Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 21 Mar 2007.

To cite this article: Edward C.-H. Hsu & Julian F. Johnson (1974): Prediction of Eutectic Temperatures, Compositions and Phase Diagrams for Binary Mesophase Systemst, Molecular Crystals and Liquid Crystals, 27:1-2, 95-104

To link to this article: http://dx.doi.org/10.1080/15421407408083122

Mol. Cryst. Liq. Cryst., Vol. 27. pp. 95–104

Printed in Dordrecht, Holland

Prediction of Eutectic Temperatures, Compositions and Phase Diagrams for Binary Mesophase Systems†

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(Received September 7, 1973)

Examination of a number of binary mesophase systems shows that the Schröder-van Laar equations for predicting the liquidus temperature and the eutectic temperature and composition are widely applicable. Additionally emperical correlations between the melting point and eutectic composition and temperature for binary mixtures having one common component are shown to be applicable to a considerable number of systems.

INTRODUCTION

The thermodynamic properties of binary mesophase (liquid crystal) systems have been discussed, for example, in the book of Gray[1] and have been recently reviewed[2]. Since the crystal-mesophase transition for many mesomorphic compounds is above room temperature, lowering of this transition temperature into the ambient region can be achieved by use of binary or ternary systems. It has been shown that two components with the same morphologies, i.e. nematic-nematic or smetic A-smetic A, are completely miscible and form a uniform "comesophase" over essentially the entire composition range. However, binary mixtures with different morphologies, i.e. nematic-smetic or smetic A-smetic B, are not continuously miscible. The mesophase-isotropic liquid transition tem-

† Part XXXVIII of series "Order and Flow in Mesophases"

peratures for the structurally similar compounds vary almost linearly with changes in composition, but dissimilar compounds deviate from linearity. Normally, the crystal-mesophase transition temperatures for the binary mixtures are decreased more than the mesophase - isotropic liquid transition temperatures. Therefore, the binary mixtures lower the crystal-mesophase transition temperature and give an expanded temperature range of mesophase stability.

In order to test the nature of the binary mesophase systems and to formulate some general rules, some mesophase systems which have been previously reported in the literature are re-examined by use of the Schröder-van Laar equations. The relationships between eutectic composition and eutectic temperature, melting point (crystal → mesophase transition) and eutectic composition, and melting point and eutectic temperature are also calculable. Therefore, the eutectic temperatures, eutectic compositions and phase diagrams for binary mesophase systems can be predicted easily and accurately.

PROCEDURE AND RESULTS

Figure 1 shows the temperature-composition phase diagram of the p-azoxyanisole-p-azoxyphenetole system.[3] This type of phase diagram which is usually

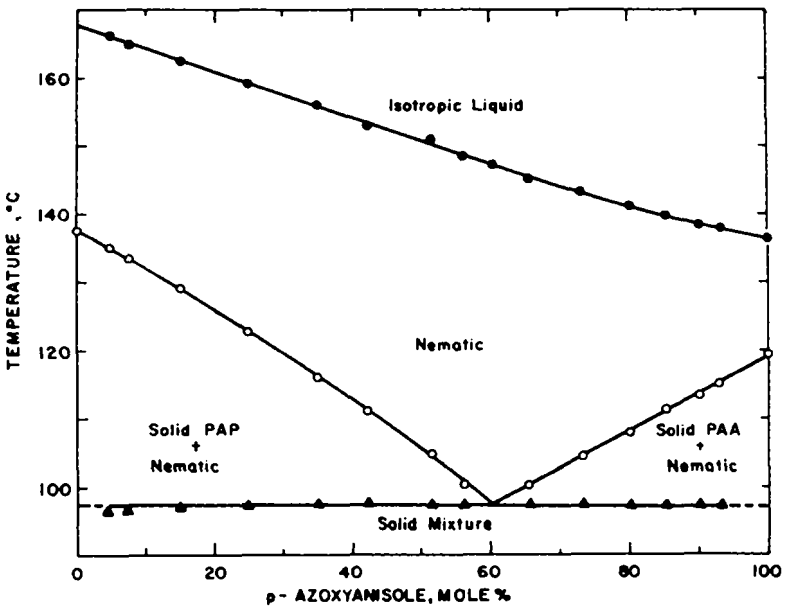

FIGURE 1 Phase Diagram of p-Azoxyanisole-p-Azoxyphenetole System

encountered in binary mixtures of simple mesophase systems is known as the "simple-eutectic" type. It shows that the two components do not form solid solutions in the solid state and are completely miscible in the mesomorphic state which is referred to as "comesophase". Both components are also completely miscible in the isotropic liquid state. The lowest melting mixture is the eutectic which crystallizes as a mechanical mixture of the two pure components.

If a phase diagram is of the simple-eutectic type, the mesophase-liquidus curves, eutectic temperature and composition can be calculated by means of the Schröder-van Laar equations which are also referred to as the freezing point depression equations, using only the crystal mesophase transition heats and temperatures of the two pure components. The Schröder-van Laar equations are:

$$-\ln x_1 = \frac{\Delta H_{f1}}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right) \tag{1}$$

$$-\ln (1-x_1) = \frac{\Delta H_{f2}}{R}\left(\frac{1}{T} - \frac{1}{T_2}\right) \tag{2}$$

where ΔH_{f1}, T_1 and ΔH_{f2}, T_2 are the heats of fusion and transition temperatures of pure components 1 and 2 from the crystalline solid to the mesophase, T is the transition temperature for a two component system containing x_1 mole fraction of component 1, and R is the gas constant. Simultaneous solution of the two equations with $X_1 = X_e$ and $T = T_e$ also permits calculation of the eutectic temperature, T_e, and composition, X_e, for the simple eutectic binary system.

For the system p-azoxyanisole-p-azoxyphenetole the nematic liquidus values, eutectic temperature and composition calculated by use of the Schröder-van Laar equations, together with the experimental results, are presented in Table 1. The agreement between calculated and experimental results is good.

In order to test the application of the Schröder-van Laar equations for binary mesophase systems which are of the "simple-eutectic" type, some binary mesophase systems which have been reported in the literature were re-examined. In each system the eutectic temperature and eutectic composition were calculated by simultaneous solution of the Schröder-van Laar equations. A comparison of calculated and measured results is given in Table 2 and shows good agreement. This demonstrates that the Schröder-van Laar equations can be used to predict the eutectic temperatures, compositions and phase diagrams for the simple-eutectic binary mesophase systems. These equations can be used, of course, only when the transition temperatures and heats of the two components are known. Conversely, the transition heats of components can be calculated using these equations if the eutectic composition and temperature are known.

In order to gain a better insight into the features of binary mesophase systems, an attempt was also made to find the relationship between melting point and eutectic composition, melting point and eutectic temperature and eutectic

TABLE I

Calculated and Measured Nematic Liquidus Temperatures for the System p-Azoxyanisole (PAA) – p-Azoxyphenetole (PAP)

No.	Mole % PAA	Mole % PAP	Transition Temperature, °C Crystal Calculated	Transition Temperature, °C Nematic Measured
1	100.0	–	–	119.5
2	93.0	7.0	116.3	116.2
3	90.1	9.9	114.9	114.6
4	85.3	14.7	112.6	111.9
5	80.2	19.8	109.9	108.9
6	73.2	26.8	106.1	105.6
7	65.4	34.6	101.4	101.0
8	60.4	39.6	98.2	97.5
9	56.1	43.9	99.1	100.0
10	51.4	48.6	103.4	104.8
11	42.2	57.8	111.0	111.0
12	34.8	65.2	116.5	116.0
13	24.9	75.1	125.6	124.8
14	15.1	84.9	129.0	129.0
15	7.5	92.5	133.3	133.2
16	4.8	95.2	134.7	134.9
17	–	100.0	–	137.8
Eutectic Temperature, °C			96.9	97.4
Eutectic Composition, Mole % PAA			59.2	60.0

temperature and eutectic composition. Figure 2 shows the eutectic compositions of a number of binary nematic mesophase systems having one common second component, p-azoxyanisole, plotted as a function of the melting points of the first components. All components fall on or close to a straight line with a slope 1.625° C/mole % which intersects the zero mole % axis at 38°C. This implies that those components form nearly ideal mesophase solutions with p-azoxyanisole due to structural similarities. A similar plot with p-azoxyphenetole as one common second component is shown in Figure 3. Comparison of Figures 2 and 3 shows that both lines have identical slopes. The temperature difference between the intersections at the zero mole % axis of the two plots is exactly equal to that between the melting points of p-azoxyanisole and p-azoxyhenetole, 18°C.

Based on the eutectic composition-melting point straight line relationship shown in Figures 2 and 3, the approximate eutectic composition of a compound mixed with a structurally similar component can be predicted.

TABLE II

Calculated and Measured Eutectic Temperatures and Compositions

System A – B	Eutectic Temperature, °C		Eutectic Composition Mole % Component A		Reference
	Calculated	Measured	Calculated	Measured	
p-Azoxyanisole – p-Azoxyphenetole	96.6	97.4	59	60	(3)
p-Azoxyanisole – p,p'-Di-n-propoxyazoxybenzene	90.0	92.2	49	48	(3)
p-Azoxyanisole – p,p'-Di-n-butoxyazoxybenzene	80.5	83.5	38	37	(3)
p-Azoxyanisole – p,p'-Di-n-hexyloxyazoxybenzene	71.5	73.2	26	24	(3)
p-Azoxyanisole – p-Anisalazine	106.6	107.8	78	81	(4)
p-Azoxyphenetole – p-Anisalazine	119.1	120.8	70	72	(4)
p-Azoxyanisole – p-[(p-Methoxybenzylidene) amino]-phenyl Acetate	68.4	68.4	26	23	(4)
p-Azoxyanisole – N-(p-Ethoxybenzylidene)-p-butylaniline	30.9	31.5	7	5	(4)
Cholesteryl Myristate-Cholesteryl Sterate	62.5	60.0	71	70	(5)
Cholesteryl Myristate-Cholesteryl Undecanoate	61.7	59.0	65.2	60	(5)

Figure 4 shows the eutectic temperatures of a number of binary nematic mesophase systems having one common second component, p-azoxyanisole, plotted as a function of melting point of the first component. A smooth curve is obtained. Based on this curve, the eutectic temperature of a compound mixed with a structurally similar component may be predicted.

If no transition heat data exist for both pure components, another approximate prediction of the eutectic composition can be made by the following equation when the eutectic temperature of a binary system is known[6]

$$x_1 = \frac{100(T_2 - T_e)}{T_1 + T_2 - 2T_e} \tag{3}$$

where T_1 and T_2 = melting point of the lower and higher melting components

T_e = eutectic temperature

x_1 = mole fraction of the lower melting component in the eutectic.

Since the eutectic temperature of a binary system which forms the simple-eutectic type phase diagram can be determined by measuring only one mixture

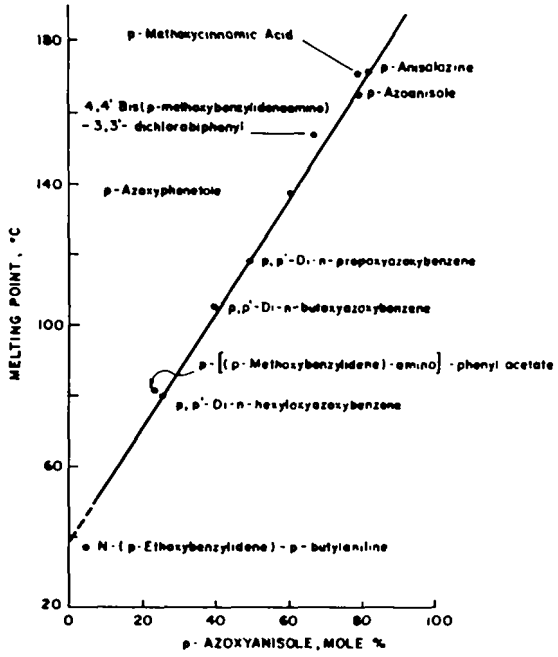

FIGURE 2 Eutectic Compositions in a Number of Binary Systems Having One Common Second Component, p-Azoxyanisole, as a Function of Melting Point of the First Component. The Abscissa is the Mole % p-Azoxyanisole in the Eutectic, the Ordinate is the Solid to Nematic Transition Temperature

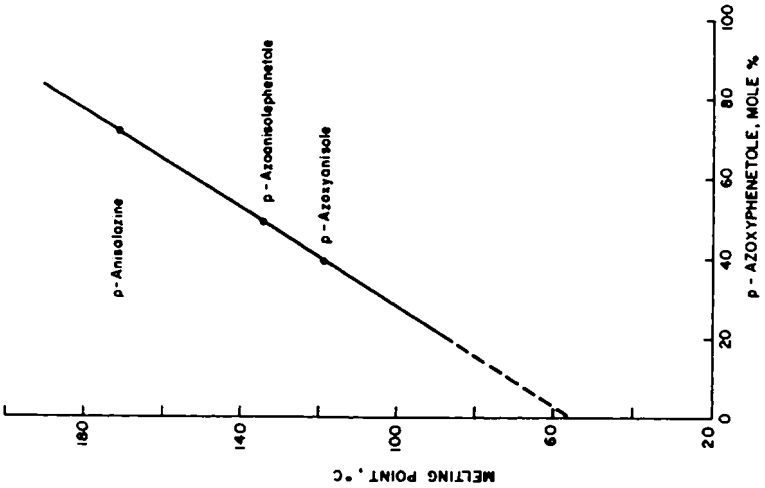

FIGURE 3 Eutectic Compositions in a Number of Binary Systems Having One Common Second Component, p-Azoxyphenetole, as a Function of Melting Point of the First Component. The Abscissa is the Mole % p-Azoxyphenetole in the Eutectic, the Ordinate is the Solid to Nematic Transition Temperature

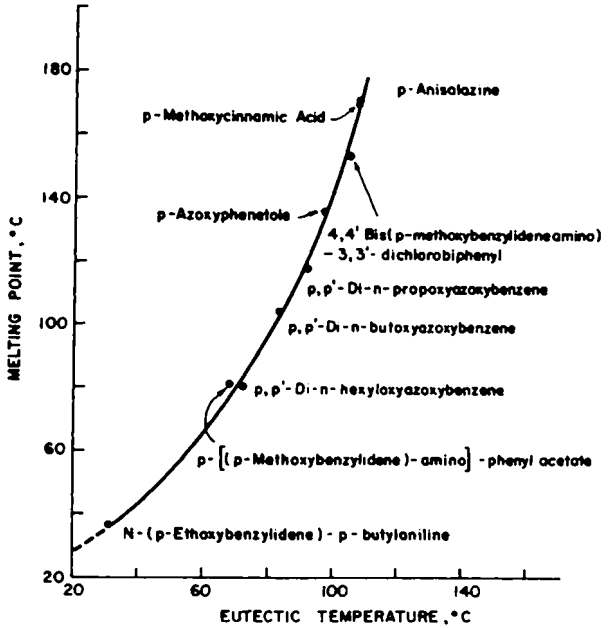

FIGURE 4 Eutectic Temperatures in a Number of Binary Systems Having One Common Second Component, p-Azoxyanisole, as a Function of Melting Point of the First Components. The Ordinate is Referred to the Solid to Nematic Transition Temperature

TABLE III

Calculated and Measured Eutectic Compositions (From Equation 3)

Component A + Component B	Eutectic Temperature °C Measured	Eutectic Composition Mole % Component A Calculated	Measured	Reference
p-Azoxyanisole + p-Azoxyphenetole	97.4	61	60	(3)
p-Azoxyanisole + p,p'-Di-n-propoxyazoxybenzene	92.2	49	48	(3)
p-Azoxyanisole + p,p'-Di-n-butoxyazoxybenzene	83.5	39	37	(3)
p-Azoxyanisole + p,p'-Di-n-hexyloxyazoxybenzene	73.2	23	24	(3)
p-Azoxyanisole + p-Anisalazine	107.8	83	81	(4)
p-Azoxyphenetole + p-Anisalazine	120.8	74	72	(4)
p-Azoxyanisole + p-[(p-Methoxybenzylidene)amino]-phenyl Acetate	68.4	21	23	(4)
p-Azoxyanisole + N-(p-Ethoxybenzylidene)-p-butylaniline	31.5	6	5	(4)
Cholesteryl Myristate + Cholesteryl Sterare	60.0	68	70	(5)
Cholesteryl Myristate + Cholesteryl Undecancate	59.0	74	60	(5)
p-Azoxyanisole + p-Azoanisolephenetole	102.0	68	71	(7)

TABLE III (*cont'd*)

Calculated and Measured Eutectic Compositions

System Component A + Component B	Eutectic Temperature °C Measured	Eutectic Composition Mole % Component A Calculated	Measured	Reference
p-Azoxyphenetole + p-Azoanisolephenetole	117.8	50	52	(7)
p-Azoxyanisole + Methoxycinnamic Acid	107.5	78	78	(8)
p-Azoanisolephenetole + p-Di-n-propoxyazobenzene	113.0	62	60	(7)
n-Butyl 4′-ethoxyazobenzene-4-carboxylate + n-Propyl 4′-methoxybenzylidene-4-amino-α-methylcinnamate	34.0	40	39	(9)
n-Butyl 4′-ethoxyazobenzene-4-carboxylate + (4′-methoxyazobenzene-4-oxy)hexanoate	42.0	51	53	(9)
n-Propyl 4′-methoxybenzylidene-4-amino-α-methyl-cinnamate + (4′-methoxyazobenzene-4-oxy) hexanoate	38.0	64	62	(9)
p-n-Hexylcarbonato-p′-n-hexylphenyl Benzoate + p-n-Heptylcarbonato-p′-n-hexylphenyl Benzoate	26.5	35	37	(10)

without weighing, the eutectic composition can be predicted using the above relationship. Conversely, the eutectic temperature can be calculated when the eutectic composition of a binary system is known. A comparison of the calculated and measured results is given in Table 3 and shows good agreement.

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