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MECHANISM OF GAS–LIQUID CHROMATOGRAPHIC SEPARATION OF DISUBSTITUTED BENZENE ISOMERS USING NEMATIC LIQUID PHASES

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SUMMARY

From measurement and analysis of specific retention volumes of four pairs of *meta* and *para* isomers at four well controlled temperatures in the liquid-crystalline stationary phase *p,p'*-dihexoxyazoxybenzene, precise solute free energy, enthalpy and entropy parameters are obtained. It is found that the *para* isomer is more soluble and is retained longer, due to its more favorable excess enthalpy and enthalpy of solution. This behavior is interpreted in the light of current theories of nematic solutions, and a plausible separation mechanism is proposed. The extent to which this mechanism may be extended to other geometric isomers is discussed.

INTRODUCTION

Nematic liquid crystals are unique stationary liquid phases in that they exhibit long-range (thousands of Ångstroms) orientational order, wherein the rodlike molecules tend towards mutually parallel alignment. It is well known[1,2] that such phases selectively differentiate on the basis of solute shape. For example, using nematic phases, the gas–liquid chromatographic (GLC) separation of *meta* and *para* disubstituted benzenes can usually be effected or, at least, enhanced, with the more rodlike *para* isomer invariably being retained longer. A good illustration of this is an analysis performed in this laboratory[3], where a retention-time ratio (*para/meta*) of 1.3 was attained for the divinylbenzenes. Earlier attempts, using more conventional liquid phases or adsorbents, never managed to realize a value of even 1.1.

One could cite other prominent examples of successful separations of geometric isomers (monosubstituted phenols[4], naphthalene homologs[5], 3–5-ring polycyclic aromatic hydrocarbons[6,7], etc.[1,2]) using nematic stationary phases. Again, all of these have been attributed, in a general manner, to differences in molecular shape among the isomers. Yet, with a few exceptions[3,4,8-12], the understanding of the separation mechanism has advanced little beyond the concept that more rodlike isomers "fit better" into the ordered nematic array. These few exceptions were all based on a solution model proposed[8] and subsequently developed[13] by one of us several years ago. It became clear at that time that a more detailed understanding required precise knowledge (from GLC) of not only the infinite dilution solute partial molar excess

free energies (G_2^s) [or activity coefficients (γ_2^∞)], and of the related enthalpies (H_2^s) and entropies (S_2^s), but also of the molar enthalpies $(\varDelta H_2^s)$ and entropies $(\varDelta S_2^s)$ of solution.

For the following reasons, it is an appropriate time to reconsider the mechanistic question: (1) there have been recent developments in the theory of solutions of nonmesomorphic solutes in nematic solvents[14]; (2) all the previously cited thermodynamic GLC experiments[3,8-12] utilized air-baths, where column temperature control was less than optimum, thus affecting the precision of the determined thermodynamic parameters; and, relatedly, (3) the factors governing the precision and accuracy of thermodynamic measurements by GLC have recently been further clarified and quantified[15].

The test systems considered in the present study are four pairs of *meta* and *para* disubstituted benzenes in the nematic phase of p,p'-dihexoxyazoxybenzene (DHAB). The latter is a particularly attractive solvent because of the location and width of its nematic temperature range[16], and its previous use in thermodynamic studies and shape-selective separations[3,8]. While only this class of solutes will be examined in any detail, the extent to which the proposed separation mechanism may be applied to other geometric isomers will be discussed.

EXPERIMENTAL

The source, purification procedure and purity of DHAB are given elsewhere[16]. The solid → nematic and nematic → isotropic phase transitions occur at 81.0° and 128.2°, respectively. The solutes, listed in Table I, were all sufficiently volatile at the experimental temperatures and were used without further purification.

The support material employed was Johns-Manville 60–80 mesh, acid-washed and DMCS-treated Chromosorb G. The weight percent of liquid phase in the packing of coated support was 8.92 ± 0.06%, which was precisely determined from the weight loss of five separately ashed samples of coated support[17], with a small but necessary correction for the weight loss of ashed bare support[15].

The gas chromatograph was of laboratory construction, with precision control of inlet carrier gas (helium) pressure and hot-wire thermal conductivity detection[15]. The column temperature was controlled to better than ±0.05° through immersion in a well regulated ethylene glycol bath.

TABLE I.

LIST OF SOLUTES

Number	Name	Dipole moment (D)*
1	*m*-Xylene	0.33
2	*p*-Xylene	0
3	*m*-Ethyltoluene	0.33
4	*p*-Ethyltoluene	0
5	*m*-Chlorotoluene	1.77
6	*p*-Chlorotoluene	1.92
7	*m*-Dichlorobenzene	1.59
8	*p*-Dichlorobenzene	0

* Values from A. L. McClellan, *Tables of Experimental Dipole Moments*, Freeman, San Francisco, Calif., 1963.

The general procedure used to obtain meaningful and accurate solute specific retention volumes (V_g^0) is described elsewhere[8,15-17]. Suffice it to note that ample precautions were taken to minimize random error and, insofar as possible, to eliminate sources of systematic error.

RESULTS

The expression relating V_g^0 to the experimental variables may be written in the form[15]

$$V_g^0 = \frac{t'\bar{F}_c^0}{g_1} \tag{1}$$

where t' is the solute retention time corrected for dead space, $\bar{F}_c^0$ is the volume flow-rate of the carrier gas adjusted to the mean column pressure and $0°$ and g_1 is the weight of liquid phase in the column. V_g^0's were obtained at $83.0°$, $93.0°$, $103.0°$ and $113.0°$, all within the nematic phase of DHAB. The temperature region immediately below $(ca.\ 15°)$ the nematic–isotropic transition was not studied in order to avoid any pretransitional effects inherent in the pure nematogen, which, independently or when coupled with the concentration effect of the solute band moving through the column, can produce anomalous results[18]. Moreover, this temperature region is not of prime importance in practical GLC separations[2,3] (see later).

The V_g^0's reported in Table II represent the average of at least three separate t' measurements and six $\bar{F}_c^0$ measurements for each point. The relative random error in V_g^0 may be estimated from those in t', $\bar{F}_c^0$ and g_1 through propagation-of-errors analysis[15]:

$$\left(\frac{\sigma_{V_g^0}}{V_g^0}\right) = \left[\left(\frac{\sigma_{t'}}{t'}\right)^2 + \left(\frac{\sigma_{F_c^0}}{\bar{F}_c^0}\right)^2 + \left(\frac{\sigma_{g_1}}{g_1}\right)^2\right]^{1/2} \tag{2}$$

Since the total weight of packing in the column is known to high precision, the error in g_1 is governed by the error in the determination (by ashing) of the weight percent

TABLE II

SOLUTE SPECIFIC RETENTION VOLUMES (V_g^0) AND STANDARD MOLAR ENTHALPIES $(\varDelta H_2^s)$ AND ENTROPIES $(\varDelta S_2)$ OF SOLUTION

Solutes are numbered according to Table I.

Solute	V_g^0 (ml carrier gas/g liquid phase)				$-\varDelta H_2^s$ (kcal/mole)	$-\varDelta S_2^s$ (cal/mole·degree)
	$83°$	$93°$	$103°$	$113°$		
1	184.7	142.9	111.8	90.51	6.52	15.96
2	195.1	150.1	117.8	93.61	6.69	16.30
3	325.0	245.3	188.7	148.8	7.12	16.53
4	356.3	268.2	206.1	160.3	7.27	16.75
5	403.4	305.1	236.2	186.8	7.02	15.80
6	451.9	339.3	261.6	203.6	7.25	16.23
7	613.3	463.8	355.3	277.6	7.23	15.55
8	687.8	515.0	394.2	304.8	7.41	15.82

of liquid phase. Accordingly, from the percent standard deviations estimated through multiple measurements of t' (0.24%), $\bar{F}_c^0$ (0.17%) and g_1 (0.70%), the relative standard deviation is calculated to be 0.76%, the dominant factor clearly being the uncertainty in g_1[15].

The standard solute molar enthalpies (ΔH_2^s) and entropies (ΔS_2^s) of solution listed in Table II were determined from[19]

$$\ln V_g^0 = \frac{-\Delta H_2^s}{RT} + \frac{\Delta S_2^s}{R} - \ln \left(\frac{M_1}{273.2R}\right) \tag{3}$$

where M_1 is the liquid phase molecular weight. The correlation coefficients of the linear regression analyses ($\ln V_g^0$ vs. T^{-1}) were all in excess of 0.9998. The standard deviations in ΔH_2^s and ΔS_2^s are essentially the same (within rounding errors) as those for H_2^c and S_2^c, respectively (Table III).

The solute activity coefficients (γ_2^x), based on deviations from Raoult's law, were calculated from the V_g^0 data via[8]

$$\ln \gamma_2^\infty = \ln (273.2R/M_1 f_2^0 V_g^0) \tag{4}$$

where

$$\ln f_2^0 = \ln p_2^0 + (B_{22}p_2^0/RT) \tag{5}$$

and where f_2^0, p_2^0 and B_{22} are, respectively, the fugacity, saturated vapor pressure and second virial coefficient of the pure solute at the experimental temperature T. The vapor pressures and second virial coefficients were determined using the sources and procedure described in ref. 8. The resulting γ_2^x's are reported in Table III. Also:

$$\left(\frac{\sigma_{\gamma_2^\infty}}{\gamma_2^\infty}\right) = \left[\left(\frac{\sigma_{V_g^0}}{V_g^0}\right)^2 + \left(\frac{\sigma_{f_2^0}}{f_2^0}\right)^2\right]^{1/2} \tag{6}$$

Since the uncertainty in f_2^0 is estimated to be less than 0.15%, the percent standard deviation in γ_2^x is ca. 0.8%.

TABLE III

SOLUTE INFINITE-DILUTION SOLUTE ACTIVITY COEFFICIENTS (γ_2^x) AND PARTIAL MOLAR EXCESS ENTHALPIES (H_2^c) AND ENTROPIES (S_2^c)

Solutes are numbered according to Table I.

Solute	γ_2^x				H_2^c (kcal/mole)	S_2^c (cal/mole·degree)
	$83°$	$93°$	$103°$	$113°$		
1	1.849	1.662	1.514	1.363	2.76 ± 0.07	6.51 ± 0.17
2	1.693	1.536	1.398	1.284	2.52 ± 0.02	6.04 ± 0.05
3	2.253	2.005	1.798	1.611	3.05 ± 0.04	6.95 ± 0.10
4	2.070	1.851	1.663	1.513	2.86 ± 0.03	6.60 ± 0.07
5	1.782	1.575	1.394	1.236	3.33 ± 0.05	8.20 ± 0.12
6	1.599	1.433	1.282	1.165	2.90 ± 0.04	7.22 ± 0.09
7	1.712	1.502	1.337	1.196	3.26 ± 0.02	8.10 ± 0.06
8	1.605	1.417	1.258	1.134	3.17 ± 0.03	7.96 ± 0.07

From the thermodynamics[2,8], we have

$$\ln \gamma_2^\infty = \frac{G_2^c}{RT} = \frac{H_2^c}{RT} - \frac{S_2^c}{R} \tag{7}$$

where the symbols have already been identified. Linear regression analysis of $\ln \gamma_2^\infty$ as a function of T^{-1} yielded the H_2^c and S_2^c values listed, with their standard deviations, in Table III. The high linear correlation coefficients (all in excess of 0.9995) and the small standard deviations reflect the quality of the data. The standard deviations of the fits, which range from 0.001 to 0.005 and average *ca.* 0.003 or 0.3%, measure the scatter of the experimental $\ln \gamma_2^\infty$ values about the least-squares line. The average or typical value correlates well with the percent standard deviation calculated using eqns. 2 and 6, excluding the contribution of the g_1 term which does not affect this scatter.

Poorer temperature control (say, $\pm 0.3°$, which would be respectable for a forced-air oven) would affect the overall precision of γ_2^∞ only slightly (raising it to *ca.* 1.1 %[9]), but the precision of H_2^c and S_2^c more radically. Indeed, relatively higher errors are reported in earlier thermodynamic studies[2,3,8-12,18], with the results of Bocquet and Pommier[18] being perhaps the most precise to date. We note also that, while the agreement with our previous V_g^0 measurements is quite good, the earlier H_2^c and S_2^c values are uniformly higher than the present ones (for the systems in common) by *ca.* 0.2-0.3 kcal/mole and 0.6-0.7 cal/mole · degree, respectively. This is attributed partly to the less effective temperature control, but mainly to the inclusion of data points closer to the nematic–isotropic transition temperature (T_{NI}) in the earlier study[8]. Since $\ln \gamma_2^\infty$ begins to decrease more steeply with increasing temperatures as T_{NI} is approached[2,18], data points included from this region would lead to somewhat steeper slopes and more negative intercepts (hence, to larger H_2^c and S_2^c) and, undoubtedly, to a biasing of the presumed linear fit.

For present purposes, additional parameters must be defined and tabulated. The retention-time ratio or separation factor ($\alpha_{p/m}$) may be written as the product of a "selectivity factor" ($S_{m/p}$) and a fugacity-ratio term ($F_{m/p}$), *i.e.*, from eqn. 4

$$\alpha_{p/m} = \frac{t_p'}{t_m'} = \frac{(V_g^0)_p}{(V_g^0)_m} = \left(\frac{\gamma_m^\infty}{\gamma_p^\infty}\right) \cdot \left(\frac{f_m^0}{f_p^0}\right) = S_{m/p} \cdot F_{m/p} \tag{8}$$

where p and m refer to the *para* and *meta* isomers, respectively. Values of $\alpha_{p/m}$ and $S_{m/p}$ at 83° and 113°, calculated from the results in Tables II and III, are given in Table IV. Finally, listed in Table V are differences (*meta* value minus *para* value)

TABLE IV

SEPARATION ($\alpha_{p/m}$) AND "SELECTIVITY" ($S_{m/p}$) FACTORS AT 83.0 AND 113.0°

See eqn. 8 for definition of $\alpha_{p/m}$ and $S_{m/p}$. Solutes are numbered according to Table I.

Solute pair	83.0°		113.0°	
	$\alpha_{p/m}$	$S_{m/p}$	$\alpha_{p/m}$	$S_{m/p}$
1–2	1.056	1.092	1.034	1.062
3–4	1.096	1.088	1.077	1.065
5–6	1.120	1.114	1.090	1.061
7–8	1.122	1.067	1.098	1.055

TABLE V

ENTHALPY AND ENTROPY DIFFERENCES BETWEEN *meta* AND *para* SOLUTE PAIRS

The differences are the *meta* value minus *para* value; units as in Tables II and III. Solutes are numbered according to Table I.

Solute pair	$\Delta(\Delta H_2^v)$ *	ΔH_2^c **	$\Delta(\Delta H_2^s)$ ***	$\Delta(\Delta S_2^v)$ *	ΔS_2^c **	$\Delta(\Delta S_2^s)$ ***
1–2	0.17	0.24 ± 0.07	0.07	0.34	0.47 ± 0.18	0.13
3–4	0.15	0.19 ± 0.05	0.04	0.22	0.35 ± 0.12	0.13
5–6	0.23	0.43 ± 0.06	0.20	0.43	0.98 ± 0.14	0.55
7–8	0.18	0.09 ± 0.04	−0.09	0.27	0.14 ± 0.09	−0.13

     * From data in Table II.
     ** From data in Table III.
     *** Calculated using eqns. 12 and 13.

between various enthalpy and entropy parameters. It follows from eqns. 3 and 7, and the Clausius–Clapeyron equation that

$$\ln \alpha_{p/m} = \frac{-\Delta H_p^s + \Delta H_m^s}{RT} + \frac{\Delta S_p^s - \Delta S_m^s}{R} = \frac{\Delta(\Delta H_2^s)}{RT} - \frac{\Delta(\Delta S_2^s)}{R} \tag{9}$$

$$\ln S_{m/p} = \frac{H_m^c - H_p^c}{RT} - \frac{S_m^c - S_p^c}{R} = \frac{\Delta H_2^c}{RT} - \frac{\Delta S_2^c}{R} \tag{10}$$

$$\ln F_{m/p} = \frac{-\Delta H_m^v + \Delta H_p^v}{RT} + \frac{\Delta S_m^v - \Delta S_p^v}{R} = \frac{-\Delta(\Delta H_2^v)}{RT} + \frac{\Delta(\Delta S_2^v)}{R} \tag{11}$$

where ΔH_2^v and ΔS_2^v refer to the standard molar enthalpy and entropy of vaporization of the pure solute. Hence, in the light of eqn. 8:

$$\Delta(\Delta H_2^s) = \Delta H_2^c - \Delta(\Delta H_2^v) \tag{12}$$

$$\Delta(\Delta S_2^s) = \Delta S_2^c - \Delta(\Delta S_2^v) \tag{13}$$

Again, the random errors in $\Delta(\Delta H_2^s)$ and $\Delta(\Delta S_2^s)$ are essentially the same as those in ΔH_2^c and ΔS_2^c, respectively. By comparison, both $\Delta(\Delta H_2^v)$ and $\Delta(\Delta S_2^v)$ are precisely known (negligible error).

THEORETICAL

In the theoretical model developed several years ago[8,13], it was assumed that there are four main sources of deviation from ideal solution behavior in nematic binary mixtures: combinatorial, conformational, rotational and energetic. The existence of these effects has been confirmed by more recent theory[14], which further reveals that the last three contributions are coupled (see later).

The combinatorial contribution, which is purely entropic, arises from the difference in molecular size between the solute and solvent (liquid phase). If one were considering absolute thermodynamic quantities, this term should not, in general, be neglected. However, since we shall ultimately be analyzing the separation of isomeric

solute pairs of roughly the same size and, hence, only relative values, the combinatorial effect is of little consequence. Moreover, since the internal rotational motions (as opposed to rotation of the molecule as a whole) of those "rigid" solute molecules involve no major changes in positional coordinates, the conformational contribution, which is largely entropic, is negligible as well[8,13]. This is a considerable simplification, leaving only the rotational and energetic contributions to contend with.

Since the rotational contribution to H_2^e is negligible[13], the bulk of the observed H_2^e is provided by the energetic term[8,13], which is given by the following approximate form[8,20].

$$H_2^e = c_2 \Delta w/2 = c_2(\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12})/2 \tag{14}$$

where c_2 is proportional to the size of the solute molecule and is constant for a given isomeric solute pair, ε_{ij} is a segmental attactive interaction energy (1 = solvent; 2 = solute) and Δw is the segmental interchange energy. Thus, for example, weaker (less positive) 1–2 attractive interactions relative to the arithmetic mean of 1–1 and 2–2 attractive interactions yield positive Δw values, which lead to positive H_2^e and, normally, to positive S_2^e and positive deviations from Raoult's law ($\gamma_2^\infty > 1$).

It is clear from eqn. 14 that, in a common solvent (ε_{11} fixed), the magnitude of H_2^e (and S_2^e) depends on ε_{22}. For example, a less positive H_2^e could be due to a larger ε_{12} and/or a smaller ε_{22}. To sort out the effect of ε_{12}, one focuses on the molar enthalpies (and entropies) of solution[8]:

$$\Delta H_2^s = c_2(\varepsilon_{11} - 2\varepsilon_{12})/2 \tag{15}$$

Thus, the larger is ε_{12}, the more negative is ΔH_2^s and, generally, ΔS_2^s. The picture becomes complete with the relation for ΔH_2^v

$$\Delta H_2^v = c_2(\varepsilon_{22})/2 \tag{16}$$

which is consistent with eqns. 12, 14 and 15.

As with conventional mixtures, the strength of 1–2 interactions is governed by the electrostatic and dispersion forces between the solute and solvent molecules (assuming, of course, the absence of charge-transfer forces). In nematic solvents, however, it also depends on the shape of the solute molecule. According to both an expandable lattice model and a recent extension of the Maier–Saupe theory[14], ε_{12} will be larger for solutes which align better within the host nematic solvent. Thus, all else being equal, more rodlike solute molecules should experience relatively stronger 1–2 interactions. It is important to note that it is the repulsive interactions or "packing" that primarily determine the orientational order in nematic system[14] and thus lead to these shape- dependent 1–2 attractive interactions. That is, because they experience less intermolecular repulsion, more rodlike solutes can, on the average, approach the solvent molecules more closely, thereby promoting effectively stronger electrostatic and dispersion (attractive) interactions. Concomitantly, however, the greater orientational order and larger ε_{12} lead to lower translational and rotational entropy[8,13]. (Accordingly, the energetic and rotational contributions are coupled.) Therefore, shape-dependent effects *per se* produce more negative ΔH_2^s and ΔS_2^s values for the more rodlike isomer of the solute pair.

Finally, to address directly the separation mechanism of *meta* and *para* di-substituted benzenes in a given nematic liquid phase, differences (*meta* value minus *para* value) in the respective thermodynamic parameters need to be considered. For the enthalpy terms, for example, eqns. 14–16 give

$$\Delta H_2^c = c_2[(\varepsilon_{mm} - \varepsilon_{pp}) + 2(\varepsilon_{1p} - \varepsilon_{1m})]/2 \tag{17}$$

$$\Delta(\Delta H_2^s) = c_2(\varepsilon_{1p} - \varepsilon_{1m}) \tag{18}$$

$$\Delta(\Delta H_2^v) = c_2(\varepsilon_{mm} - \varepsilon_{pp})/2 \tag{19}$$

which are consistent with eqn. 12. Generally, the corresponding entropy terms follow the above enthalpy terms in their sign and magnitude (see Table V). Examining the above equations along with eqns. 8–11, one sees that the truest measure of "solvent selectivity" is $\alpha_{p/m}$, because it reflects only the difference in solute–solvent interactions. What is commonly referred to as the "selectivity factor" ($S_{m/p}$) measures the enhancement of the actual separation over what would have been achieved solely on the basis of the vapor pressures of the pure components, *i.e.*, with the $F_{m/p}$ term alone, as in a "boiling-point" separation. Perhaps, a better definition for $S_{m/p}$ might be an "enhancement factor".

DISCUSSION

For all the solutes studied, $\gamma_2^\infty > 1$, $H_2^c > 0$ and $S_2^c > 0$. This indicates that all the nonmesomorphic solutes are incompatible with the ordered nematic solvent. (Some activity coefficients are close to unity. However, in view of the relatively large H_2^c and S_2^c values, such solutions should be regarded merely as pseudoideal.) We note that, without exception, the *para* isomers have the lower values of γ_2^∞, H_2^c, S_2^c, ΔH_2^c and ΔS_2^c; thus, they are less incompatible with the liquid phase. Moreover, the lower γ_2^∞ (higher solubility) is a consequence of the more favorable enthalpy outweighing the less favorable entropy.

For the most part, the above general trends have been noted in previous thermodynamic GLC studies. However, with the possible exception of the trend in γ_2^∞, the larger experimental error in these earlier studies usually precluded an unqualified identification of those trends. The differences in H_2^c, S_2^c, ΔH_2^c and ΔS_2^c are quite small, but, in the present study, they are clearly larger than the relevant experimenal errors (see Table V). This point needs to be established, because the proposed mechanism deals with these small, but important, differences.

From Table IV, we see that, in all cases: (a) the *para* isomer is retained longer, *i.e.*, $\alpha_{p/m} > 1$; (b) the separation factor is higher at 83° than at 113°; (c) the separation factor is greater than what would have been attained simply on the basis of boiling point, *i.e.*, $S_{m/p} > 1$. Therefore, DHAB is a selective liquid phase for the separation of these isomers, particularly in the temperature region immediately above its melting point[3].

Except for *p*-chlorotoluene, the *para* isomers have zero dipole moment (Table I). One might expect that the *meta* isomers of the three remaining pairs would experience stronger solute–solvent interactions, because, in addition to dispersion interactions, there would be a dipolar contribution (dipole–dipole and dipole–induced

dipole) to the overall interaction energy. However, as discussed earlier, the 1–2 interactions of the more globular *meta* isomers should operate at slightly greater average distances than those (primarily dispersion interactions) of the rodlike *para* isomers, which are better accommodated in the ordered domain of DHAB. Without knowledge of the detailed structure of nematic solutions, it is not possible to determine, *a priori*, which of these two effects will dominate to give effectively stronger 1–2 interactions. However, the thermodynamic evidence (Table V) shows that $\Delta(\Delta H_2^s)$ is positive for all isomeric pairs, indicating that $\varepsilon_{1p} > \varepsilon_{1m}$ (eqn. 18). Therefore, the shape-dependent effect dominates, and the *para* isomer, by virtue of its better alignment, interacts more strongly. Note, however, that the positive H_2^e's suggest that the liquid-crystalline solvent would prefer to interact with itself rather than with any of these solutes, but it is less hostile towards the *para* isomers.

Unfortunately, the stronger 1–2 interactions and higher orientational order of the *para* isomers also result in greater translational and rotational entropy losses (more negative ΔS_2^s) upon solvation, making $\Delta(\Delta S_2^s)$ positive as well (Table V). However, the favorable enthalpy difference is only partly counteracted by the unfavorable entropy difference, as the *para* isomer is always retained longer (see eqn. 9). At higher temperatures, this enthalpy advantage is diminished and the separation factor decreases (Table IV). At temperatures even closer to T_{NI} (the "pre-transition" region), it is well known that the orientational order of nematic solvents begins to decrease sharply with increasing temperature. One would expect the nematic liquid phase to be yet less selective (much smaller $\alpha_{p/m}$) in this region. Indeed, preliminary studies at a few degrees below T_{NI} confirm this expectation.

Finally, we note from Table V that ΔH_2^e does not necessarily correlate with $\Delta(\Delta H_2^s)$ [or ΔS_2^e with $\Delta(\Delta S_2^s)$], since the former contains the additional term $\varepsilon_{mm} - \varepsilon_{pp}$, as measured by $\Delta(\Delta H_2^e)$ (see eqns. 17–19). The relative nonideality of the isomers is determined by differences in their excess properties, but the relative retention by differences in their solution properties. In any event, it is clear that it is the enthalpy terms, and not the entropy terms, which promote the lower activity coefficients and enhanced retention of the *para* isomers. Although the *para* isomer certainly "fits better" within the nematic liquid phase, the separation mechanism is energetically controlled rather than entropically controlled, as the expression in quotes would seem to imply.

The proposed mechanism provides a reasonable and defensible explanation for the separation of a pair of rigid geometric isomers, where one is more rodlike and the other is more globular in shape. It would be worthwhile to examine the extent to which it may be generalized to the separation of other geometric isomers using nematic liquid phases.

Consider, for example, the separation of alkane isomers —say, an *n*-alkane and a fairly branched alkane. Our studies[8,20] on C_7 and C_9 alkanes and four nematic liquids reveal that the *n*-alkanes invariably have more negative ΔH_2^s and ΔS_2^s values, as would be predicted on the basis of solute shape. However, in addition to greater translational and rotational entropy losses, the conformational restrictions imposed on *n*-alkanes by the aligned nematic solvent generate another major source of solute entropy loss[8,13,20]. It is found that, in some cases, the unfavorable $\Delta(\Delta S_2^s)$ and ΔS_2^e terms overwhelm the favorable $\Delta(\Delta H_2^s)$ and ΔH_2^e terms, respectively, leading to both shorter retention time and lower solubility for the more "rodlike" isomer[20]. Hence,

the conformational contribution introduces a further complication and precludes any generalizations. It is currently not possible to predict the order of retention when one or both of the isomers has appreciable molecular flexibility. On the other hand, most fused, multiring aromatic solutes[6,7] are rigid, but they are more platelike, rather than rodlike or globular, in molecular shape. As such, they have two principal long molecular axes, *i.e.*, they are biaxial. Accordingly, their alignment in nematic solvents cannot be described by a single orientational order parameter, as is possible for *para* disubstituted benzenes which are, more or less, cylindrically symmetric. Also, it appears that their nematic solution behavior is more complex than that of rodlike solutes[21]. However, it is conceivable that the separation mechanism of such polycyclic isomers may also be energetically controlled. To test this, it would be of interest to study the temperature dependence of the relative retention volumes of these isomers, via eqn. 9.

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