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LIQUID CRYSTALS

III. 4,4'-DI-*n*-ALKOXYAZOXYBENZENES AND THEIR MIXTURES AS STATIONARY LIQUID PHASES IN GAS-LIQUID CHROMATOGRAPHY*,**

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SUMMARY

The 4,4'-di-*n*-alkoxyazoxybenzene (I) homologs in which the alkyl group is methyl, ethyl, *n*-butyl and *n*-hexyl and mixtures of these compounds have been studied as stationary phases in gas-liquid chromatography. The nematic mesophases of the materials are selective toward solutes on the basis of molecular shape. Specifically, they effect good separations of close-boiling *meta*- and *para*-disubstituted benzene isomers, the more linear *para* isomer being eluted last. The results support earlier evidence that the use of nematic mixtures is a promising approach to maximum selectivity of this type because it makes lower operating temperatures possible. Previously unreported phase diagrams of four binary systems of homologs of I and criteria for choosing components of highly selective nematic mixtures are presented.

INTRODUCTION

The liquid crystalline (mesomorphic) state[1,2] is a state of matter intermediate between crystalline solids and isotropic liquids. The phenomenon is exhibited by certain compounds having relatively rigid, rodshaped, polar molecules that tend to be oriented with their long axes parallel due to mutual attractive forces. When such a substance is heated, the crystalline solid melts to an anisotropic liquid (a mesophase) in which adjoining molecules lie parallel to one another. At a higher temperature, the melt undergoes transition to "normal" isotropic liquid. Two common varieties of liquid crystals are the nematic and smectic types. Whereas nematic mesophases have only the parallel molecular arrangement, the molecules in smectic liquids are additionally constrained to be arranged in layers with their

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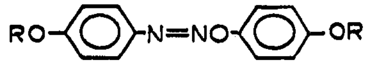
long axes more or less perpendicular to the layer planes. A third type, cholesteric or twisted nematic, is related in molecular organization to the nematic type. Compounds that exhibit cholesteric mesomorphism are always optically active.

Liquid crystals are of interest as solvents because of their anisotropic nature. Among the solvent applications that have been studied is their use as stationary liquid phases in gas–liquid chromatography (GLC)[3]. 4,4′-Di-*n*-alkoxyazoxybenzenes (I) were some of the first liquid crystalline



Ia, R = CH_3; Ib, R = C_2H_5; Ic, R = n-C_4H_9; Id, R = n-C_6H_{13}.

compounds to be investigated in this regard. The nematic mesophases of the methyl (Ia),[4–11] ethyl (Ib)[5,7,9,10,12,13] and *n*-hexyl (Id)[6,8,10,11,14] homologs were found to be selective toward solutes on the basis of molecular shape. *E.g.*, close-boiling *meta* and *para* isomers of disubstituted benzenes are separated readily, the more linear *para* isomer invariably being eluted last.

Thermodynamic studies[4,5,9,14,15] provide an explanation of this behavior. The enthalpy and entropy of solution in the mesophase are lower for the *para* isomer, indicating, respectively, stronger solvent–solute interactions and a better ordered solution state compared to the *meta* isomer. This is consistent with the relatively linear *para*-substituted molecules fitting more readily into, and, therefore, interacting more strongly with, the parallel molecular arrangement of the nematic solvent. In GLC, proceeding from the completely disordered vapor (similar for both isomers) to the ordered solution state, the *para*-substituted molecule sacrifices more translational rotational freedom, but its favorable geometry allows stronger interaction with the mesophase. On balance, the entropy loss is overcome by the enthalpy difference and the *para* isomer is more soluble than the *meta* isomer[15].

An inherent limitation of a mesophase in practical applications is its restricted temperature range. Depressing the lower limit of the range is particularly desirable. In GLC, the selectivity of a nematic stationary phase toward solutes on the basis of molecular shape increases with decreasing temperature[5–7,10]. In other applications that depend on nematic liquids, such as optical devices[16] and NMR spectrometry in nematic solvents[17], the stable existence of the mesophase at or near room temperature is advantageous.

The use of mixtures is a convenient means of obtaining nematic mesophases that are stable at relatively low temperatures[18]. Like other crystalline solids, a nematogenic compound undergoes melting point depression on addition of a substance with which it is miscible. A mixed nematic mesophase originating at a lower temperature is the result. If the molecular structure of the added substance is similar to that of the nematogenic compound, there is little disruption of the nematic mesophase, which may persist to a high concentration of the second component. In particular, if the added substance is also nematogenic, the mixed system often exhibits nematic mesomorphism at all compositions.

Mixtures of 4,4′-di-*n*-alkoxyazoxybenzene (I) homologs are examples of such compatible nematic blends. The phase diagrams of the systems Ia–Ib[19,20], Ia–Id[10] and eight others containing higher homologs of I (n-C_7H_{15} through n-$C_{12}H_{25}$)[20,21] have been determined. In every instance, the system exhibits mesomorphism at all compositions but, for mixtures of the higher homologs, this is predominantly or entirely smectic. Therefore, the blends of the lower homologs are best suited for a study of mixed nematic mesophases. The systems Ia–Ib[7,10] and Ia–Id[8,10] were investigated earlier as stationary liquid phases in GLC. Nematic mixtures were obtained that can be used at relatively low temperatures and display high selectivity toward *meta*- and *para*-disubstituted benzene isomers. In this paper, comparable data (including phase diagrams) for the systems Ia–Ic, Ib–Ic, Ib–Id and Ic–Id are presented and the results for all binary systems based on Ia, Ib, Ic and Id are discussed.

EXPERIMENTAL

Materials

Three of the homologs of I (Ia, Ib and Id) were commercial products. The Ia and Ib were recrystallized from benzene before use; the Id was pure as received. 4,4'-Di-*n*-butoxyazoxybenzene (Ic) was synthesized. 4-*n*-Butyloxynitrobenzene, prepared from *p*-nitrophenol (0.10 mole) and *n*-butyl bromide (0.16 mole) by a modified Williamson reaction[22], was reduced to Ic with $LiAlH_4$[23]. The crude product (60 % yield based on *p*-nitrophenol) was recrystallized from 95 % ethanol. The transition temperatures of the pure materials are given in Table I.

TABLE I

TRANSITION TEMPERATURES OF SOME HOMOLOGS OF 4,4'-DI-*n*-ALKOXYAZOXYBENZENE

Ia = 4,4'-di-methoxyazoxybenzene; Ib = 4,4'-di-ethoxyazoxybenzene; Ic = 4,4'-di-*n*-butoxyazoxybenzene; Id = 4,4'-di-*n*-hexoxyazoxybenzene. Literature values are given between parentheses.

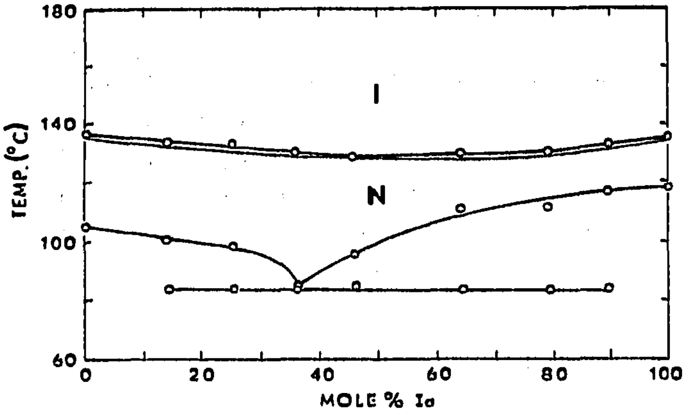
Compound	*Solid–nematic (°C)*		*Nematic–isotropic (°C)*	
Ia	119.5	(118.5)[a]	135	(135)[a]
Ib	138.5	(138.5)[b]	169.5	(168)[b]
Ic	104.5	(105)[c]	136	(136.5)[c]
Id	81	(81)[d]	129	(127)[d]

[a] Refs. 24, 25.
[b] Ref. 26.
[c] Ref. 27.
[d] Ref. 28.

The GLC solutes were commercial products which were not purified further. No major contaminants were observed in their chromatograms.

Procedure and apparatus

The experimental methods were, in general, the same as those described earlier[8,10,20]. Mixtures for determining the phase diagrams (Figs. 1–4) were prepared by weighing the components accurately into a small beaker, melting, and cooling the liquid with stirring until solidification occurred. Phase transition temperatures of the pure compounds and mixtures were measured with a calibrated Nalge-Axelrod hot-stage polarizing microscope. The heating rate was *ca.* 0.5°/min while observing the transitions.



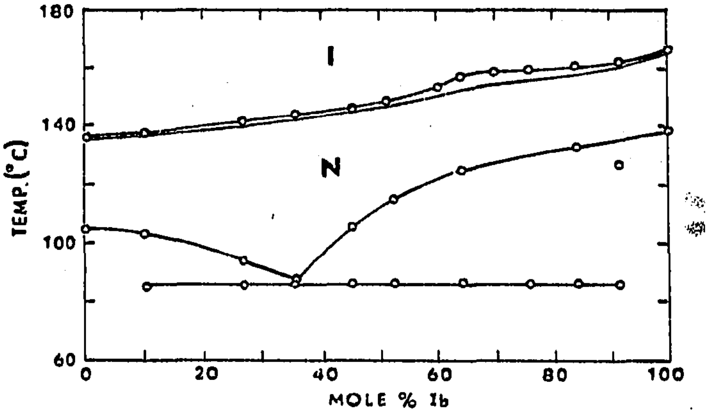
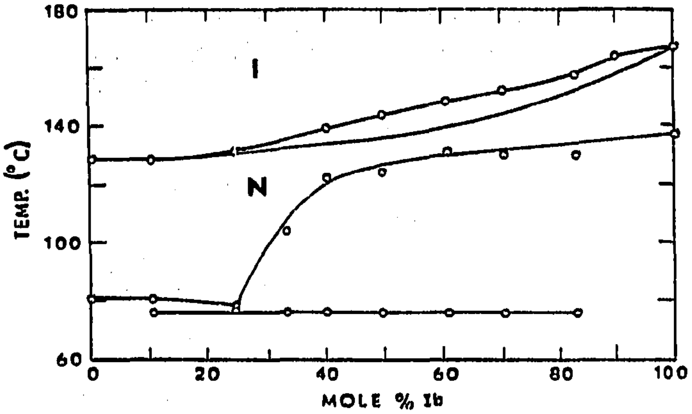


Fig. 1. Phase diagram of system 4,4'-dimethoxyazoxybenzene (Ia)–4,4'-di-*n*-butoxyazoxybenzene (Ic). I = isotropic, N = nematic.

Fig. 2. Phase diagram of system 4,4'-diethoxyazoxybenzene (Ib)–4,4'-di-*n*-butoxyazoxybenzene (Ic). I = isotropic, N = nematic.



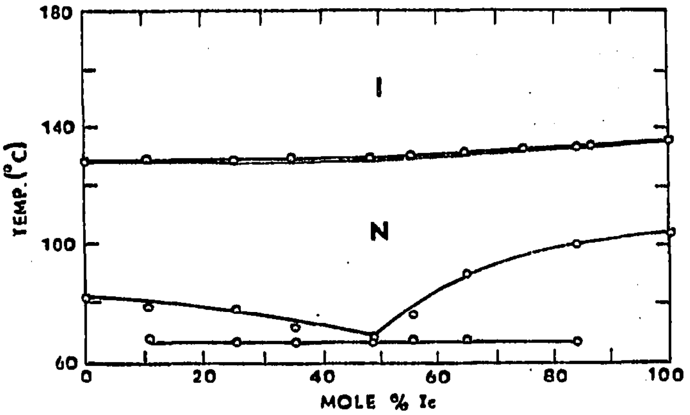
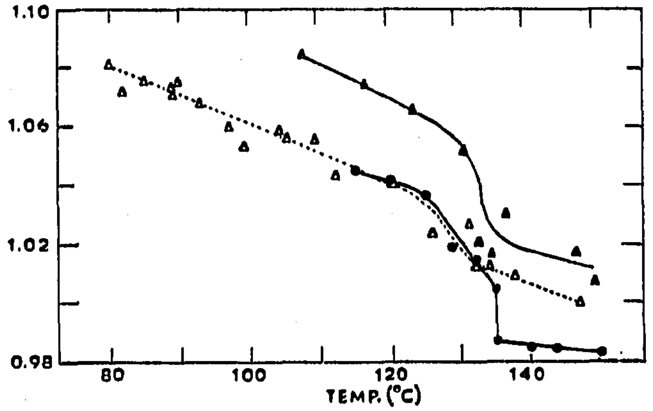


Fig. 3. Phase diagram of system 4,4'-diethoxyazoxybenzene (Ib)–4,4'-di-*n*-hexoxyazoxybenzene (Id). I = isotropic, N = nematic.

Fig. 4. Phase diagram of system 4,4'-di-*n*-butoxyazoxybenzene (Ic)–4,4'-di-*n*-hexoxyazoxybenzene (Id). I = isotropic, N = nematic.

Gas–liquid chromatograms were obtained with an Aerograph Hy-Fi gas chromatograph, Model No. 600-D, using nitrogen as carrier gas (flow-rate *ca.* 20 ml/min) and a flame ionization detector. The injection chamber was at 250° and the sample size was 0.4 μl of a 1 % solution in CS_2 for all runs. (Small sample size minimizes disruptive solute effects on mesomorphic stationary liquid phases.) The GLC columns were made from 3.2 mm O.D., 1.8 mm I.D. annealed copper tubing and were 5 m in length. The tubing was washed with CH_2Cl_2 to remove oil before packing. The column packings contained 15 wt. % of stationary liquid phase deposited on the solid support, Chromosorb W (60–80 mesh), from solution in CH_2Cl_2. The columns were conditioned at 15° above the nematic–isotropic (N–I) transition temperature of the stationary liquid phase for 1–2 h before use.

Retention times (t_R) of the solutes were determined first at a column temperature well above the N–I transition point of the stationary phase and then at successively lower temperatures until crystallization of the phase occurred as signaled by a drop in t_R. Relative retentions (α) were calculated from t_R values corrected for column dead space by subtracting the t_R for methane under the same conditions. Within the precision of our measurements, methane is not absorbed by the relatively polar homologs of I of this study. Usually, the α values (Figs. 5–8) were reproducible to a precision of ± 0.5 % in successive runs. However, in plotting α *vs.* temperature,



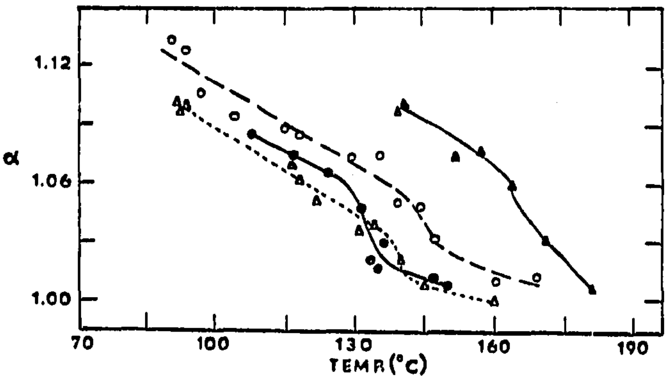
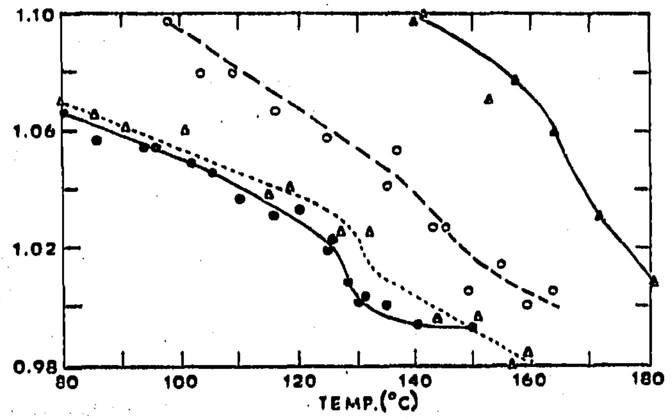


Fig. 5. Variation of relative retention (α) of *p*-xylene (*m*-xylene = 1.00) with temperature using Ia, Ic and the Ia–Ic eutectic mixture as stationary liquid phases. ●—●, Ia; ▲—▲, Ic; △- - -△, eutectic (36 mole % Ia).

Fig. 6. Variation of relative retention (α) of *p*-xylene (*m*-xylene = 1.00) with temperature using Ib, Ic and their mixtures as stationary liquid phases. ▲—▲, Ib; ●—●, Ic; △- - -△, eutectic (34 mole % Ib); ○ — — ○, 55 mole % Ib.



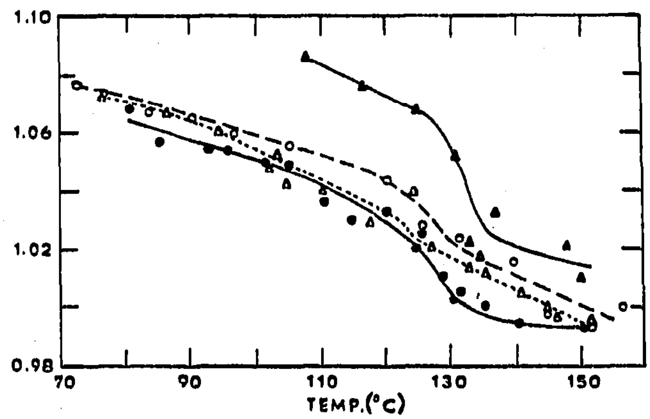


Fig. 7. Variation of relative retention (α) of *p*-xylene (*m*-xylene = 1.00) with temperature using Ib, Id and their mixtures as stationary liquid phases. ▲—▲, Ib; ●—●, Id; △- - -△, eutectic (22 mole % Ib); ○ — — ○, 64 mole% Ib.

Fig. 8. Variation of relative retention (α) of *p*-xylene (*m*-xylene = 1.00) with temperature using Ic, Id and their mixtures as stationary liquid phases. ▲—▲, Ic; ●—● Id; △- - -△, eutectic (48 mole % Ic); ○ — — ○, 55 mole % Ic.

a number of points fell far away from what was obviously the general trend of the data. Because they are confusing, these "sports" have been omitted from Figs. 5–8. While we must confess to some uneasiness at their appearance and our inability to explain them, it should be stressed that an overwhelming majority of the data points gave meaningful α *vs.* temperature correlations.

RESULTS AND DISCUSSION

The phase diagrams of the systems Ia–Ic, Ib–Ic, Ib–Id and Ic–Id are presented in Figs. 1–4. When these are considered along with the previously determined diagrams for Ia–Ib[10,29] and Ia–Id,[10] it is seen that all six systems exhibit nematic mesomorphism at all compositions and a eutectic composition that melts below either pure component. The principal variation between diagrams is in the shape of the nematic–isotropic transition curve. This is strongly concave upward for the system Ia–Id, almost linear for Ia–Ib and Ic–Id, and slightly concave for the other three systems. These results are consistent with the supposition[10,30,31] that concavity reflects disruption of the mixed mesophase. Thus disruption appears to be greatest when the components are relatively dissimilar structurally (Ia–Id), and least when they are similar (Ia–Ib and Ic–Id). Further support of this view is provided by data for binary mixtures of higher homologs of I. The N–I transition curves for C_4–C_{12} and C_2–C_8 mixtures are highly concave, those for C_4–C_8 and C_8–C_{12} are less so, while the curves for C_8–C_9 and C_8–C_{10} are linear[29]. Another factor that seems to play a role is the stabilizing effect on a mixed mesophase of a component that exhibits a very stable nematic mesophase as a pure compound[10]. The N–I transition temperature is a reasonable measure of mesophase stability. For the compounds under consideration here, the stability order based on this criterion is Ib$>$Ic$>$Ia$>$Id, and the three systems containing Ib display N–I transition curves that are, at most, only slightly concave. Also, there is a maximum in the Ib–Ic N–I curve at *ca.* 65 mole percent Ib and the hint of two maxima at *ca.* 65 and 90 mole percent Ib in the Ib–Id curve. This "buttressing" effect on nematic mesophase stability in mixtures at certain compositions has been observed before[29,32]. It was attributed to enhanced intermolecular attraction at these specific compositions resulting from optimum geometric arrangements of the parallel molecules. It is not illogical that such buttressing should be accomplished best by a component like Ib with a proven ability to exert strong intermolecular attractive forces, *i.e.*, one that exhibits a highly stable nematic mesophase as a pure compound.

If the selective affinity of nematic solvents toward linear, rodlike solute molecules is, as it appears to be, the result of a steric discrimination by the parallel molecular alignment in the mesophase, the regularity of that alignment should influence the degree of selectivity. Based on these premises, the relative molecular order in several nematic mesophases as a function of temperature has been estimated, using the difficult separation of *meta-* and *para*-xylene by GLC as the experimental criterion[10]. A convenient way to present the data is to plot relative retention (α) of *p*-xylene (*m*-xylene = 1.00) against temperature. Plots of this type for several compositions of the systems Ia–Ic, Ib–Ic, Ib–Id and Ic–Id, including the pure components and eutectic mixtures, are presented in Figs. 5–8. The selectivities of the various stationary liquid phases were determined at temperatures ranging from above the N–I transition point downward until crystallization occurred.

When these figures are considered together with analogous plots for Ia–Ib and Ia–Id[10], several conclusions may be drawn. At a given temperature, the selectivities of the nematic mesophases of the pure components are in the order Ib$>$Ic$>$Ia$>$Id. (It is necessary to extrapolate the Ib curve for this comparison.) This order is the same as that of their N–I transition temperatures, suggesting that both parameters are measures of molecular regularity in the mesophase. However, the data for Ia and Ic indicate that the N–I transition temperature is only a rough indicator of molecular order. Although the transition points of these compounds are almost identical (135° and 136°), Ic is far more selective. Ia is unique in this group of substances in two respects: it is the lowest member of the homologous series and the only one of the four with an odd number of carbon atoms in the alkyl moiety. Other odd-numbered homologs should be studied to see if they, too, are poorly selective relative to even-numbered homologs with comparable N–I transition points.

In all of the plots, α increases gradually on cooling the isotropic liquid, which may be due, in part, to the increasing difference between the vapor pressures of *m*- and *p*-xylene with decreasing temperature[33]. However, it is also consistent with the development of some nematic molecular order in the stationary phase above the usually assigned N–I transition point[34]. This must certainly be the explanation of the high selectivity ($\alpha = 1.03$) displayed by Ib just above its N–I transition temperature (Figs. 6 and 7).

On further cooling, there is a rapid increase in α at the transition point as the nematic mesophase forms and displays a strong preference for the *para* isomer. Below the transition temperature, α continues to increase with cooling until the nematic liquid crystallizes. Thus, the value of α is maximal at the lowest possible operating temperature. From a practical standpoint, this $\alpha_{max.}$ value is optimum and it is a convenient parameter for comparison of the various nematic stationary phases in terms of maximum selectivity and molecular order. In Table II, the mesophases that were studied in this work and in ref. 10 are listed with their compositions, $\alpha_{max.}$ values, and the temperatures at which these values were obtained.

TABLE II

MAXIMUM VALUES OF α FOR *p*-XYLENE (*m*-XYLENE = 1.00) OBTAINED WITH NEMATIC STATIONARY LIQUID PHASES IN GLC

Stationary liquid phase	*Column temp.* (°C)	$\alpha_{max.}$
Ib–Ic (55 mole % Ib)	90	1.13
Ib–Ia (40 mole % Ib; eutectic)[a]	90 (99)[b]	1.11 (1.10)[b]
Ib–Ic (34 mole % Ib; eutectic)	92	1.10
Ib[a]	140 (140)[b]	1.10 (1.09)[b]
Ib–Id (64 mole % Ib)	98	1.10
Ic	108	1.085
Ic–Ia (64 mole % Ic; eutectic)	80	1.08
Ic–Id (55 mole % Ic)	72	1.08
Ib–Id (22 mole % Ib; eutectic)	79	1.07
Ic–Id (48 mole % Ic; eutectic)	76	1.07
Id[a]	80	1.07
Id–Ia (73 mole % Id; eutectic)[a]	70	1.07
Id–Ia (66 mole % Id)[a]	80	1.06
Id–Ia (39 mole % Id)[a]	86	1.05
Ia[a]	115 (119)[b]	1.04 (1.04)[b]
Id–Ia (18 mole % Id)[a]	110	1.03

[a] Ref. 10.

[b] Values reported by KELKER *et al.*[7].

It should be stressed that the separation of *m*- and *p*-xylene by GLC is a classically difficult one so that α values greater than 1.05 are outstanding. On this basis, most of the stationary phases in Table II can be classified as highly selective and several are exceptionally so. The $\alpha_{max.}$ values of the pure homologs are in the order Ib>Ic>Id>Ia (the positions of Ia and Id are reversed relative to the order for α determined at a given temperature because the minimum operating temperature for Id is so much lower: 80° *vs.* 115°). On examining the table further, one sees that the order in which the pure components contribute to the selectivities of the mixed mesophases is also Ib>Ic>Id>Ia. *I.e.*, Ib mixtures have, in general, higher $\alpha_{max.}$ values than Ic mixtures, etc. Also, in the systems for which several mixed compositions were studied, selectivity increases with increasing concentration of the more selective component. Similarly, the Ic–Ia eutectic mixture, which has a high content of Ic, is very selective ($\alpha_{max.}$ = 1.08). These results negate the rule of thumb that the eutectic composition is likely to be the most selective mixture in a binary nematic system since it has the lowest melting point[10]. Apparently, a balance must be struck between the molecular ordering effects of the more selective component and of the minimum operating temperature in order to achieve maximum selectivity. *E.g.*, it seems probable that Ib–Ia mixtures rich in Ib, which have not been studied, would display higher selectivity than the eutectic composition.

The data in Table II further show that nematic mixtures of homologs of I are most selective when the pure components are highly selective and have alkyl groups of comparable length. Thus Ib–Ic and Ib–Ia mixtures have the highest $\alpha_{max.}$ values in the table. Even when the alkyl groups differ considerably in length, as in Ib–Id mixtures, performance is excellent if one component is highly selective and present in high concentration.

Having established the selectivities of these nematic stationary phases toward *m*- and *p*-xylene, their effectiveness in the separation of other close-boiling *meta*–*para* isomer pairs was determined. The data are summarized in Table III along with results for a silicone stationary phase for comparison. The nematic phases are arranged in the same order as in Table II, *i.e.*, descending order of effectiveness in separating *m*- and *p*-xylene, and it is seen that the relative retentions follow a general trend in the same direction in Table III also. All of the nematic liquids are highly selective (α values 1.09–1.28).

CONCLUSION

The use of nematic mixtures appears to be a promising route to stationary liquid phases that are highly selective toward solutes on the basis of molecular shape. The results for homologs of I suggest the following guidelines for choosing components for such "superselective" mixtures:

(1) At least one component (A) should exhibit a very stable nematic mesophase (have a high N–I transition point).

(2) The other component(s) should be compatible with A in the sense that the mixture also has a very stable, well ordered nematic mesophase.

(3) Ideally, the mixture should have a high concentration of A and a low freezing point. In these circumstances, advantage may be taken of the molecular ordering effects of both A and low temperature.

TABLE III

VALUES OF α FOR *p*-ETHYLTOLUENE, *p*-DICHLOROBENZENE AND *p*-METHYLANISOLE (*meta* ISOMER = 1.00) ON NEMATIC STATIONARY LIQUID PHASES

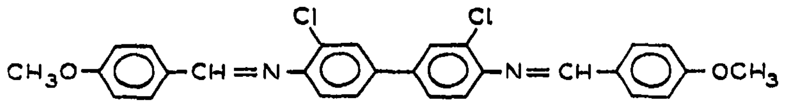
Stationary liquid phase	*Column temp.* (°C)[a]	α		
		p-EtC_6H_4Me	p-ClC_6H_4Cl	p-$MeOC_6H_4Me$
Ib–Ic (55 mole % Ib)	90	1.17	1.22	1.21
Ib–Ia (40 mole % Ib)[b]	100	1.18[c]	1.28	1.23
Ib–Ic (34 mole % Ib)	92	1.19	1.25	1.19
Ib[b]	141	1.15	1.26	1.18
Ic	108	1.12	1.18	1.14
Ic–Ia (64 mole % Ic)	96	1.12	1.22	1.15
Ic–Id (55 mole % Ic)	87	1.11	1.14	1.14
Ib–Id (22 mole % Ib)	86	1.11	1.15	1.15
Ic–Id (48 mole % Ic)	94	1.10	1.15	1.14
Id[b]	85	1.09	1.11	1.13
Id–Ia (73 mole % Id)[b]	75	1.11	1.17	1.16
Ia[b]	120	1.09	1.17	1.12
SE-30 Silicone	100	1.01	1.04	1.02

[a] For the mesomorphic stationary phases, the column temperature is in the lower part of the nematic range.

[b] Ref. 10.

[c] KELKER *et al.*[7] reported the same α value at 99°.

Criterion (1) is easy to apply, but at the present state of knowledge, criteria (2) and (3) require an empirical, trial-and-error approach. *E.g.*, the anil II (N–I transition point 363°) is obviously a likely choice for component A. However, its compatibility with the structurally dissimilar Ia (the N–I transition curve for this binary system is convex upward) and the very low operating temperature of the eutectic composition (60°) were not anticipated[10]. Ternary, quaternary or even more complex mixtures are attractive in that one can imagine relatively small amounts of several components disrupting the crystalline lattice of A, and thus lowering the melting point substantially, while being quite compatible with A in the mesophase.



(II)

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