Liquid Crystal Formation in Binary Systems. I. An Interpretation of the Phase Diagrams of the Azoxydianisole–Schiff Base Systems

Kotaro ARAYA and Yoshio MATSUNAGA*

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received August 25, 1979)

In order to confirm the presence of a transition at the temperature where the liquid crystal-isotropic liquid transition curve in the nematogen-rich region is met by the other transition curve, five binary systems comprising azoxydianisole (AA) and a Schiff base were examined by means of differential scanning calorimetry. A small but sharp endothermic peak due to a phase change is observable at the expected temperature upon heating, provided that it is well separated from the eutectic temperature. When the above-mentioned curve intersects the solid-liquid transition curve on the Schiff base-rich side, a liquid crystal coexisting with the solid base is transformed into an isotropic liquid coexisting with the same solid at this temperature. The presence of a nematic phase below this temperature could be demonstrated by measuring the separation of the outer hyperfine extrema in the ESR spectrum of bis(acetylacetonato)oxovanadium(IV) dissolved in the mixtures. The sequence of the transformation is entirely different when the intersection occurs on the AA-rich side. However, attempts to confirm the transition of the latter type by ESR were not successful.

Liquid crystal formation in binary systems, in which both, or one, or none of the component compounds give a mesomorphic phase, has been extensively studied by many workers. Nevertheless, the majority of reported phase diagrams are far from complete. For example, the system comprising azoxydianisole (AA), a mesomorphic compound, and *N*-(*p*-methoxybenzylidene)-*p*-anisidine, a non-mesomorphic compound, has been examined by Dave and Dewar employing the optical and thermal methods.[1] Although the nematic liquid crystal-isotropic liquid (N-L) transition curve on the AA-rich side is met well above the eutectic temperature by the solid-liquid (S-L) transition curve on the Schiff base-rich side, it is not clear whether or not the transition from the nematic liquid crystal (N) to the isotropic liquid (L) with the coexisting solid can be observed at the temperature of the intersection.

In the present series of papers, we are planning to report on the mesomorphic phases induced by some sort of molecular complexing in binary systems. In order to interpret our results, we felt that the subject mentioned above is of fundamental importance and should be clarified. For this purpose, we chose five representative systems of AA mixed with Schiff bases. As it is well known that an N phase can serve as an orienting solvent in magnetic resonance studies, measurements of the degree of alignment of the bis(acetylacetonato)oxovanadium(IV) molecules dissolved in the systems were attempted on the basis of the ESR spectrum. This particular chelate has been noted by Glarum and Marshall to be ordered to about the same extent as AA.[2] In this way, we hoped to establish the temperature ranges where an N phase exists with or without a solid-component compound.

Experimental

Materials. The AA was obtained from the Tokyo Chemical Industry Co. and was purified by recrystallization from ethanol. On the calorimetric curves, it melted at 117.5 °C and had an N-L transition point of 135 °C. These values are in good agreement with the literature values.[1] The Schiff bases were prepared by a condensation reaction between a *p*-X derivative of benzaldehyde and *p*-Y derivative of aniline; they were then recrystallized several times from ethanol and finally sublimed in a vacuum if necessary. Mixtures of AA and a Schiff base in known proportions were melted in small test tubes, shaken well to insure homogeneity, and then rapidly cooled.

Measurements. The calorimetric curves were recorded on a Rigaku Denki Thermoflex differential scanning calorimeter during the processes of heating and cooling. The heating rate in this work was 2.5 °C min^{-1}. The temperature was calibrated with the transition points of hexachloroethane (45 and 71 °C) and hexamethylbenzene (111 °C) and the melting points of naphthalene (80 °C), pyrene (150 °C), and indium (157 °C). The ESR spectra were recorded on a JEOL model JES-ME-3X (X band) spectrometer with 100 kHz modulation in the range between a temperature below the eutectic and a temperature above the S-L or N-L transition. The magnetic-field span was calibrated with Mn^{2+}-doped MgO powder.

Results and Discussion

*AA–*N-*(*p-*Methoxybenzylidene)*-p-*anisidine (X=Y=CH_3O) System.* The phase diagram has been reported by Dave and Dewar.[1] According to them, the N-L transition curve is met at 116.5 °C by the S-L transition curve on the Schiff base-rich side. They have drawn a horizontal dashed line at this temperature and marked four points observed in the cooling process above 40 mol% of AA. The eutectic point was located at 105 °C and about 72 mol% of AA. Our results are presented in Fig. 1. The open and shaded circles indicate the transitions found during the processes of heating and cooling respectively. The shaded circles are omitted when they coincide exactly with the open circles. The N-L transition above 60 mol% of AA is reversible, but the N phase is readily supercooled below the eutectic temperature and is suddenly solidified. When the AA content is less than 50 mol%, a sharp endothermic peak assignable to the N-L transition with the coexisting solid is observed at 117 °C on heating. This temperature is that of the intersection between the N-L transition curve and the S-L transition curve. Contrary to the observation reported by Dave and Dewar, the L phase in this composition range is super-

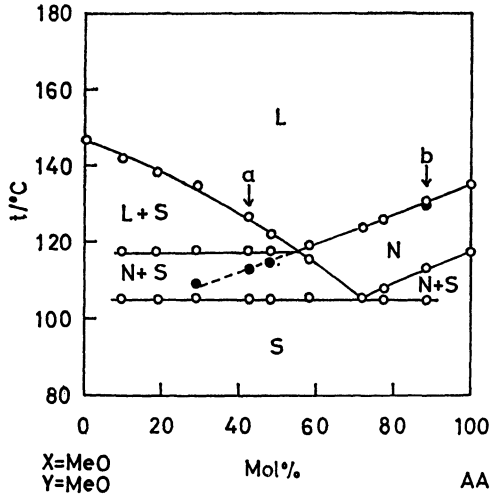

Fig. 1. The system azoxydianisole(AA)–*N*-(*p*-methoxybenzylidene)-*p*-anisidine.
The open and shaded circles are transitions observed in the processes of heating and cooling respectively.

cooled and changes into the N phase. The transformation takes place at temperatures on a continuation of the reversible N-L transition curve, which is almost straight. Such a linear relationship has also been observed for a number of binary N systems when there is no significant difference in the molar volumes or densities of the components.[3-7] The value at 0 mol% of AA found by extrapolation may be considered to be the latent L-N transition temperature of the Schiff base. If the molten base could be cooled without solidification, the N phase would monotropically appear at about 97 °C.

In the N phase, the spin-probe molecules are not distributed uniformly in θ, the angle between the V=O bond direction of the chelate molecule and the magnetic field. The order parameter, S, defined by $<3\cos^2\theta-1>/2$, can be approximated by $(<A>-a)/2(a-A_\perp)$, where $A_\perp$ is the component perpendicular to the V=O bond direction of the nearly axial hyperfine tensor, a is the isotropic hyperfine constant, and $<A>$ is one-seventh of the separation of the outer hyperfine extrema. If the alignment of the probe is perfect, the parameter, S, is $-1/2$, because $<A>=A_\perp$. When the medium becomes isotropic, the probe molecules may rapidly tumble, and one may observe $S=0$. Thus, a marked difference in the S value can be expected below and above the N-L transition temperature. The ESR spectrum was measured at 42.5 and 88.5 mol% of AA (they are indicated by Arrows a and b in Fig. 1) as a function of the temperature. The parameter was calculated with the values of $A_\perp$ and a estimated from the ESR spectra in molten *o*-terphenyl, namely, 68 and 108 G (1 G=10^{-4} T). The results, shown in Figs. 2a and b, clearly support our interpretation of the phase diagram. Here again, the open circles were obtained in the process of heating, and the shaded ones, in the process of cooling. The vertical lines represent the transition temperatures taken from Fig. 1. In Fig. 2a, a sudden change in the order parameter is found at the N-L transition temperature, even in the presence of a

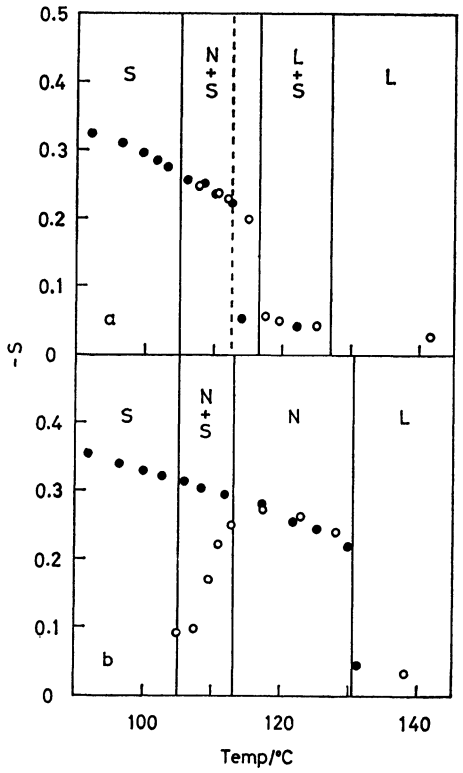

Fig. 2. Temperature dependence of the parameter S in AA–*N*-(*p*-methoxybenzylidene)-*p*-anisidine, (a) 42.5 and (b) 88.5 mol% of AA.
As to the open and shaded circles, see the caption of Fig. 1.

solid Schiff base. Furthermore, the supercooling of the L phase is clearly demonstrated by a shaded circle located between the dashed line and the N-L transition line. In the other temperature ranges, the open and shaded circles are nearly on the same curve, indicating the reversibility. As the S value estimated using the above-mentioned $A_\perp$ and a is essentially zero in the L phase of pure AA, there must be some changes in $A_\perp$ and a upon mixing with the Schiff base. At 88.5 mol% of AA, a large hysteresis is seen in the heterogeneous region where the N phase coexists with solid AA (see Fig. 2b). The rapid change in the order parameter upon heating suggests that the coexisting solid AA strongly disturbs the alignment of the N phase. To avoid such a complication, the measurement at a lower content of AA seemed to be desirable. However, the temperature range where the N phase coexists with solid AA is too narrow to carry out the desired measurement, as the eutectic point is located at about 72 mol% of AA. Consequently, two more similar systems with eutectics at lower AA contents were examined.

AA–N-(p-*Nitrobenzylidene)*-p-*anisidine* (*X*=NO_2, *Y*=CH_3O) *System.* Dave and Dewar have reported the eutectic at 93 °C and 57 mol% of AA for this system.[5] The diagram reproduced by the S-L and L-N transition temperatures tabulated in their paper is in fair agreement with ours, shown in Fig. 3. Although the temperatures of the intersection of the L-S and N-L transition curves and of the eutectic agree well with

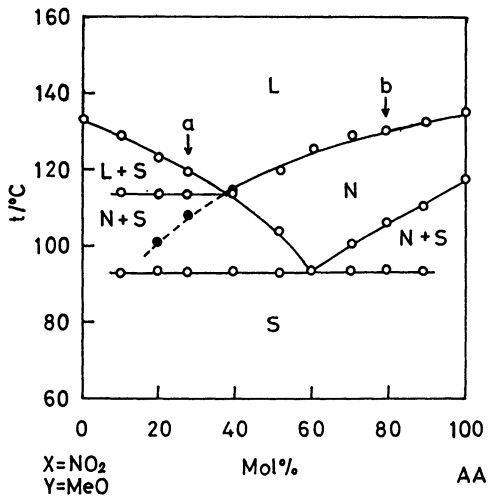

Fig. 3. The system AA–*N*-(*p*-nitrobenzylidene)-*p*-anisidine.

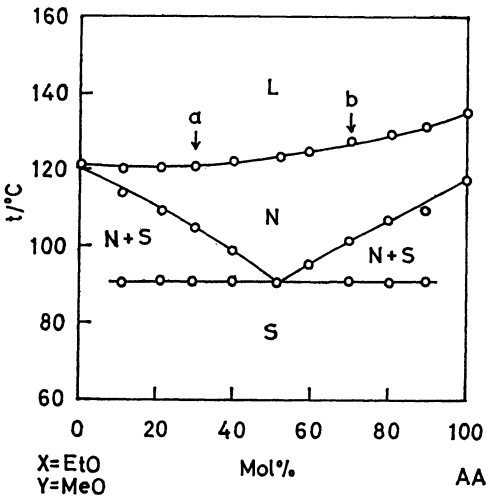

Fig. 4. The system AA–*N*-(*p*-ethoxybenzylidene)-*p*-anisidine.

those of Dave and Dewar, the compositions obtained by us are a little higher. It must be emphasized, however, that Dave and Dewar have reported neither the transitions at the horizontal N-L line of 113.5 °C on the Schiff base-rich side nor the transitions on the extrapolated part of the N-L curve on the AA-rich side. Contrary to the AA-*N*-(*p*-methoxybenzylidene)-*p*-anisidine system, the N-L curve on the AA-rich side is markedly convex upwards. The latent N-L transition temperature of about 80 °C is deduced by extrapolation to 0 mol% of AA.

The order parameter of the spin probe was measured at 27.6 and 79.3 mol% of AA (a and b in Fig. 3 respectively). At the former composition, the results are similar to those presented in Fig. 2a; however, the *S* values in the N+S region obtained during the process of heating are definitely higher than those in the supercooled N phase, possibly because of a larger difference between the two transition temperatures. As we hoped, the difference in the *S* value between the heating and cooling processes at the latter composition is much less than that found in Fig. 2b. The parameters measured on heating are about −0.23 throughout the N+S region and also in a part of the N phase.

AA-N-(p-*Ethoxybenzylidene*)-p-*anisidine* ($X=C_2H_5O$, $Y=CH_3O$) *System.* The Schiff base melts at 121.5 °C. When the melt is cooled, a monotropic transition to the N phase occurs at 121 °C. Therefore, the N-L transition curve looks as if it is met by the S-L transition curve at 0 mol% of AA. As is shown in Fig. 4, the N-L transition curve is slightly concave upwards; in other words, it shows a negative deviation from a linear relationship between the N-L transition temperatures of the two components. The eutectic is at 91 °C and about 51 mol% of AA. The order parameters of the spin probe examined at the compositions a and b are presented in Fig. 5. There is no supercooling of the L phase at either of the compositions. At 29.3 mol% of AA, the temperature variation in *S* is nearly reversible. On the other hand, a small but definite difference in the *S* value can be seen between the processes of heating

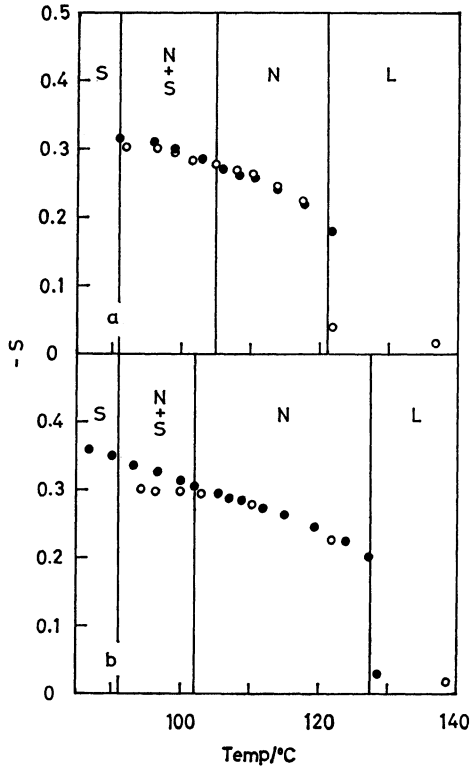

Fig. 5. Temperature dependence of the parameter *S* in AA–*N*-(*p*-ethoxybenzylidene)-*p*-anisidine, (a) 29.3 and (b) 70.5 mol% of AA.

and cooling in the N+S region at 70.5 mol% of AA. As the compositions a and b are selected almost symmetrically to the eutectic, the amount of the coexisting solid Schiff base at the composition a must be about the same as that of solid AA at the composition b. Therefore, the results in Fig. 5 indicate that the orientation of the AA-rich N phase by the magnetic field is more strongly disturbed by the coexisting solid AA than is the orientation of the Schiff base-rich N phase by the coexisting solid base.

The negative deviation of the N-L transition curve

from the ideal linear relationship may be due to the slightly repulsive interaction between the AA and Schiff-base molecules compared to the interaction between like molecules. On the other hand, the deviation found in the AA–*N*-(*p*-nitrobenzylidene)-*p*-anisidine system is in the direction opposite to the above-mentioned and is as much as 14 ° in the range of 40 to 50 mol% of AA, reflecting a strong attractive interaction between the AA and Schiff-base molecules in the N phase. A similar enhancement of the N-phase stability has been found by Park *et al.* in the binary system *N*-(*p*-methoxybenzylidene)-*p*-butylaniline and 4-cyano-4′-pentylbiphenyl and several other, closely related systems.[8] They have attributed the enhancement to molecular complexing by a weak charge-transfer interaction. This sort of intermolecular interaction may be more significant if one of the components carries a strong electron-donating substituent such as a dimethylamino group and the other, a strong electron-accepting substituent such as a nitro group. Work along this line will be reported in forthcoming papers of this series.

AA–N-(p-*Methylbenzylidene*)-p-*anisidine* (*X*=CH_3, *Y*=CH_3O) *System.* According to the work by Dave and Dewar, the eutectic is located at 72 °C and 25 mol% of AA, and the N-L transition curve is met by the transition curve on the AA-rich side at 100 °C and 62 mol% of AA.[5] In this case, the phase diagram is expected to be more complicated than those of the three systems described above. Below the temperature of the intersection, the isotropic L phase should coexist with solid AA, as is indicated by the endings of the isothermal tie-lines. Upon heating, this mixture is transformed into a mixture of the N phase and solid AA at the temperature of the intersection, then into the N phase only, and finally into the L phase. Thus, the sequence of the transformation at the temperature of the intersection is reversed compared with that we have found in the previous diagrams. Dave and Dewar reported neither the expected horizontal transition line nor the L-N transition to be shown by supercooled melts in the composition range below the intersection.

These missing transitions could, however, be detected by the present calorimetric measurements. The results are plotted in Fig. 6. The N-L transition curve observed with supercooled melts is slightly bent below 50 mol% of AA. The boundary between the N phase and the heterogeneous region where the N phase coexists with solid AA is straight. On the other hand, the S-L transition curve is really curved. The last two curves are of a different nature; that is, one of them represents the solubility of AA in the N phase, and the other, the solubility of AA in the L phase. Therefore, the discontinuity of the slope at the intersection is not unexpected, The eutectic was found at 72.5 °C and 27 mol% of AA, and the intersection, at 102 °C and 60 mol% of AA. The ESR measurements attempted at 68.2 and at 80.0 mol% of AA failed to prove the N phase to coexist with solid AA, probably because of the narrow temperature range and/or the disturbance from the relatively large amounts of solid AA. However, the L-N transition at 102 °C could be visually confirmed with the aid of a hot stage equipped with a polarizing microscope.

AA–N-(p-*Methoxybenzylidene*)-p-*chloroaniline* (*X*=CH_3O, *Y*=*Cl*) *System.* The binary system consisting of AA and *N*-(*p*-chlorobenzylidene)-*p*-anisidine gives a phase diagram of the same type. The intersection occurs at 98.5 °C and 60 mol% of AA, in good agreement with the results reported by Dave and Dewar.[5] This temperature is so close to the eutectic temperature, 92 °C, that the expected small endothermic peak is not detectable because of overlapping with a much larger peak due to the eutectic. The present system comprising AA and the isomeric Schiff base is, consequently, included as a further example. The eutectic has been located at 79.5 °C and 35 mol% of AA, and the intersection, at 99 °C and about 62 mol% of AA, by Dave and Dewar.[5] They made no mention of the horizontal transition line expected at the latter temperature and the L-N transition of supercooled melts. As is shown in Fig. 7, our measurements could indicate more complete relations for this system. The temperature of the intersection is firmly established at 100.5 °C by the transitions observed between 69.5 and 88.5 mol%

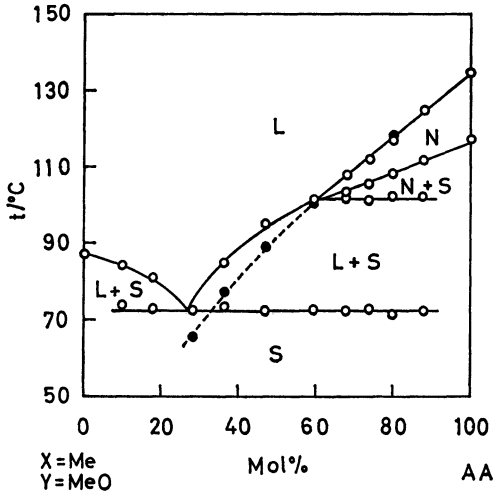

Fig. 6. The system AA–*N*-(*p*-methylbenzylidene)-*p*-anisidine.

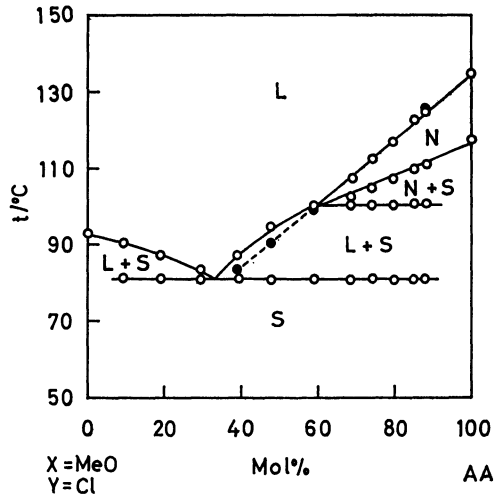

Fig. 7. The system AA–*N*-(*p*-methoxybenzylidene)-*p*-chloroaniline.

of AA. The N-L transition curve, now extended to 40 mol% of AA by the observations of the monotropic transformation of the supercooled melts, is essentially straight. If the curve is not bent below this composition, the latent L-N transition temperature of this Schiff base may be about 50 °C. The S-N transition curve is essentially straight, and its slope is considerably different from that of the S-L transition curve at the intersection. Attempts to confirm the N phase coexisting with solid AA by the ordering of the spin probe at 74.3, 79.8, and 85.6 mol% of AA did not meet with any success.

References

1) J. S. Dave and M. J. S. Dewar, *J Chem. Soc.*, **1954**, 4616.
2) S. H. Glarum and J. H. Marshall, *J. Chem. Phys.*, **46**, 55 (1967).
3) A. Bogojawlensky and N. Winogradow, *Z. Phys. Chem.*, **64**, 229 (1908).
4) R. Walter, *Ber.*, **58**, 2303 (1925).
5) J. S. Dave and M. J. S. Dewar, *J. Chem. Soc.*, **1955**, 4305.
6) J. S. Dave and J. M. Lohar, *J. Chem. Soc., A*, **1967**, 1473.
7) E. C. H. Hsu and J. F. Johnson, *Mol. Cryst. Liq. Cryst.*, **20**, 177 (1973).
8) J. W. Park, C. S. Bak, and M. M. Labes, *J. Am. Chem. Soc.*, **97**, 4398 (1975).