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J. M. Lohar [a] & D. S. Shah [a]
[a] Chemistry Department, Faculty of Technology and Engineering, M.S. University of Baroda, Baroda, India

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Studies in Mixed Mesomorphism: Determination of Latent Transition Temperatures by Extrapolation

J. M. LOHAR and D. S. SHAH[‡]

Chemistry Department, Faculty of Technology and Engineering,
M.S. University of Baroda, Baroda, India

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In binary systems, consisting of two structually similar components of which one is a liquid crystal, extrapolation of the transition curves should yield values for latent transition temperatures of the non-liquid crystalline substances. The reliability of this method of arriving at the latent transition temperatures has been questioned by some research workers. An attempt has been made under this investigation to arrive at some conclusive evidence in regard to the reliability of the method. Several binary systems with suitable Schiff's bases as one component and the well-known *p*-azoxyanisole or *p*-azoxyphenetole as the other liquid-crystal component have been studied from which a fair conclusion in favour of the dependability of the extrapolation method may be drawn. Yet, there cannot be a final word since some of the binary systems under study pose a difficulty in understanding their behaviour although discrepancies observed have been accounted for in terms of polarity and non-ideality of the mixtures besides an overall combined effect accruing from structural aspects working for or against the exhibition of mixed mesomorphism. It can be readily seen that whenever the transition curves are more or less straight, the reliability is high. Incidentally the present study also clearly supports the view of 'additive effect' of terminal polar groups in exhibiting mixed mesomorphism; the values of initial slopes of the transition curves and 'group slope values' for the terminal polar groups of Schiff's bases obtained from the phase diagrams of their binary mixtures with *p*-azoxyanisole are comparable with those obtained from the phase diagrams of their binary mixtures with *p*-azoxyphenetole. Though some of the values vary slightly, the order of 'group efficiency' remains the same.

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[‡] Presently in U.S.A.

INTRODUCTION

A nematic liquid is so oriented in its molecular disposition as to give rise to a coexistence of certain specific properties of isotropic liquids and crystalline solids over a range of temperature. Such an intermediate state of existence has been designated as a mesophase which behaves mechanically as a liquid but differs from isotropic liquids in that the molecules in them get oriented in a rod-like parallel formation. Display of crystalline properties has been attributed to the regularity in alignment of molecules due to the residual forces which do not disappear sharply at the melting point of the substance on heating but continue to be operative until a certain higher temperature known as transition point is reached when finally the turbird liquid is transformed into an isotropic liquid. Several molecular features have been generally accepted as minimum conditions for giving rise to liquid crystallinity in substances, but often even all of them together fail to endow substances with mesomorphic properties. However, since mesomorphism is an intermediate state of existence, all such substances should exhibit liquid crystallinity under favourable conditions. This would lead to the assumption that non-mesomorphic substances, which apparently satisfy the minimum conditions for the occurrence of mesophase, have transition points below their freezing points; naturally a search for their virtual transition temperatures thus acquires importance. An attempt has been made in this investigation to study binary mixtures of structurally similar components with a view to ascertain the transition temperatures of non-liquid crystalline substances by the method of extrapolation of transition curves in phase diagrams of such systems.

EXPERIMENTAL: PREPARATION OF COMPOUNDS

1) *p-Azoxyphenetole:p*-Nitrophenetole[1] was prepared by boiling under reflux for several hours one mole of *p*-nitrophenol in acetone to which some potassium carbonate was added, with one mole of diethyl sulphate. The reaction mixture was stirred by a magnetic stirrer. After the reaction was complete, the reaction mixture was poured into a large quantity of water when *p*-nitrophenetole separated as a white precipitate which on recrystallisation from alcohol gave white crystals, sharply melting at 59°C. A calculated quantity of *p*-nitrophenetole was mixed with requisite amount of sodium ethoxide. Some hydrazine hydrate was added at the same time. The reaction mixture was heated cautiously with constant stirring. After half an hour of heating, the mixture was diluted with water. *p*-Azoxyphenetole separated as yellow substance. It was recrystallised from alcohol. C–N.–137.0; N–L.–167.5°C.

2) *p-Azoxyanisole:* It was similarly prepared with proper starting materials and

recrystallised from alcohol. C–N.–118.0; N–L.–136.0°C.

3) *Schiff's bases:* The Schiff's bases were prepared by heating alcoholic solution of equimolar amounts of appropriate aldehyde and amine until reaction was complete. The products were isolated by distilling off the solvent. Recrystallised from suitable solvent, the fine crystals obtained melted sharply.

Method of study: The binary mixtures of varying compositions of Schiff's bases and a liquid crystalline substance, *p*-azoxyanisole or *p*-azoxyphenetole, were carefully prepared and studied by an optical method after Dave and Dewar.[2]

TABLE 1

Component A: *p*-Azoxyanisole (118-136°C) or *p*-Azoxyphenetole (137-167.5°C).
Mixed with Component B: Schiff's Bases (listed as below):

1.	p-Anisal-p-phenetidine	(128.4°C)
2.	p-Anisal-p-anisidine	(147.8°C)
3.	p-Anisal-p-toluidine	(92.0°C)
4.	p-Chlorobenzal-p-phenetidine	(121.0°C)
5.	p-Chlorobenzal-p-toluidine	(126.1°C)
6.	p-Dimethylaminobenzal-p-phenetidine	(147.5°C)
7.	p-Dimethylaminobenzal-p-anisidine	(140.7°C)
8.	p-Dimethylaminobenzal-p-toluidine	(120.2°C)
9.	p-Ethoxybenzal-p-anisidine	(122.3°C)
10.	p-Ethoxybenzal-p-toluidine	(94.9°C)

Twenty binary systems were investigated.

RESULTS AND DISCUSSION

Bogojawlensky and Winogrodow[3] deduced from their study of binary systems in which one component was a liquid crystal by itself that the second component, a non-liquid crystalline substance as such, would form a mesophase if the liquid was supercooled sufficiently and that the corresponding latent transition temperatures could be determined by extrapolation of the transition line. Walter[4] reported similar cases and stated that the hypothetical transition line obtained by joining two latent transition temperatures could be concurrent with a real one in binary mixtures of non-liquid crystalline substances. Dave and Dewar[2] ruled out any possibility of reliable extrapolation for they obtained different values for the latent transition temperatures for the same non-liquid crystalline substance depending whether *p*-azoxyanisole or *p*-azoxyphenetole was the liquid crystal component. Later Dave and Lohar[5] reported a case wherein extrapolation of the transition curve was found quite reliable for determining the latent transition temperature of a non-liquid substance. Lohar[6] has shown that the method is in fact reliable in cases of a number of Schiff's bases. Dewar and Goldberg[7] now report in a recent study that reliable extrapolation is possible

TABLE 2

Solid-liquid Transition Temperatures for the Binary systems *p*-Azoxyanisole and Schiff's Bases. The Eutectic Temperatures and Melting Points of Pure Components are Direct Experimental Values; The Other Temperatures are Read from the Phase Diagrams.

Sr. No.	Mole % *p*-Azoxyanisole (A)											Eutectic	
	0	10	20	30	40	50	60	70	80	90	100	Mole %A	Temp. °C.
1.	128.4	124.0	119.0	113.0	106.5	99.5	97.0	103.5	109.0	113.8	118.0	57.0	94.8
2.	147.8	143.0	138.3	113.1	127.7	121.6	114.5	105.8	111.4	115.0	118.0	70.3	105.7
3.	92.0	87.7	82.2	76.0	83.9	92.0	98.5	104.0	109.0	113.4	118.0	31.2	74.9
4.	121.0	116.7	112.3	107.2	101.4	91.3	97.6	104.6	110.5	115.2	118.0	52.8	91.8
5.	126.1	120.9	115.0	117.8	100.0	93.8	100.5	106.4	111.5	115.5	118.0	48.0	93.0
6.	147.5	142.5	137.5	132.1	126.2	119.2	111.0	103.5	109.5	114.5	118.0	67.7	101.9
7.	140.7	136.0	131.2	126.0	120.0	113.1	104.5	103.6	109.4	114.4	118.0	64.0	99.7
8.	120.2	114.4	108.0	101.2	93.1	93.2	99.2	104.9	110.0	114.4	118.0	44.0	89.5
9.	122.3	117.7	112.7	107.0	100.3	92.4	98.4	106.5	111.4	115.0	118.0	53.4	89.2
10.	94.9	90.5	85.9	81.4	79.7	91.9	99.3	105.0	109.9	114.0	118.0	38.7	77.4

TABLE 3

Isotropic Liquid-Nematic Liquid Transition Temperatures. The Values are Read from Phase Diagrams.

Sr. No.	Mole % *p*-Azoxyanisole (A)														Triple-point	
	0	10	20	30	40	50	60	70	75	80	85	90	95	100	Mole %A	Temp. °C
1.	(121.0)	(120.7)	121.0	121.8	122.8	124.1	125.5	127.4	128.5	130.0	131.4	133.0	134.5	136.0	16.7	120.7
2.	---	---	---	---	---	---	120.2	123.6	125.5	127.4	129.5	131.5	133.5	136.0	54.5	118.5
3.	---	---	---	---	(76.8)	(87.8)	(98.3)	108.0	113.0	118.0	122.9	127.0	131.5	136.0	61.2	99.5
4.	---	---	---	---	(97.0)	101.8	107.6	114.3	117.0	121.3	124.8	128.5	132.2	136.0	43.7	98.7
5.	---	---	---	---	---	---	---	---	---	(108.7)	115.5	122.2	129.0	136.0	83.2	113.0
6.	---	---	---	---	---	(110.5)	113.6	117.9	120.4	123.1	126.0	129.3	132.5	136.0	58.1	113.0
7.	---	---	---	---	---	(95.5)	(104.1)	112.5	116.5	120.6	124.7	128.5	132.4	136.0	60.0	104.5
8.	---	---	---	---	---	---	---	---	---	---	114.5	121.5	128.6	136.0	82.8	111.5
9.	(120.8)	121.1	121.6	122.3	123.0	124.0	125.5	127.4	128.4	129.5	130.7	132.3	134.0	136.0	3.5	120.8
10.	(76.1)	(79.0)	(83.0)	87.6	93.2	99.5	106.2	113.2	116.7	120.3	124.0	127.7	131.7	136.0	23.2	84.5

TABLE 4

Solid-Liquid Transition Temperatures for Binary Systems *p*-Azoxyphenetole and Schiff's Bases. The Eutectic Temperatures and Melting Points of Pure Components are Direct Experimentals Values; the Other Temperatures are Read from Phase Diagrams.

Sr. No.	Mole % *p*-Azoxyphenetole (A)											Eutectic	
	0	10	20	30	40	50	60	70	80	90	100	Mole %(A)	Temp. °C.
1.	128.4	124.5	120.0	115.0	109.0	107.5	113.4	119.3	125.2	131.0	137.0	45.7	104.8
2.	147.8	141.0	135.6	130.3	125.0	118.3	114.4	120.0	125.6	131.4	137.0	56.2	112.0
3.	92.0	86.1	80.7	88.0	97.9	106.0	113.0	119.6	125.5	131.3	137.0	22.5	79.0
4.	121.0	116.7	116.6	106.0	99.6	106.0	114.0	120.9	126.6	132.0	137.0	42.8	98.0
5.	126.1	120.5	114.2	107.4	103.9	110.0	115.7	121.5	126.9	132.0	137.0	37.5	101.8
6.	147.5	143.0	138.3	133.0	127.0	120.0	110.5	118.7	124.3	129.5	137.0	63.3	110.1
7.	140.7	135.4	130.0	124.8	119.6	114.4	110.0	117.7	124.5	130.9	137.0	59.5	109.4
8.	120.2	113.9	107.5	101.3	104.3	109.5	115.1	120.6	126.0	131.5	137.0	32.2	99.8
9.	122.3	118.0	113.5	109.0	104.6	109.5	116.2	122.5	128.3	133.0	137.0	42.0	103.9
10.	94.9	90.4	85.7	78.9	95.9	105.5	113.3	120.0	126.0	131.5	137.0	31.0	78.0

TABLE 5

Isotropic Liquid-Nematic Liquid Transition Temperatures. The Values are Read from Phase Diagrams.

Sr. No.	Mole % *p*-Azoxyphenetole (A)														Triple-point	
	0	10	20	30	40	50	60	70	75	80	85	90	95	100	Mole %A	Temp. °C
1.	(121.01)	124.8	129.5	134.2	133.9	143.6	148.4	153.0	155.4	157.7	160.0	162.5	164.8	167.5	9.5	124.5
2.	–––	–––	–––	–––	129.3	135.5	142.0	148.5	151.5	154.8	158.0	161.2	164.5	167.5	36.5	127.0
3.	–––	–––	–––	89.8	104.2	118.0	129.0	139.5	144.2	149.0	153.5	158.0	162.5	167.5	26.5	84.0
4.	–––	–––	(103.5)	113.0	121.9	130.0	137.6	145.4	149.0	152.7	156.2	159.5	163.7	167.5	25.4	108.7
5.	–––	–––	–––	–––	–––	–––	119.9	134.3	140.5	146.2	151.7	157.0	162.2	167.5	56.3	113.7
6.	–––	–––	–––	–––	129.4	136.4	143.0	148.6	151.5	154.2	157.0	160.0	163.3	167.5	38.2	128.0
7.	–––	–––	–––	–––	–––	124.6	133.8	142.4	146.5	150.6	154.7	158.5	162.5	167.5	43.2	118.0
8.	–––	–––	–––	–––	–––	–––	121.5	133.0	138.6	144.5	150.2	156.0	161.7	167.5	50.0	109.5
9.	(120.8)	125.5	130.2	134.8	139.5	144.1	159.0	153.5	156.0	158.2	160.6	163.0	165.4	167.5	1.8	121.6
10.	(76.1)	(87.5)	98.0	108.3	118.2	127.4	135.7	144.0	148.0	152.0	155.7	159.4	162.6	167.5	12.0	89.7

and that similar values for the same substance from its binary systems with different liquid crystal components can be obtained. In the present investigation we have two series of binary systems in which the liquid crystal component is either *p*-azoxyanisole (series I) or *p*-azoxyphenetole (series II) and the other component is a Schiff's base. Both the liquid crystaline substances comprising the component A of the series are very much themselves structurally similar and have great resemblance constitutionally to the Schiff's bases in general. The central group of the Schiff's bases differs from that of *p*-azoxyanisole or *p*-azoxyphenetole; but being common in both series of binary systems, its contribution can be neglected for all practical purposes. The only differences effective from system to system is the one of *p-p'*-substituted terminal groups which possess different polarity. Tables 2, 3, 4 and 5 record the melting points, transition points, eutectic points and triple points of the various mixed melts as read from the phase diagrams of the binary systems. Table 6 shows that the values for latent transition temperatures of Schiff's bases obtained by extrapolation of the transition curves in the phase diagrams of both the series of binary systems compare very well. In Table 6, series I and series II refer to binary systems of Schiff's bases with *p*-azoxyanisole and *p*-azoxyphenetole, respectively, as component A.

For both series, the extrapolated values for the first four Schiff's bases (Table 6) (Figures 1a, 1b, 2a, 2b, 3a, 3b and 4a, 4b) are mutually comparable. In all but two (system no. 2 Table 6; Figures 2a and 2b) of these phase diagrams, the eutectic point is in equilibrium with the nematic liquid phase; thus transition curves meet melting curves to the left of respective eutectic. These transition curves display

TABLE 6

Latent Transition Temperatures

		Extrapolated transition temperature in °C	
		Series I	Series II
1.	*p*-Anisal-*p*-anisidine	103.5	103.5
2.	*p*-Anisal-*p*-toluidine	39.0	39.0
3.	*p*-Chlorobenzal-*p*-phenetidine	80.7	83.3
4.	*p*-Dimethylaminobenzal-*p*-phenetidine	97.0	97.5
5.	*p*-Dimethylaminobenzal-*p*-anisidine	52.3	74.5
6.	*p*-Chlorobenzal-*p*-toluidine	–	–
7.	*p*-Dimethylaminobenzal-*p*-toluidine	–	–
8.	*p*-Ethoxybenzal-*p*-toluidine	(76.1)	(76.1)
9.	*p*-Anisal-*p*-phenetidine	(121.0)	(121.0)
10.	*p*-Ethoxybenzal-*p*-anisidine	(120.8)	(120.8)

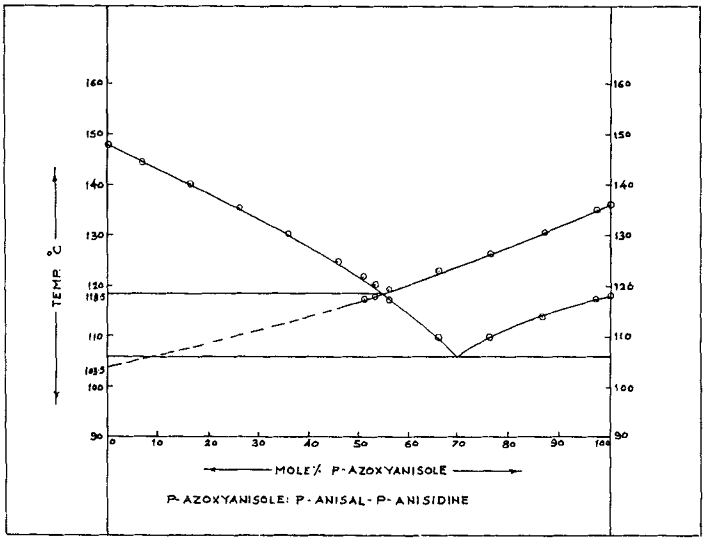

FIGURE 1a Extrapolated value of latent transition temperature for *p*-anisal-*p*-anisidine from its phase diagram with *p*-azoxyanisole as liquud crystal component.

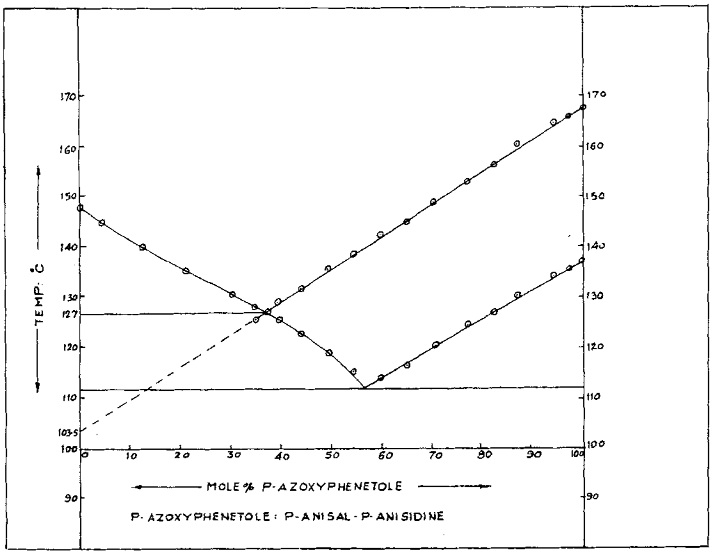

FIGURE 1b Extrapolated value of latent transition temperature for *p*-anisal-*p*-anisidine from its phase diagram with *p*-azoxyphenetole as liquid crystal component.

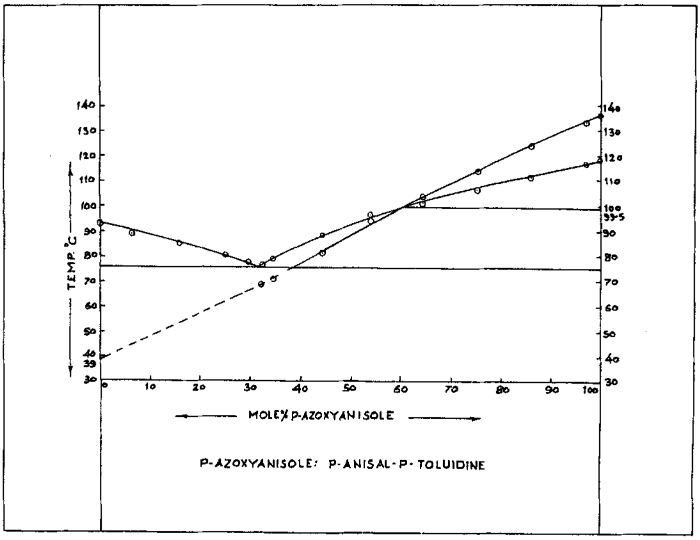

FIGURE 2a Extrapolated value of latent transition temperature for *p*-anisal-*p*-toluidine from its phase diagram with *p*-azoxyanisole as liquid crystal component.

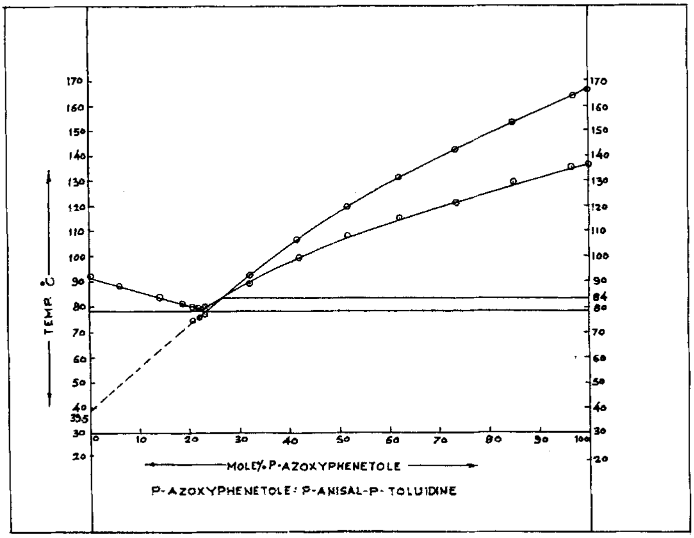

FIGURE 2b Extrapolated value of latent transition temperautere for *p*-anisal-*p*-toluidine from its phase diagram with *p*-azoxyphenetole as liquid crystal component.

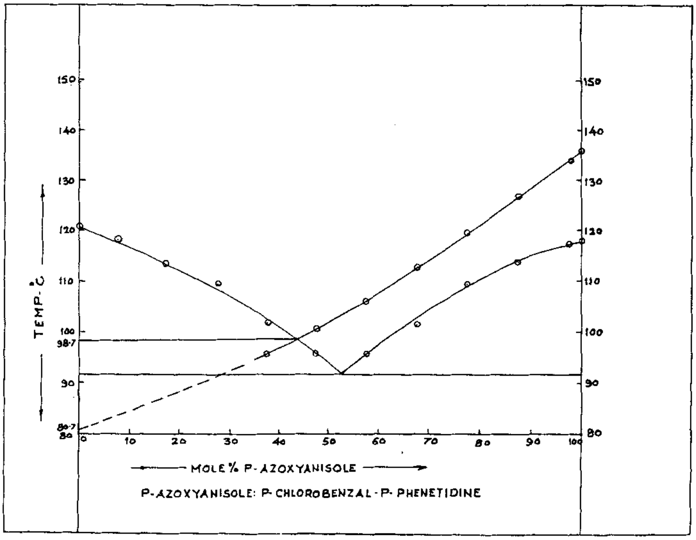

FIGURE 3a Extrapolated value of latent transition temperature for *p*-chlorobenzal-*p*-phenetidine from its phase diagram with *p*-azoxyanisole as liquid crystal component.

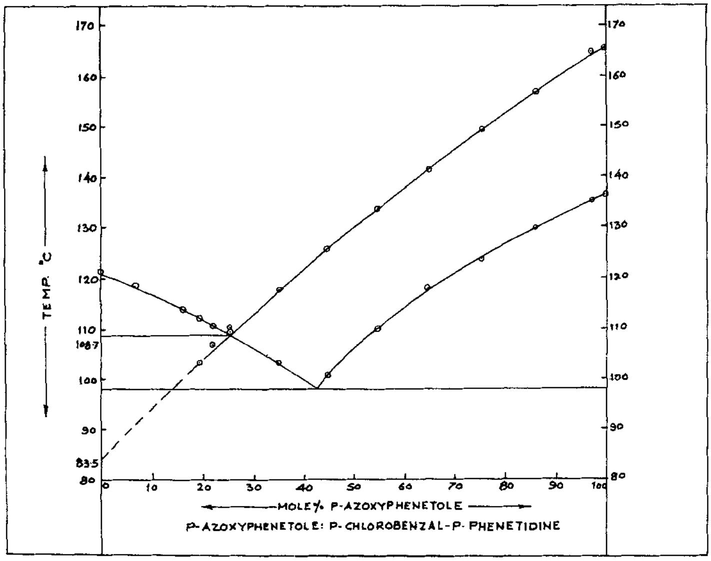

FIGURE 3b Extrapolated value of latent transition temperature for *p*-chlorobenzal-*p*-phenetidine from its phase diagram with *p*-azoxyphenetole as liquid crystal component.

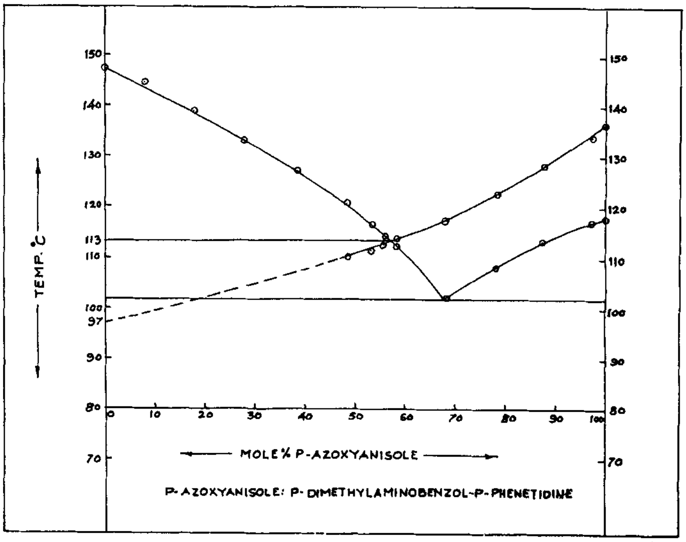

FIGURE 4a Extrapolated value of latent transition temperature for *p*-dimethylaminobenzal-*p*-phenetidine from its phase diagram with *p*-azoxyanisole as liquid crystal component.

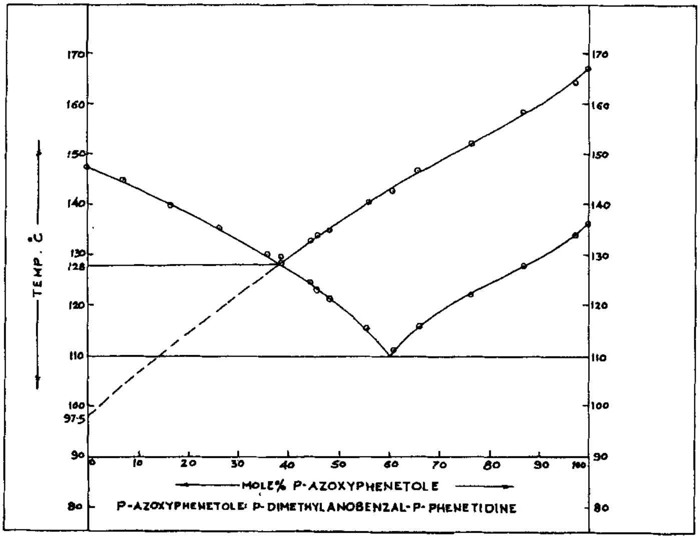

FIGURE 4b Extrapolated value of latent transition temperature for *p*-dimethylaminobenzal-*p*-phenetidine from its phase diagram with *p*-azoxyphenetole as liquid crystal component.

low slopes. Since the monotropic mesophase can be easily pursued further into the supercooled region, the transition curves could be smoothly extrapolated. Even in system No. 2 (Table 6) (Figs. 2a and 2b) where the eutectics are in equilibrium with the isotropic liquid, the metastable monotropic mesophase is easily pursued to a considerable extent, thus permitting smooth extrapolation. All these Schiff's bases possess sufficiently polar terminal groups. The effect of polarity on mixed liquid crystal formation is well known.[2,8] The higher the polarity of the terminal groups the lower is the slope of the transition curves. The lower the slope of the transition curves, the greater the possibility of the non-liquid crystalline substance to be potentially capable of showing mesomorphism under favourable conditions. The virtual transition temperatures of such substances would then be nearer to their melting points; if such a situation could be obtained, the extrapolation of transition curves could be surely more dependable. In case of *p*-dimethylaminobenzal-*p*-anisidine (Figures 5a and 5b), the extrapolated values differ widely. The eutectic points in both of these diagrams are in equilibrium with the nematic liquid. But while the monotropic nematic mesophase could be studied into the supercooled region up to 55 mole % of *p*-dimethylaminobenzal-*p*-anisidine in a mixture with *p*-azoxyanisole, which is approximately 13 mole % away from the triple point of the system, the same substance in *a* mixture with *p*-azoxyphenetole offers difficulty in studying monotropic anisotropy even a little beyond the triple point. Would it have been possible to pursue the monotropic nematic liquid property in both the binary systems considerably beyond the triple point, the extrapolation could have been more smooth and reliable. Then, the transition curves in the two corresponding phase diagrams might be expected to show bends leading to concurrent extrapolated values. In the case of *p*-chlorobenzal-*p*-toluidine and *p*-dimethylaminobenzal-*p*-toluidine (No. 6 and No. 7, Table 6), extrapolation is rendered difficult as the eutectics in both these phase diagrams happen to be in equilibrium with the isotropic liquid; consequently the transition curves meeting the melting curves considerably to the right of the eutectic. These transition curves are also very steep. No monotropic nematic mesophase could be seen on supercooling the mixed melts. Compounds with terminal groups (i.e. Cl, CH_3 and $N(CH_3)_2$) offer weak resistance to thermal breakdown of the forces of aligment on heating. Thus their mixture melt easily and the nematic property cannot persist beyond a certain minimum which is insufficient for extrapolation of the transition curves. Besides, the crystallizing tendency is so great that the mixed melts freeze before the monotropic nematic property could show up. As it is, extrapolation in such cases can be misleading to a great extent. Further, the last three Schiff's bases (Table 6) exhibit metastable monotropic nematic properties and the transition curves in these phase diagrams of their binary mixtures with *p*-azoxyanisole and *p*-azoxyphenetole could smoothly be extrapolated with concurrent values even if the monotropic nematic liquid behaviour is not pursued beyond a certain limit.

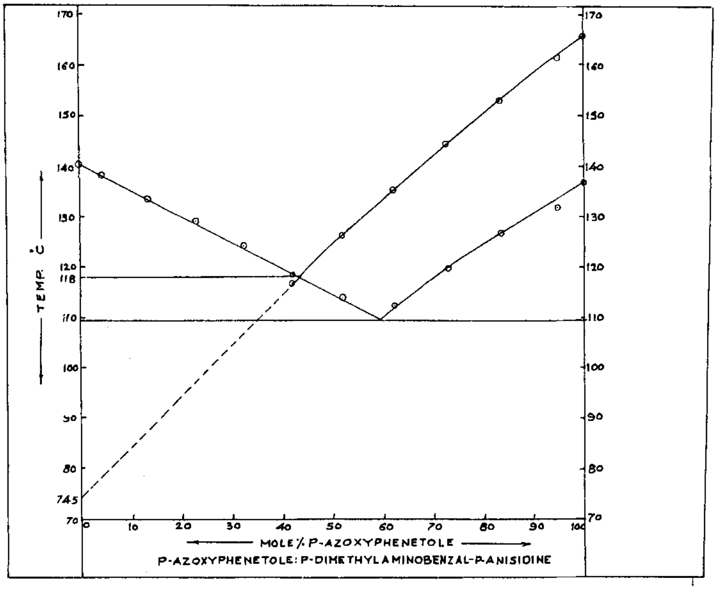

FIGURE 5a Extrapolated value of latent transition temperature for *p*-dimethylamino-benzal-*p*-anisidine from its phase diagram with *p*-azoxyanisole as liquid crystal component.

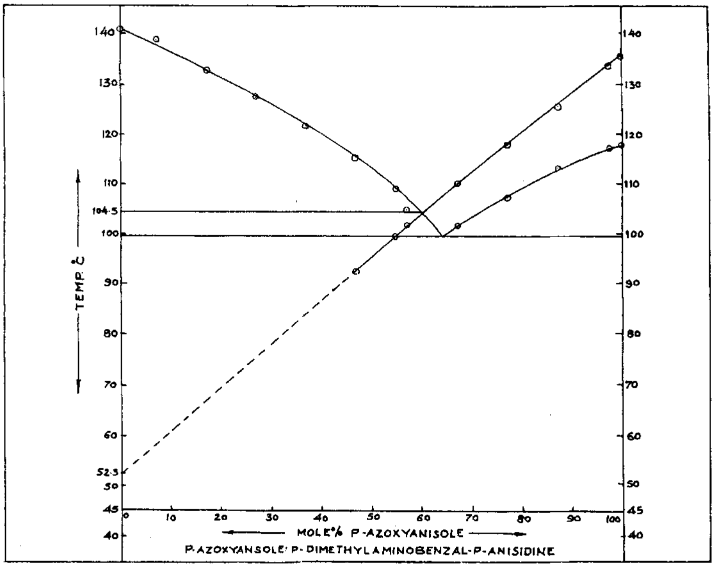

FIGURE 5b Extrapolated value of latent transition temperature for *p*-dimethylamino-benzal-*p*anisidine from its phase diagram with *p*-azoxyphenetole as liquid crystal component.

All three Schiff's bases possess end groups whose polarity seems to be sufficient to offer resistance to the forces of breakdown on heating, and to endow the pure melts of these Schiff's bases with enough lateral forces to keep aligment intact.

From the above discussion, we can fairly conclude that the extrapolation method for determining the latent transition temperatures of non-liquid crystalline substances can be quite dependable when the non-liquid crystalline substances are structurally similar to the liquid crystalline substance concerned and possess sufficiently polar terminal groups. In such binary systems the transition curves follow the law of mixtures ideally and the eutectic points are generally in equilibrium with anisotropic liquid. Even in binary systems where the transition curves are not straight and deviate somewhat from the ideality of mixtures and, also where eutectic points are not in equilibrium with the nematic liquid, the extrapolation method is dependable provided monotropic liquid crystallinity can be pursued to an extent which would assure the smooth trend of the bend in transition curves.

Incidentally, the present study supports some of the conclusions drawn in earleir studies.[2,8] The initial slopes of the transition curves given in Table 7 have been deduced for the various Schiff's bases from their phase diagrams of both series of binary systems.

In the present study Schiff's base No. 2, series II (Table 7), which has OCH_3 as the terminal group at both ends, is selected for calculating the "group slope" value for the OCH_3 group. The initial slope for this system in series II is 6,

TABLE 7

Initial Slopes of the Transition Curves (°C./mole %) × 10.

		I[a]	II[b]	III[c]
1. $OCH_3 \cdot C_6H_4 \cdot CH$	$= N \cdot C_6H_4 \cdot OC_2H_5$	3.0	4.5	3.0
2. $OCH_3 \cdot C_6H_4 \cdot CH$	$= N \cdot C_6H_4 \cdot OCH_3$	4.2	6.0	4.0
3. $OCH_3 \cdot C_6H_4 \cdot CH$	$= N \cdot C_6H_4 \cdot CH_3$	9.0	9.5	9.2
4. $Cl \cdot C_6H_4 \cdot CH$	$= N \cdot C_6H_4 \cdot OC_2H_5$	7.8	8.0	8.0
5. $Cl \cdot C_6H_4 \cdot CH$	$= N \cdot C_6H_4 \cdot CH_3$	13.8	10.5	14.2
6. $(CH_3)_2N \cdot C_6H_4 \cdot CH$	$= N \cdot C_6H_4 \cdot OC_2H_5$	6.5	7.0	6.5
7. $(CH_3)_2N \cdot C_6H_4 \cdot CH$	$= N \cdot C_6H_4 \cdot OCH_3$	7.5	8.5	7.5
8. $(CH_3)_2N \cdot C_6H_4 \cdot CH$	$= N \cdot C_6H_4 \cdot CH_3$	12.5	11.8	12.7
9. $OC_2H_5 \cdot C_6H_4 \cdot CH$	$= N \cdot C_6H_4OCH_3$	3.5	4.5	3.0
10. $OC_2H_5 \cdot C_6H_4 \cdot CH$	$= N \cdot C_6H_4 \cdot CH_3$	8.0	8.0	8.2

[a] I: Initial slopes of the transition curves for the Schiff's bases from the binary systems with *p*-azoxyanisole as the liquid crystalline component.

[b] II: Initial slopes of the transition curves for Schiff's bases from the binary systems with *p*-azoxyphenetole as the liquid crystalline component.

[c] III: Hypothetical slopes of the transition curves for the Schiff's bases calculated on the additive effect of the terminal polar groups, worked out from earlier studies.[2,8]

therefore, the group slope value for OCH_3 comes to be 3. On this basis other group slopes are calculated. On the whole, the values for series I are comparable with those of series II. There is a noticeable variation in the case of system No. 5 in series II, which may be due to experimental error. A normal expectation that *p*-azoxyphenetole, with end groups more polar than those of *p*-azoxyanisole, should be more effective in arriving at the initial slope value with greater ease is quite logical. But that this is not so may be attributed to the high transition points. The advantage offered by end groups of high polarity seems to be balanced by the increase of transition and melting points.

The effect of polar groups has been found to be additive.[8] That the present study supports this view is evident from the difference values obtained from the series of binary systems with one common group at one end and a different group at the other end in the case of both series of binary systems. The additive[8] effect of the polar group in such binary systems is also very clearly borne out in Table 8.

The difference values in series I are comparable with those arrived at in an earlier study[8]; the values for series II, although slightly varying from those of series I, are quite consistent. 'Group slope' values arrived at in the present study for both series of systems are given in Table 9. This order is the order of decreasing

TABLE 8

Additive Effect of Polar Groups: Difference Values.

	Series I			Series II		
	OCH_3	OC_2H_5	$N(CH_3)_2$	OCH_3	OC_2H_5	$N(CH_3)_2$
CH_3	9.0	8.0	12.5	9.5	8.0	11.8
OCH_3	4.2	3.0	7.5	6.0	4.5	8.5
Difference	4.8	5.0	5.0	3.5	3.5	3.3
	OCH_3	$N(CH_3)_2$	Cl	OCH_3	$N(CH_3)_2$	Cl
CH_3	9.0	12.5	13.8	9.5	11.8	--
OC_2H_5	3.0	6.5	7.8	4.5	7.0	--
Difference	6.0	6.0	6.0	5.0	4.8	--
	OCH_3	$N(CH_3)_2$		OCH_3	$N(CH_3)_2$	
OCH_3	4.2	7.5		6.0	8.5	
OC_2H_5	3.0	6.5		4.5	8.0	
Difference	1.2	1.0		1.5	0.5	

TABLE 9

Order of 'Group Slopes' and 'Group Efficiency'.

	OC_2H_5 >	OCH_3 >	$N(CH_3)_2$ >	CH_3	=	Cl
Series I	0.9	2.1	5.4	7.1		6.9
Series II	1.5	3.0	5.5	6.5		7.3

polarity of the groups regardless of sign. The main factor thus is the magnitude of the group dipole and not its direction.[2]

These values are not only mutually comparable but hold good when compared with those obtained in earlier studies.[4,8]

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