal-isotropic liquid transition points measured are presented as open circles in Figure 1a. Although there are few experimental points, the T-x curve is clearly convex upwards. The best fitting T-x curve, shown as a solid line in Figure 1a, was calculated using these experimental points. The A value was calculated as -1.0. This means that based

TABLE I

Melting points, clearing points, and transition entropies at the clearing point of PAA and Schiff bases[a]

Compounds	t_{fus} / °C [b]	t_c / °C [c]	ΔS / J mol^{-1} K^{-1}
PAA	118.0	135.0	1.48
(nitro, butoxy)	77.5	(66.7)	0.45
(dimethylamino, butoxy)	112.0	(98.4)	6.19
(methoxy, butoxy)	113.8	(108.0)	2.49
(methoxy, ethoxy)	128.3	(120.9)	2.21
(nitro, ethoxy)	123.5	[85.0]	0.40 [d]
(dimethylamino, ethoxy)	147.4	[97.5]	5.50 [d]

[a] Parentheses denote a monotropic phase transition and square brackets a latent phase transition. [b] Melting point. [c] Clearing point. [d] Assumed from the comparison between (methoxy, butoxy) and (methoxy, ethoxy).

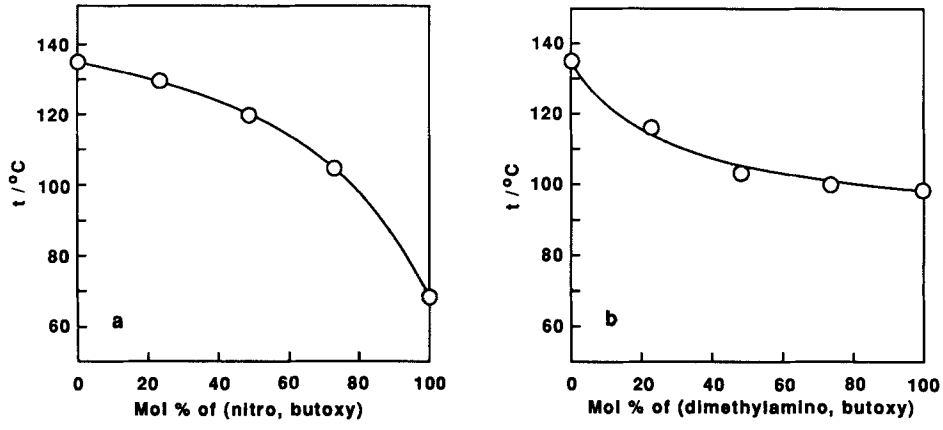

FIGURE 1 Phase diagrams of the systems of PAA with (a) (nitro, butoxy), (b) (dimethylamino, butoxy). The solid lines are the calculated nematic liquid crystal-isotropic liquid transition temperature-composition curves. The open circles are the experimental points.

on Equation (2) the temperature deviation from the ideal system at 50 mol% is −0.4°C. This value is negligibly small, which indicates that this binary system is ideal. Therefore, the convexity of the *T-x* curve is attributed only to the small transition entropy of (nitro, butoxy).

(b) PAA-(dimethylamino, butoxy) System

The monotropic liquid crystal (dimethylamino, butoxy) has a liquid crystal-isotropic liquid transition entropy that is very large compared with PAA. The entropy ratio, *S*, of this system is 4.2. The open circles in Figure 1b represent the liquid crystal-isotropic liquid transition points measured, and the solid line depicts the fitting *T-x* curve, which was calculated using these experimental points. Contrary to the PAA-(nitro, butoxy) system, the *T-x* curve is concave upwards. The calculated *A* value was −2.3 for the fitting curve. This means that based on Equation (2) the temperature deviation from ideal system at 50 mol% is −0.2°C. This value is so small that this binary system is also considered to be ideal. Therefore, the concavity of the *T-x* curve in this system is also attributed to the large transition entropy of (dimethylamino, butoxy).

The binary system containing a non-mesomorphic component was difficult to calculate. Because the transition temperature and transition entropy of the non-mesomorphic Schiff bases were unknown values. We assumed that the *A* value was equal to zero, which was a reasonable assumption judging from the calculations for the two binary systems described above.

(c) PAA-(nitro, ethoxy) System

In a previous paper, we reported that the virtual transition temperature of a non-mesomorphic compound could be calculated, if the transition entropy was estimated in advance. As seen in Table I, the transition entropy of (methoxy, ethoxy) is

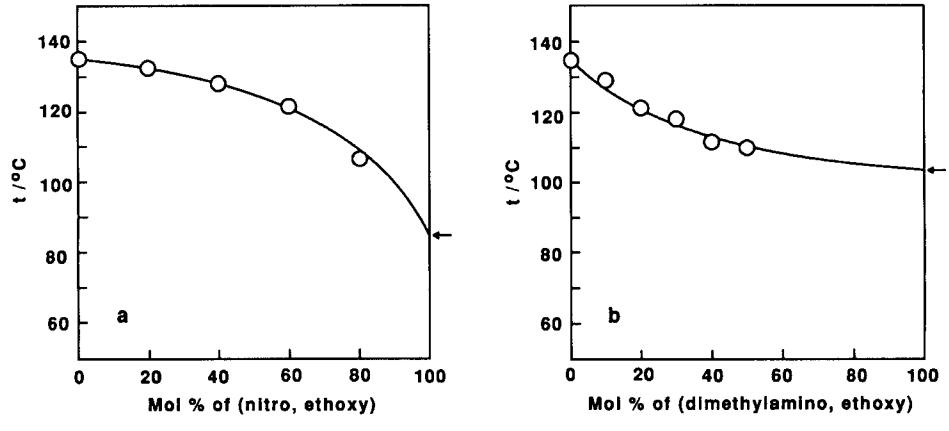

FIGURE 2 Phase diagrams of the systems of PAA with (a) (nitro, ethoxy), (b) (dimethylamino, ethoxy). The solid lines are the calculated nematic liquid crystal-isotropic liquid transition temperature-composition curves. The open circles are the experimental points redrawn from Reference 8. Arrows indicate the virtual nematic liquid crystal-isotropic liquid transition temperature.

similar to that of (methoxy, butoxy). From this example and other reported examples,[11,12] it could be expected that the transition entropy of an ethoxy derivative would be equal to that of a butoxy derivative. We assumed that the transition entropy of (nitro, ethoxy) is 0.4 and the entropy ratio, S, of this system is 0.3. This binary system was already reported by Lohar.[8,9] The transition points were measured up to 80% of the Schiff base as shown in Figure 2a. The virtual liquid crystal-isotropic liquid transition temperature of (nitro, ethoxy) was 85.0°C based on extrapolation of the T-x curve.[9] As mentioned above, the interaction between PAA and a Schiff base was first pointed out for this binary system. Figure 2a shows the best fitting T-x curve calculated using their experimental points. The curve is convex upwards like the system between PAA and (nitro, butoxy) and the virtual transition temperature calculated was 83.4°C. This value coincided with the extrapolated one, supporting the assumption of the transition entropy of (nitro, ethoxy) as correct. If this assumption is correct, then the deviation from linearity of the T-x curve can also be assigned to the small entropy of (nitro, ethoxy).

(d) PAA-(dimethylamino, ethoxy) System

This binary system was also reported by Lohar.[8,9] The transition points measured are presented in Figure 2b. The virtual transition temperature of (dimethylamino, ethoxy) was 97.5°C based on extrapolation method.[9] According to the above system, we assumed that the entropy ratio, S, of this system is 3.7. Figure 2b also shows the best fitting T-x curve calculated. The curve is concave upwards like the system between PAA and (dimethylamino, butoxy). The virtual transition temperature calculated was 103°C, which does not coincide with the extrapolated one. As the transition points measured were up to 50% of the Schiff base, it would be difficult to extrapolate the virtual transition point in this system. In either case, the deviation from linearity of the T-x curve would also be attributed to the large entropy of the Schiff base judging from the system between PAA and (dimethylamino, butoxy).

CONCLUSIONS

For the four binary systems between p-azoxyanisole and a Schiff base, the liquid crystal-isotropic liquid transition temperature-composition curves were investigated using equal G analysis. As a result, it was found that the transition temperature-composition curve's deviation from linearity can be attributed to the difference between the transition entropy of PAA and the Schiff base. Moreover, it was concluded that the interaction between p-azoxyanisole and a Schiff base accepted so far, is negligibly small.

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