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Phase Diagrams and the Metathetic Reactions of Schiff Bases

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Phase Diagrams and the Metathetic Reactions of Schiff Bases

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La présence des reactions metathétiques altére le diagramme de phase des cristaux liquides a base(s) de Schiff et á composants multiples. Au lieu d'un point eutetique les diagrammes de phase montrent un minimum. Pour observer ce minimum, la mètathèses doit conduire à des produits à structures homologues. Les bases de Schiff de la famille des *p-n*-alkoxybenzylaniline-*p-n*-alkylaniline forment des systèmes homologues si, soit la chaine "alkyl," soit la chaine "alkoxy" (mais pas tous les deux) differe par pas plus d'une unité de méthyléne.

Les diagramme de phase avec un minimum sont obtenus quand le nombre de pairs de ces molecules homologues est un de moins que celui de réactions metathétiques, ou trois (3) de moins du nombre total des composants.

En accord avec ces considérations des mixtures à quatre composants ayant deux groupes de structures homologues binaires montrent un minimum dans leur courbes de fusion (voir Table I).

The presence of metathetical reactions alters the phase diagram of multicomponent Schiff base liquid crystals.† Instead of a eutectic point, phase diagrams with a minimum are observed. To observe the minimum, the metathetical reaction must lead to products with homologous structure. Schiff bases of the *p-n*-alkoxybenylidene-*p-n*-alkylaniline family form homologous systems if either the alkyl or alkoxy chain but not both differ by not more than one methylene unit.

Phase diagrams with a minimum obtain when the number of pairs of such homologous molecules is one less than the number of metathetical reactions or three less than the total number of components.

In agreement with these considerations four component mixtures having two sets of binary homologous structures exhibit melting curves with a minimum point (Table I).

† The concentration in the phase diagrams are corrected for metathesis when applicable. For the equilibrium

$$A + B = C + D$$

The equilibrium constant K is one

$$K = \frac{x^2}{(a - x)(b - x)}$$

The terms a and b are the initial mole fraction of components A and B. Consequently the corrected mole fractions are $a - x$ and $b - x$ where $x = (a)(b)$.

TABLE I

Binary mixtures with minimum associated with metathesis

System 1	2	$T_{CN}{}^1$	$T_{CN}{}^2$	Minimum temperature
EBBA/BBPeA		34.5	39.5	−15°
MBBA/BBPrA		19.5	24.0	−28°
EBBA/MBAP		34.5	47.5	−10°
MBBA/BBPeA		19.5	43.0	−34°
MBBA/EBBA		19.5	34.5	+10°
MBBA/BMZB		19.5	32.0	+10°
PrBBA/EBBA		31.0	34.5	6.2°
EBBA/EBPeA		34.5	63.0	16.0°

INTRODUCTION

The Schroder–Van Laar equation (Eq. 7) as normally employed in calculating eutectic composition and temperature is simplified by neglecting the heat of mixing in both the liquidus and solidus phase.

Since the enthalpy in the exponential factor receives contributions from both fusion and mixing, the shape of the temperature–composition curve for a given material is determined by the heat of mixing in both phases. The shape of the temperature–composition curve can vary from a smooth curve with a minimum point for positive heats of mixing to a temperature–composition curve representing compound formation with large negative heats of mixing. A single equation, a generalized form of the Schroder–Van Laar equation was derived which includes not only these extremes but also describes the more commonly observed eutectoid phase diagram.

EXPERIMENTAL OBSERVATIONS

The phase diagram of MBBA/BBPeA (Figure 1) was expected to resemble that of MBBA/EBBA with perhaps a lower eutectic point (Table II). However, instead of the V-pattern of two lines intersecting at an eutectic point, a flat-bottomed U-shaped curve was observed. Curves with a minimum were described many years ago by van Laar[1] and recently by Cox.[2]

To complicate matters further, gas chromatographic analysis of the MBBA/BBPeA mixture showed four instead of two components (Eq. 1). The two new components were

$$\text{MBBA} + \text{BBPeA} = \text{MBPeA} + \text{BBBA} \qquad (1)$$

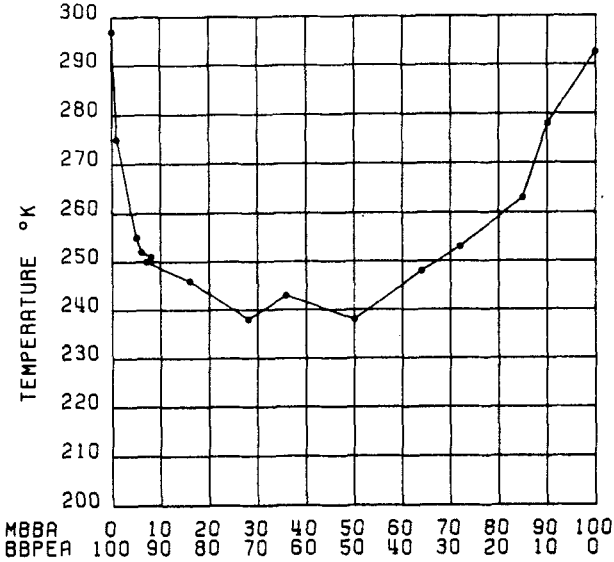


FIGURE 1 The phase diagram of MBBA/BBPeA. The melting temperature was obtained on the DuPont 990 Thermal Analyzer. The concentration of MBBA was corrected for metathesis (1).

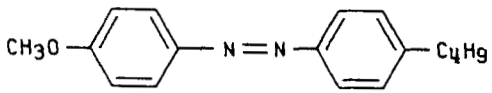
TABLE II

Acronyms

MBBA	*p*-methoxybenzylidene-*p*-*n*-butylaniline
EBBA	*p*-ethoxybenzylidene-*p*-*n*-butylaniline
BBPeA	*p*-*n*-butoxybenzylidene-*p*-*n*-pentylaniline
BBPrA	*p*-*n*-butoxybenzylidene-*p*-*n*-propylaniline
MBAP	*p*-methoxybenzylidene-*p*-*n*-butyryloxyaniline
MBPrA	*p*-methoxybenzylidene-*p*-*n*-propylaniline
MBPeA	*p*-methoxybenzylidene-*p*-*n*-pentylaniline
EBPeA	*p*-ethoxybenzylidene-*p*-*n*-pentylaniline
BBBA	*p*-*n*-butoxybenzylidene-*p*-*n*-butylaniline
BBAP	*p*-*n*-butoxybenzylidene-*p*-*n*-butyryloxyaniline
BMZB	*p*-methoxyphenyl-azo-*p*-*n*-butylbenzene
EBEA	*p*-ethoxybenzylidene-*p*-ethylaniline
BBEA	*p*-*n*-butoxybenzylidene-*p*-ethylaniline
PrBPeA	*p*-*n*-propoxybenzylidene-*p*-*n*-pentylaniline
BBBN	*p*-*n*-butoxybenzylidene
EBPeA	*p*-ethoxybenzylidene-*p*-*n*-pentylaniline
PrBBA	*p*-*n*-propylbenzylidene-*p*-*n*-butylaniline

MBPeA and BBBA. A metathesis had occurred. Metathesis in Schiff bases and its effect upon the melting of liquid crystal mixtures was discussed by Sorkin and Denny.[3] They observed that the melting point for any mixture of two or more Schiff bases depending on the composition of the mixture changed through metathesis.

To determine whether the metathetical reaction was responsible for the unusual phase diagram, a series of mixtures composed of BMZB, *p*-methoxyphenyl-azo-*p*-*n*-butylbenzene (I) and BBPeA was studied. Compound I is an analog of MBBA but the azo-linkage is stable towards metathesis.



1

A phase diagram with an eutectic point was obtained (Figure 2).

Curiously, a mixture of EBEA and BBPeA also formed an eutectic point (Eq. 2), although metathesis also took place. This was interpreted to mean that metathesis per se is not a sufficient condition to alter the shape of the phase diagram.

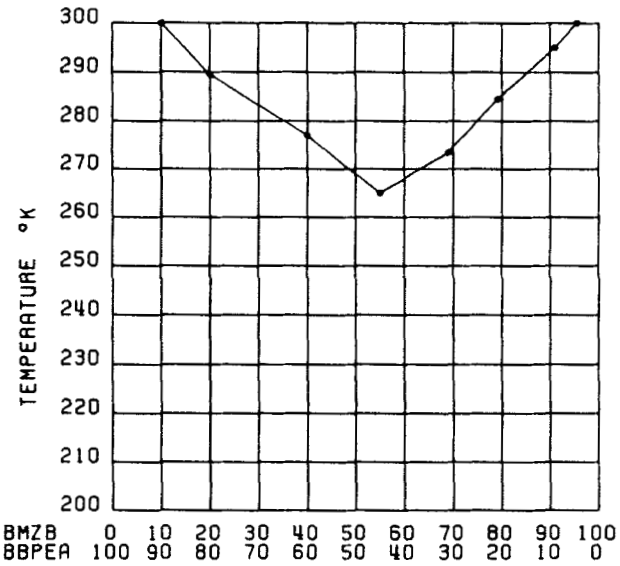


FIGURE 2 The phase diagram of BMZB/BBPeA. The stable azo-linkage in BMZB does not permit metathesis, thus a eutectic point is found.

$$\text{EBEA} + \text{BBPeA} = \text{EBPeA} + \text{BBEA} \quad (2)$$

The reaction between MBBA and BBPeA formed products which were adjacent members in an homologous series to MBBA and BBPeA, MBPeA and BBBA, respectively. The couples MBBA/MBPeA and BBBA/BBPeA differ by only one methylene group in the anilino-portion of the Schiff base. In contrast the reaction between EBEA and BBPeA (Eq. 2) yielded products EBPeA and BBEA which differ by three methylene units in each case.

Adjacent members in an homologous series often exhibit temperature–composition curves without a eutectic point.[4] Solid solutions might be expected to form between such members of an homologous series due to either similarity in heat of fusion or similarity in size. Heat of fusion was eliminated as a parameter through comparison of Schiff bases with similar heat of fusion for the crystalline to nematic transition but differing widely in aspect ratios (Table III). The Schiff base MBBA with a heat of fusion of 3063 cal/mole was mixed with BMZB with a heat of fusion of 3194 cal/mole (Table III) to form a phase diagram without a eutectic point (Figure 3) whereas the mixture of BMZB and BBBA with an associated heat of fusion of 3027 cal/mole gave the eutectic containing curve.

Similarity in size and shape was shown to be an important factor through choosing Schiff bases which were adjacent members of homologous series.

TABLE III

Enthalpies and transition temperatures of Schiff bases

Compound	ΔH_{CN} (cal/mole)[a]	T_{CN} (°K)[b]
MBBA	3063	292.5
EBBA	5930	307.5
BBBA	3027	314.0
BBPeA	3402	312.5
BMZB	3194	305.0
MBAP	3620	319.7
EBEA	4321	335.0
BBEA	1676	314.0
BBPRA	1772	297.0
BBAP	2810	344.0
MBPeA	4868	312.5
EBPeA	5934	336.0
PRBBA	—	304.0

[a] ΔH is the enthalpy of the crystalline to nematic (CN) transition. These values were obtained on a Dupont 990 Thermal Analyzer using Tin, Zinc and Indium as enthalpy standards.

[b] T_{CN} is the temperature of the crystalline to nematic (CN) transition.

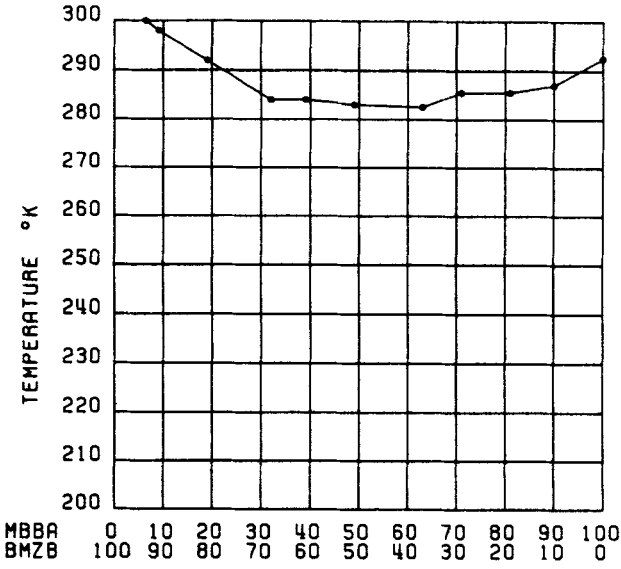


FIGURE 3 The phase diagram of MBBA/BMZB. Because of the similarity in aspect ratio MBBA and BMZB co-crystallize.

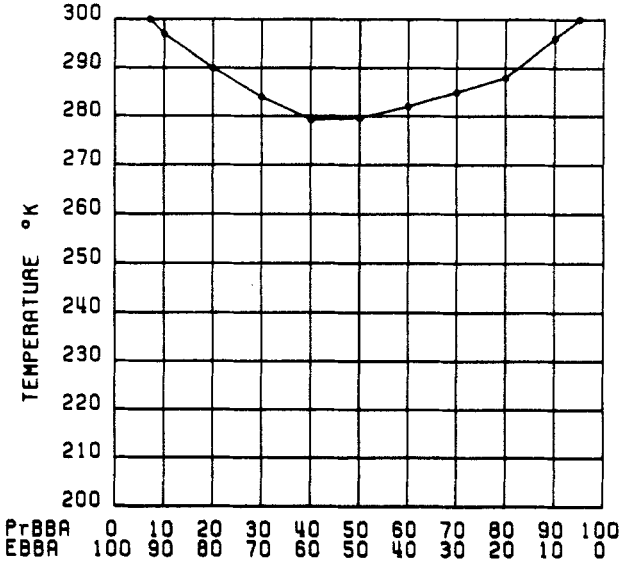


FIGURE 4 The phase diagram of PrBBA/EBBA Adjacent homology on the aldehydo-portion of the Schiff base also leads to U-shaped phase diagrams.

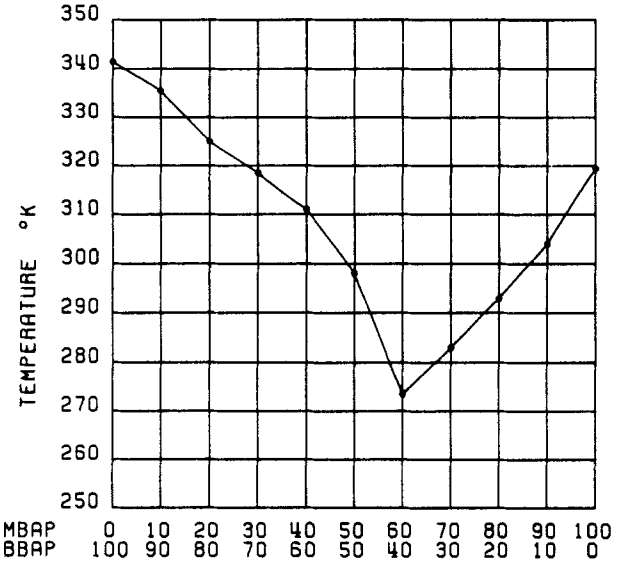


FIGURE 5 The phase diagram of MBAP/BBAP. The difference in aspect ratio between MBAP and BBAP does not permit co-crystallization thus a eutectic point is found.

The couple PrBBA/EBBA (Figure 4) showed the U-shaped phase diagram whereas the non-adjacent couple MBAP/BBAP (Figure 5) gave the familiar eutectic point.

Indeed, the requirement for co-crystallization of two Schiff bases is highly restrictive. They must differ by no more than one methylene unit.

The phenomenon of metathesis accompanied by a U-shape phase diagram was exhibited by the following binary mixtures: EBBA/BBPeA, MBBA/BBPrA, EBBA/MBAP and MBBA/BBPeA (Table I). In every case products were formed which are adjacent homologs to the starting materials.

Interestingly, the binary mixture MBBA/EBBA required annealing at $-15°C$ for 24 hours before the U-shaped phase diagram appeared. Quite often Schiff base couples which differed by one methylene unit in the aldehydo-portion of the Schiff base had less tendency to co-crystallize than the isomer with the additional methylene group in the anilino-section of the molecule.

DISCUSSION OF RESULTS

In order to understand the relationship between the U-shape phase diagram and co-crystallization, co-crystallization was considered as a solution process.

Instead of equating the heat of mixing to deviation from ideality, an equilibrium is assumed between the components of the mixture. The formation

from components of co-crystallized centers is achieved by interchanging molecules on the lattice of component i with molecules on the lattice of component j. The interchanging of molecules results in increasing the number of (i, j) co-crystallized pairs by two and in decreasing the number (i, i) and (j, j) pairs by one (Eq. 3).

$$(i, i) + (j, j) = 2(i, j) \tag{3}$$

The mole fraction N of the species in Eq. 3 are connected by an equation similar to the law of chemical equilibrium (Eq. 4)[6] with equilibrium constant K.

$$K = \frac{(2N_{ij})^2}{(N_{ii})(N_{jj})} = K_0 \exp\left(-\frac{\Delta\bar{H}^S_{ij}}{RT}\right) \tag{4}$$

The term $\Delta\bar{H}^S_{ij}$ is the partial molar heat of mixing for component i and j in the solid phase. The concentration of the co-solidified phase for an ideal solution ($\Delta\bar{H}^S_{ij} = 0$) is the product of the geometric means of the concentration of components, i and j with $K_0^{1/2}$ (Eq. 5).

$$N_{ij} = \tfrac{1}{2}((N_{ii})(N_{jj}))^{1/2} K_0^{1/2} \tag{5}$$

The moles fraction of the ith component in the liquid phase N^L_i is related to the ith component in the solid phase N^S_i in the following way (see Appendix I):

$$N^L_{ii} = (N^S_{ii})^{N_{ii}} \exp\left(\frac{N_{ii}\,\Delta H^S_{ij} - \Delta H_{f_{ii}}}{RT} + \frac{\Delta\bar{H}_{f_{ii}}}{RT_{ii}}\right) \tag{6}$$

Equation 6 transforms into the well-known Schröder–Van Laar Equation (Eq. 7) for large positive heats mixing $\Delta\bar{H}^S_{ij}$:

$$N^L_{ii} = \exp -\left(\frac{\Delta H_{f_{ii}}}{RT} + \frac{\Delta H_{f_{ii}}}{RT_{ii}}\right) \tag{7}$$

For $N_{ij} = 1$ and $\Delta\bar{H}^S_{ij} = 0$ Eq. (6) transforms into the Eq. (8), an expression employed By Cox,[3] Lee[7] and Billard[8] in prediction of phase diagrams.

$$N^L_{ii} = N^S_{ii} \exp -\left(\frac{\Delta H_{f_{ii}}}{RT} + \frac{\Delta H_{f_{ii}}}{RT_{ii}}\right) \tag{8}$$

Implicit in Eq. (8) is the assumption that the solid phase is an ideal solution. For each component N_{ii} in a mixture an expression of the form Eq. (6) relates the concentration of the components in the liquid to the solid phase. There is also an Eq. (4) for each co-crystallized component N_{ij}.

The solution to this set of equations requires at least that

$$N_{ij} = N_{ii} - 2 \tag{9}$$

the number of co-crystallized species is to be two less than the number of pure components (Eq. 9). Although N_{ij} can be as large as

$$N_{ij} = \frac{N_{ii}(N_{ii} - 1)}{2} \tag{10}$$

If a metathesis is possible among the Schiff bases, then the number of co-crystallized components depends upon the number of reactions. The number of metathetical reaction r consistent with Eq. (9) is obtained from phase rule (Eq. 11).

$$F = N_{ii} - r - Ph + 1 \tag{11}$$

Setting the degrees of freedom F equal to one and the number of phase Ph equal to two gave for r the value at constant temperature

$$r = N_{ii} - 3 \tag{12}$$

Substituting N_{ij} from Eq. 9 gave

$$r = N_{ij} - 1 \tag{13}$$

A temperature–composition curve with no eutectic point restricts the number of metathetical reactions to three less than the number of components (Eq. 12).

A metathetical reaction is a process during which chemically similar but structurally different parts are exchanged between the reactants.

$$AB + CD \rightleftharpoons AD + CB \tag{14}$$

Schiff bases are the addition products of aldehydes (m) and amines (n). Two different Schiff bases exchange their constituent parts to form new Schiff bases.

$$R_1 - CH = N - R_2 + R_3 - CH = N - R_4 \rightleftharpoons$$
$$R_1CH = N - R_4 + R_4CH = N - R_2 \tag{15}$$

A Schiff base is characterized by having an imine $CH = N$ central linking unit joining two end groups.

By designating m different aldehydes and n different amines by the row and column vectors

$$\bar{M} = (1, 2, 3, \ldots m) \quad \text{and} \quad \bar{N} = \begin{vmatrix} 1 \\ 2 \\ 3 \\ \vdots \\ n \end{vmatrix} \text{ respectively}$$

A product matrix P is generated by multiplying the vectors $\bar{M}$ and $\bar{N}$ together.

$$P = \bar{M} \times \bar{N} = \begin{vmatrix} 11 & 12 & \dots & 1m \\ 21 & 22 & \dots & \\ M^1 & M^2 & \dots & mn \end{vmatrix}$$

The number of matrix elements in P corresponds in number to Schiff bases N_{ii} produced by the r metathetical reactions.

Every metathetical reaction is equivalent mathematically to an odd transposition.

$$23 + 11 \rightleftharpoons 13 + 21 \tag{16}$$

Consequently the products and reactants found in the product matrix P are symmetrically disposed to each other.

$$P = \begin{vmatrix} 11 & 12 & 13 \\ 21 & 22 & 23 \\ 31 & 32 & 33 \end{vmatrix}$$

The number of metathetical reactions r is obtained from the product matrix P by counting one-half the total number of diagonal lines connecting elements.

$$\begin{vmatrix} 11 & 12 & 13 \\ 21 & 22 & 23 \\ 31 & 32 & 33 \end{vmatrix}$$ 9 cross terms

For nine matrix elements there are eighteen symmetrically disposed diagonal lines indicating nine non-redundant metathetical reactions, r.

The number of metathetical reactions, r is calculated from the m number of aldehydes and n number of amines. The number of cross terms for N_{ii} Schiff bases in a matrix of m rows and n columns is r where:

$$r = \frac{N_{ii}(N_{ii} - 1) - N_{ii}(m - 1) - N_{ii}(n - 1)}{4} \tag{17}$$

The divisor 4 arises from not considering both symmetrical cross reactants (11 + 22, 12 + 21) and not counting twice every cross product (11 + 22, 22 + 11). Substituting $N_{ii} = m \times n$ in Eq. (17) yields:

$$r = \frac{mn(m - 1)(n - 1)}{4} \tag{18}$$

Whereas all diagonal terms in the P matrix are equivalent to metathetical reactions, the row and columnar terms correlate to pairs of homologous molecules, N_{ij}.

$$\left|\begin{array}{ccccc} 11 & \longleftrightarrow & 12 & \longleftrightarrow & 13 \\ \updownarrow & & \updownarrow & & \updownarrow \\ 21 & \longleftrightarrow & 22 & \longleftrightarrow & 23 \\ \updownarrow & & \updownarrow & & \updownarrow \\ 21 & \longleftrightarrow & 32 & \longleftrightarrow & 33 \end{array}\right| \quad \text{12 Homologous molecules}$$

The number of homologous molecules is given by:

$$N_{ij} = m'n + n'm \tag{19}$$

m' and n' are the number of adjacent elements in the $\bar{M}$ and $\bar{N}$ vectors respectively.

If to each matrix element P_{mn} in the product matrix is assigned a quantity corresponding to the mole fraction of Schiff base mn, then a Laplace development of the product determinant in complementary minors shows that the determinant of P is zero,

$$|P = 0|$$

This is obvious since each minor corresponding to a metathetical reaction of the type discussed between Schiff bases has an equilibrium constant of one. Thus, the complementary minor of element P^{11} in the nine element P matrix discussed above is:

$$P^{11} = \left|\begin{array}{ccc} \cancel{11} & \cancel{12} & \cancel{13} \\ 21 & 22 & 23 \\ 31 & 32 & 33 \end{array}\right| = \left|\begin{array}{cc} 22 & 23 \\ 32 & 33 \end{array}\right| \tag{20}$$

$$P^{11} = 22 \cdot 33 - 23 \cdot 32 = 0 \text{ because}$$

$$K = \frac{23 \cdot 32}{22 \cdot 33} = 1$$

A nine component ($P = 9$) Schiff base mixture was constructed using the following mole fractions of three aldehydes ($m = 3$) and three amines ($n = 3$):

p-methoxybenzaldehyde (0.3227);
p-ethoxybenzaldehyde (0.0471);
p-butoxybenzaldehyde (0.1326);
p-butylaniline (0.2665);
p-pentylaniline (0.1326); and
p-butyryloxyaniline (0.1037).

At equilibrium the nine Schiff bases were found to have the following mole fractions:

MBBA (0.319); EBBA (0.036); MBPeA (0.161); EBPeA (0.023); MBAP (0.118); EBAP (0.015); BBBA (0.163); BBPeA (0.082), and BBAP (0.062).

Inserting the appropriate mole fractions gives:

$$P = \begin{vmatrix} 0.319 & 0.161 & 0.118 \\ 0.036 & 0.023 & 0.015 \\ 0.163 & 0.082 & 0.062 \end{vmatrix}$$

Expanding P in terms of minors, P^{mn} one finds all such minors are nearly identical to zero:

$$P^{11} = 0.023 \times 0.062 - 0.015 \times 0.082 = 0.000196$$
$$P^{12} = 0.036 \times 0.062 - 0.015 \times 0.163 = -0.000213$$
$$P^{13} = 0.036 \times 0.082 - 0.023 \times 0.163 = -0.000797$$
$$P^{21} = 0.161 \times 0.062 - 0.118 \times 0.082 = 0.000306$$
$$P^{22} = 0.319 \times 0.062 - 0.118 \times 0.163 = 0.000544$$
$$P^{23} = 0.319 \times 0.082 - 0.161 \times 0.163 = -0.000085$$
$$P^{31} = 0.161 \times 0.015 - 0.118 \times 0.023 = -0.000299$$
$$P^{32} = 0.319 \times 0.015 - 0.118 \times 0.036 = 0.000537$$
$$P^{33} = 0.319 \times 0.023 - 0.161 \times 0.036 = 0.001541$$

The determinant of $|P| = 2.771 \times 10^{-6}$.

CONCLUSION

A Schiff base mixture of N_{ii} components composed from m aldehydes and n amines has a U-shape phase diagram when the N_{ii} components are related to r metathetical reactions where

$$r = \frac{m(m-1)\,n(n-1)}{4}$$

The r metathetical reactions must produce at least N_{ii}-2 homologous Schiff bases N_{ij} with (Table 4)

$$N_{ij} = m'n + n'm$$

TABLE IV

Correlation of components, metathetical reactions and homologous structure

Components N_{ii}	Metathetical reaction[a] r	Homologous structures[b] N_{ij}
3	0	1
4	1	2
6	3	4
9	6	7
12	9	10

[a] $r = N_{ii} - 3$
[b] $N_{ij} = N_{ii} - 2$

Analyzing the reaction of MBBA and BBPeA there are two different aldehydes, MB, BB and two different amines, BA, PeA. The total number of product Schiff bases resulting from metathesis is $4(= 2 \times 2)$: MBBA, BBPeA, MBPeA and BBBA.

The number of metathetical reactions r among these four Schiff bases is one

$$r = \frac{2 \cdot 1 \cdot 2 \cdot 1}{4} = 1$$

This reaction is MBBA + BBPeA = MBPeA + BBBA. The number of homologous molecules is two. MBBA is an adjacent homolog to MBPeA whereas BBPeA is an homolog to BBBA.

Since r is three less and N_{ij} is two less than the number of Schiff bases a U-shape phase diagram was found.

Phase diagrams with a minimum point of multicomponent liquid crystal mixture have several definite advantages over analogous mixtures exhibiting a eutectic point. First, the minimum point phase diagram is less sensitive to compositional variation. The minimum point curves are broad and flat. Second, the minimum point phase diagram allows for selection of larger mesophase ranges than those obtained with a eutectic phase diagram. Generally, the eutectic point sits under some intermediate location on the mesophase–isotropic transition curve whereas the broader, flatter minimum point curve permits selection of a composition near both the lowest crystalline–mesophase melting point and the largest mesophase isotropic transition temperature. Finally, the composition of the liquidus and solidus phases are more similar in the instance of a minimum point than in the case of a eutectic point phase diagram. This means that cooling of the mixture will have less effect on the liquid phase composition and also upon any performance characteristics which are composition dependent.

Clearly the shape of the phase diagram is altered with the heat of mixing. The most desirable phase diagram with respect to large mesophase ranges is one in which the crystalline–mesophase transition is described by a broad flat curve with a minimum point whereas the mesophase–isotropic transition displays a broad curve with a maximum point. The maximum point type phase diagram requires strong association in the mesophase such as is obtained with charge transfer complexation. In contrast, the minimum point crystalline–mesophase type phase diagram requires weak association in the solid phase as obtained from molecules of similar shape, constitution and configuration.

CALCULATION OF PHASE DIAGRAMS

Equations 4 and 6 were solved for two components and one co-solidified phase (see Appendix II). Because of the transcendental nature of these equations a numerical method was required for their solution, the graphical bisection method. Five concentrations were calculated one for each component in the liquid and solid phases plus the concentration of the co-solidified component. The system studied was MBBA/EBBA. Two sets of curves were generated, those associated with the liquid and those with the solid composition as a function of temperature (Figures 6-1 and 6-2). As the heat of mixing

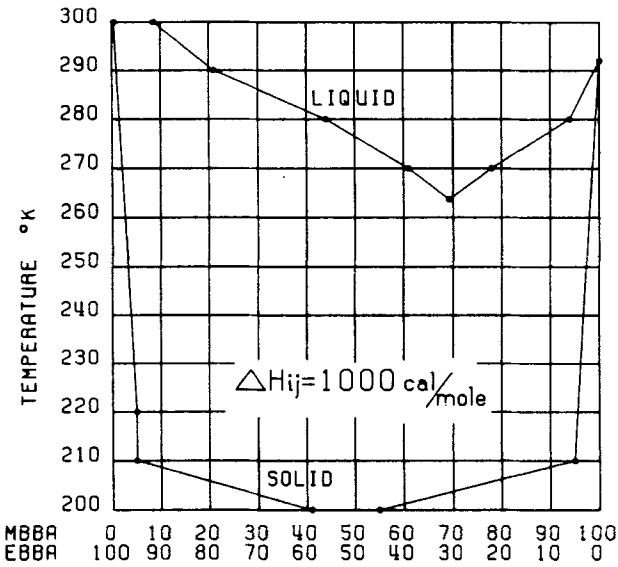


FIGURE 6(a) The upper and lower curves depict calculated values for the liquid and solid phase composition of the binary mixture MBBA/EBBA with an enthalpy of mixing in the solid of 1000 cal/mole.

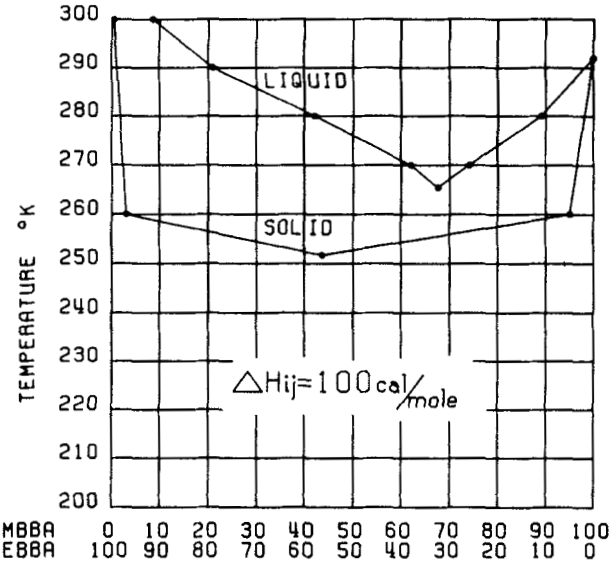


FIGURE 6(b) The upper and lower curves depict calculated values for the liquid and solid phase composition of the binary mixture MBBA/EBBA with an enthalpy of mixing in the solid of 100 cal/mole.

in the solid temperature decreases the calculated minimum solidification temperature of the liquid shifted to higher temperatures and greater concentrations of MBBA. For each value of the enthalpy of mixing, the melting temperature of the solid was reasonably flat and independent of the composition. As the enthalpy of mixing decreased the virtual melting temperature of the solid also increased. This model correctly predicted the shape of the phase diagram when co-crystallization occurred in the solid phase.

Appendix 1

DERIVATION OF EQUATION 6

Cooling curve relationship

1-1 $$H^S = N_1^S \bar{H}_1^{\cdot S} + N_2^S \bar{H}_2^{\cdot S} + N_{12}^S \Delta H_{12}^S$$

1-2 $$H^L = N_1^L \bar{H}_1^{\cdot L} + N_2^L \bar{H}_2^{\cdot L}$$

1-3 $$S^S = N_1^S \sigma_1^{\cdot S} + N_2^S \sigma_2^{\cdot S} + N_{12}^S \Delta S_{12}^S$$

1-4 $$S^L = N_1^L \sigma_1^{\cdot L} + N_2^L \sigma_2^{\cdot L} + N_{12}^L \Delta S_{12}^L$$

1-5 $$\bar{H}_2^S = \bar{H}_2^{\cdot S} + N_{12}^S \Delta \bar{H}_{12}^S$$

1-6 $\bar{H}_2^L = \bar{H}_2^L$

1-7 $\bar{S}_2^S = \sigma_2^S + N_{12}^S \Delta\bar{S}_{12}^S$

1-8 $\bar{S}_2^L = \sigma_2^L + N_{12}^L \Delta\bar{S}_{12}^L$

1-9 $$T = \frac{\Delta H_f - N_{12}^S \Delta\bar{H}_{12}^S}{\Delta S_f + N_{12}^L \Delta\bar{S}_{12}^L - N_{12}^S \Delta\bar{S}_{12}^S}$$

1-10 $$T = \frac{\Delta H_f - N_{12}^S \Delta\bar{H}_{12}^S}{\Delta S_f + N_{12}^L R \ln N_2^L - N_{12}^S R \ln N_2^S}$$

1-11 $$T = \frac{\Delta H_{f_{12}} - N_{12}^S \Delta\bar{H}_{12}^S}{\frac{\Delta H_{f_{12}}}{T_2} + N_{12}^L R \ln N_2^L - N_{12}^S R \ln N_2^S}$$

For $N_{12}^L = 1$, solving for N_2^L

1-12 $$N_2^L = (N_2^S)^{N_{12}} \operatorname{Exp}\left[\frac{-\Delta H_{f_2}}{R}\left(\frac{1}{T} - \frac{1}{T_2}\right) - \frac{N_{12}^S \Delta\bar{H}_{12}^S}{RT}\right]$$

Definitions

L	liquidus
s	solidus
N	mole fraction
N_{ij}	mole fraction of mixed solution
T	temperature
T_2	melting point of pure components
H_{12}	partial molar heat of mixing
R	gas constant
H	enthalpy
H	partial molar enthalpy of pure material
S	entropy
σ	partial molar entropy

Appendix 2

SOLUTION OF EQUATIONS (4) AND (6) FOR A BINARY MIXTURE

Define

2-1 $$K_1 = \exp\left[\frac{-\Delta H_1}{R}\ \frac{1}{T} - \frac{1}{T_1}\right]$$

$$2\text{-}2 \quad K_2 = \exp\left[\frac{-\Delta H_2}{R}\ \frac{1}{T} - \frac{1}{T_2}\right]$$

$$2\text{-}3 \quad K_3 = \exp\left(\frac{-\Delta H_3}{RT}\right)$$

Then Eq. (6) is rewritten as

$$2\text{-}4 \quad N_{11}^L = (N_{11}^S)^{N_{11}} \frac{K_1}{K_3^{N_{12}}}$$

$$2\text{-}5 \quad N_{22}^L = (N_{22}^S)^{N_{12}} \frac{K_2}{K_3^{N_{12}}}$$

$$2\text{-}6 \quad N_{12} = K_3 N_{11}^S N_{22}^S$$

Then sum of the mole fractions in each phase is equal to one

$$2\text{-}7 \quad N_{11}^L + N_{22}^L = 1$$

$$2\text{-}8 \quad N_{11}^S + N_{22}^S + N_{12}^S = 1$$

$$2\text{-}9 \quad N_{11}^S + N_{22}^S + K_3 N_{11}^S N_{22}^S = 1$$

$$2\text{-}10 \quad N_{11}^S = \frac{1 - N_{22}^S}{1 + K_2 N_{22}^S}$$

$$2\text{-}11 \quad (N_{11}^S)^{N_{12}} \frac{K_1}{K_2^{N_{12}}} + (N_{22}^S)^{N_{12}} \frac{K_2}{K_3^{N_{12}}} = 1$$

$$2\text{-}12 \quad K_1 (N_{11}^S)^{K_3 N_{12}^S N_{22}^S} + K_2 (N_{22}^S)^{K_3 N_{11}^S N_{22}^S} = K_3^{K_3 N_{11}^S N_{22}^S}$$

$$2\text{-}13 \quad \left[K_1\left(\frac{1 - N_{22}^S}{1 + K_3 N_{22}^S}\right)\right]^{K_3[(1 - N_{22}^S)/(1 + K_3 N_{22}^S)]} + K_2 (N_{22}^S)^{K_3[(1 - N_{22}^S)/(1 + K_3 N_{22}^S)]} - K_3^{K_3[(1 - N_{22}^S)/(1 + K_3 N_{22}^S)] N_{22}^S} = 0$$

Solve Eq. 2-12 for N_{22}^S. Substitute N_{22}^S into Eq. 2-10 to find N_{11}^S. From N_{11}^S and N_{22}^S compute N_{12} from Eq. 2-6. Using Eq. 2-4 and 2-5 values for N_{11}^L and N_{22}^L are calculated.

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