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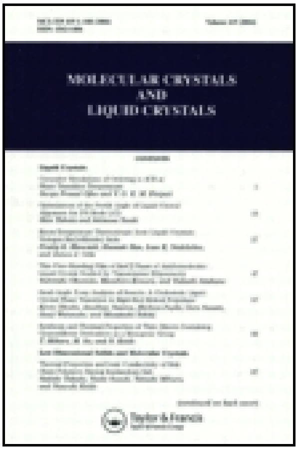

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Probe-Solute Study of Mesomorphic Polysiloxane (Mepsil) Solvents. Discontinuities in Family Retention Plots That Traverse Phase Transitions

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PROBE-SOLUTE STUDY OF MESOMORPHIC POLYSILOXANE (MEPSIL) SOLVENTS. DISCONTINUITIES IN FAMILY RETENTION PLOTS THAT TRAVERSE PHASE TRANSITIONS

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Abstract The GLC method of measurement of activity coefficients γ_A^∞, liquid-gas partition coefficients K_R^o, specific retention volumes V_g^o, capacity factors k', and excess thermodynamic properties of mixing of solutes at effective infinite dilution in polymeric solvents is considered. It is argued that while van't Hoff plots of any of the retention parameters can reveal subtle phase transitions exhibited by the solvent (the solutes are used as probes of the state of polymer aggregation), it is impractical to make measurements of most of these variables from the standpoints of both theory and experiment. A new method of characterizing the behavior of probe-solutes with polymeric solvents that is based upon evaluation of the slopes of family plots of log V_g^o against log p_A^o is therefore described; where p_A^o is the solute vapor pressure at the column temperature. The ideal slope of such plots is -1, deviations from this value being a measure of departure from solution ideality. Results obtained for plots of the readily-accessible parameter log k' (rather than log V_g^o) for a range of aromatic hydrocarbon solutes are then presented that give discontinuities with mesomorphic polysiloxane (MEPSIL) solvents, two representative examples of which are presented and discussed. The new technique is also said to have advantage as a means of gauging the utility of MEPSIL solvents as analytical gas-chromatographic stationary phases and, in addition, suggests an attractively simple method for the physicochemical measurement of vapor pressures and heats of vaporization.

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INTRODUCTION AND THEORY[1]

The extent of separation of pairs of solutes in analytical gas chromatography is commonly cast in terms of what are known as relative retentions (alpha values):

$$\alpha_{i/j} = k'_i / k'_j \tag{1}$$

where the solute capacity factors k'_A (A = solute i or solute j) can be calculated from data derived directly from stripchart recordings:

$$k' = (t_R^o - t_M)/t_M \tag{2}$$

where t_R^o and t_M are the retention times of a solute and a nonretained compound (the "air" peak) that have been corrected for the pressure drop across the column, the latter providing a measure of the void volume in the system. Over the range to which Henry's law applies, the solute capacity factor is also related to the concentration-based liquid-gas partition coefficient K_R^o that describes the equilibrium distribution of the substance between the stationary and mobile phases (i.e., the equilibrium distribution constant):

$$k' = K_R^o V_S / V_M \tag{3}$$

where the superscript zero indicates that the full correction for gas-phase virial imperfections has been made; and where V_S and V_M are the column volumes of stationary S and mobile M phases. Simple derivation then shows that the partition coefficient is related to the mole-fraction based Raoult's law activity coefficient of the solute at infinite dilution in the stationary phase via the relation:

$$K_R^o = RT / {}^x\gamma_A^\infty f_A^o \bar{V}_S \tag{4}$$

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where f_A^o is the bulk-solute fugacity, R is the gas constant, T is the column temperature, $\bar{V}_S$ is the molar volume of the stationary phase, and ${}^x\gamma_A^\infty$ is the activity coefficient.

It is generally inconvenient to determine the column volume of stationary phase, however, and so, solute specific retention volumes $V_g^o/\mathrm{cm}^3\ \mathrm{g}^{-1}$ are usually measured instead of partition coefficients:

$$V_g^o = 273\ K_R^o/\rho_S T = 273R/{}^x\gamma_A^\infty\ f_A^o\ M_S \tag{5}$$

where ρ_S and M_S are the solvent density and molecular weight. (V_g^o actually corresponds to the carrier gas volume at STP, per gram stationary phase, that must flow through the column in excess of the void volume in order to elute the solute peak maximum through the system.) The advantage of casting retentions in this form is that only the weight w_S of stationary phase need be measured, as opposed to its volume.

In any event, substitution of either Eq. (4) or (5) into Eq. (1), followed by the approximation that fugacities can be replaced with vapor pressures, yields the expression:

$$\alpha_{i/j} = \frac{\left({}^x\gamma_A^\infty\ p_A^o\right)_{\text{solute } j}}{\left({}^x\gamma_A^\infty\ p_A^o\right)_{\text{solute } i}} \tag{6}$$

For compounds of approximately equal vapor pressure (e.g., closely related structural isomers such as benzo[a]pyrene/benzo[e]pyrene), Eq. (6) reduces further to:

$$\alpha_{i/j} = \frac{\left({}^x\gamma_A^\infty\right)_{\text{solute } j}}{\left({}^x\gamma_A^\infty\right)_{\text{solute } i}} \tag{7}$$

Thus, in these instances, the ratio of activity coefficients governs entirely what separations can be achieved. Eq. (6) and (7) also re-

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veal the paramount role that solute activity coefficients play in governing gas-chromatographic separations.

A number of workers have pointed out over the years that, for polymeric stationary phases, ${}^{x}\gamma_A^\infty$ tends to zero as the stationary-phase molecular weight M_S become large. Even so, K_R^o is observed experimentally to approach a constant, that is, what decrease there is in ${}^{x}\gamma_A^\infty$ is offset by the increase in $\bar{V}_S$. As a result, Patterson, Tewari, Schreiber, and Guillett[2,3] recast Eq. (5) in terms of Raoult's law in the form of weight fractions w_A rather than mole fractions x_A:

$$p_A = p_A^o \, w_A \, {}^{w}\gamma_A \tag{8}$$

whence:

$$V_g^o = 273R/{}^{w}\gamma_A^\infty \, f_A^o \, M_A \tag{9}$$

where M_A is the solute molecular weight, and where weight- and mole-fraction based activity coefficients are related by:

$${}^{w}\gamma_A^\infty = {}^{x}\gamma_A^\infty \, M_S/M_A \tag{10}$$

The advantage of these formulations is that ${}^{w}\gamma_A^\infty$ approaches a constant value as M_S becomes large, which is in keeping with the approach to constancy of the solute retentions. However, the generality of the activity coefficient term is thereby lost. That is, while departures from unity for values of ${}^{x}\gamma_A^\infty$ indicate deviations from solution ideality regardless of the solute and solvent, virtually any value of ${}^{w}\gamma_A^\infty$ can correspond to an ideal solution depending upon the ratio of M_S to M_A. For example, supposing that ${}^{x}\gamma_A^\infty$ were unity and that M_S and M_A were 10^6 and 10^2 Da, respectively, ${}^{w}\gamma_A^\infty$ would, ideally, then be 10^4. (For solute and solvent densities of unity, lattice theory would also predict that the excess heat of mixing for such an endothermic system would be highly positive.)

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A little-used yet very powerful alternative to the above that avoids reference to activity coefficients altogether was devised more than 30 years ago by Hoare and Purnell.[4,5] Their derivation begins with the usual form of van't Hoff relation that describes the temperature-dependence of solute specific retention volumes:

$$\log V_g^o = (-\Delta\bar{H}_S/2.303RT) + C \tag{11}$$

where $\Delta\bar{H}_S$ is the molar heat of solution of the solute with the stationary phase. Next, recalling the Clausius-Clapeyron equation,

$$\log p_A^o = (-\Delta\bar{H}_V/2.303RT) + C' \tag{12}$$

where $\Delta\bar{H}_V$ is the solute molar heat of vaporization, it is a simple matter to show by combination of Eq. (5) with (11) and (12) that:

$$\log V_g^o = a \log p_A^o + C'' \tag{13}$$

where:

$$a = \Delta\bar{H}_S/\Delta\bar{H}_V \tag{14}$$

In the instance of athermal as well as ideal solutions, viz., those for which the excess heat of mixing $\bar{H}^E$ is zero, it must be the case that $\Delta\bar{H}_S + \Delta\bar{H}_V = 0$ and, hence, plots of $\log V_g^o$ against $\log p_A^o$ should exhibit slopes <u>a</u> of -1. In other instances, for example, those in which the solute and solvent interact exothermally, $\Delta\bar{H}_S$ will be more negative than $-\Delta\bar{H}_V$ and so, plots of $\log V_g^o$ against $\log p_A^o$ will be sloped more negatively than -1. These situations correspond to negative deviations from Raoult's law. Conversely, for endothermal solutions corresponding to positive deviations from Raoult's law, the slopes of the plots will be less negative than -1. Eq. (11) thereby provides the means of assessing <u>thermal</u> contributions to deviations from Raoult's law independent of the solvent molecular weight.

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Since the solute capacity factor is related to V_g^o via several constants, plots of log k' against log p_A^o should also be effective in gauging solution ideality.[6] Moreover, there is then presented the considerable advantage of obviating measurement of the column content of stationary phase (whether volume or mass), all the requisite data being available directly from stripchart tracings as mentioned earlier. Nevertheless, it is not immediately clear what advantages, if any, this mode of data reduction might have for liquid-crystalline polymer solvents nor, indeed, whether application of Eq. (13) in any form would be useful for characterizing mesomorphic substances. We therefore set out to evaluate the retention/vapor-pressure formalism cast in terms of solute k' from the particular standpoint of deviations from solution ideality associated with solvent phase transitions. We report in this work the results obtained with two mesomorphic polysiloxane (MEPSIL) GC stationary phases that are representative of materials that we have recently synthesized.[7-10]

EXPERIMENTAL

The two MEPSIL polymers considered in this work are shown below in Figure 1. The synthesis of MEPSIL I was carried out[7] as described by Finkelmann and Rehage,[11] while MEPSIL II was fabricated as described by Laub and his coworkers.[8,9] The solute capacity factor data were taken from refs. 7 and 9.

RESULTS AND DISCUSSION

The constants A, B, and C of the Antoine equation

$$\log p_A^o = A - B/(C + t) \qquad (15)$$

(t in ^oC) as well as the capacity factors k' for a number of substituted naphthalene and polycyclic aromatic hydrocarbon sol-

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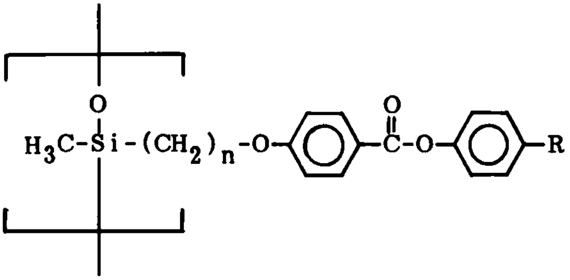


I:[7,11] n = 4, R = $-OCH_3$; T_{g-n} 288 K, T_{n-i} 368 K

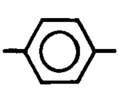
II:[8,9] n = 3, R = $-OCH_3$; T_{g-n} 412 K, T_{n-i} 592 K

FIGURE 1. Representative mesomorphic polysiloxane (MEPSIL) GC stationary phases.

utes with MEPSIL I at 343 K (nematic) and 373 K (isotropic) and MEPSIL II at 453 and 508 K are presented below in Tables I and II. Also shown for comparison in Table I are the capacity factors at 358 K with a poly(dimethylsiloxane) stationary phase, SE-30.

The plots of log k' against log p_A^o for the substituted aromatic hydrocarbon solutes with MEPSIL I are provided in Figure 2; while that obtained with SE-30 stationary phase is shown separately in Figure 3. The regression obtained for the polycyclic aromatic hydrocarbons with MEPSIL II is then illustrated in Figure 4.

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TABLE I. Antoine Constants[12,13] and Capacity Factors[7] for Listed Solutes with MEPSIL I and SE-30 Stationary Phases at Indicated Column Temperatures T/K

					k'		
		Eq. (15)			MEPSIL I		SE-30
No.	Solute	A	B	C	343 K	373 K	358 K
1.	Biphenyl	7.24541	1998.725	202.733	65.0	34.0	30.6
2.	2-Ethylnaphthalene	7.4350	2131.1	212.2	59.0	31.9	33.9
3.	1-Ethylnaphthalene	7.30532	2024.2	201.1	54.2	31.9	33.9
4.	2,6-Dimethylnaphthalene	7.3968	2080.3	200.8	90.6	41.0	36.1
5.	1,3-Dimethylnaphthalene	7.3978	2085.	200.9	82.2	43.9	39.1
6.	1,4-Dimethylnaphthalene	7.4040	2112.	201.	87.8	48.1	43.7
7.	2,3-Dimethylnaphthalene	7.40396	2111.9	201.1	109.0	53.3	43.7
8.	Diphenylmethane	7.51935	2197.1	211.6	56.8	34.0	43.4

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TABLE II. Antoine Constants[13,14] and Capacity Factors[9] for Listed Solutes with MEPSIL <u>II</u> Stationary Phase at Indicated Column Temperatures T/K

		Eq. (15)			k'	
No.	Solute	A	B	C	453 K	508 K
1.	Anthracene	7.37609	2518.815	218.509	1.07	
2.	Phenanthrene[a]				3.23	
3.	Fluorene	7.76176	2637.095	243.190	4.05	
4.	Fluoranthene	6.37310	1756.355	118.428		2.04
5.	Pyrene	5.61838	1122.025	15.158		2.73

[a] $\log p_A^o = 29.5477 - 4743.0/T - 6.7893 \log T$.

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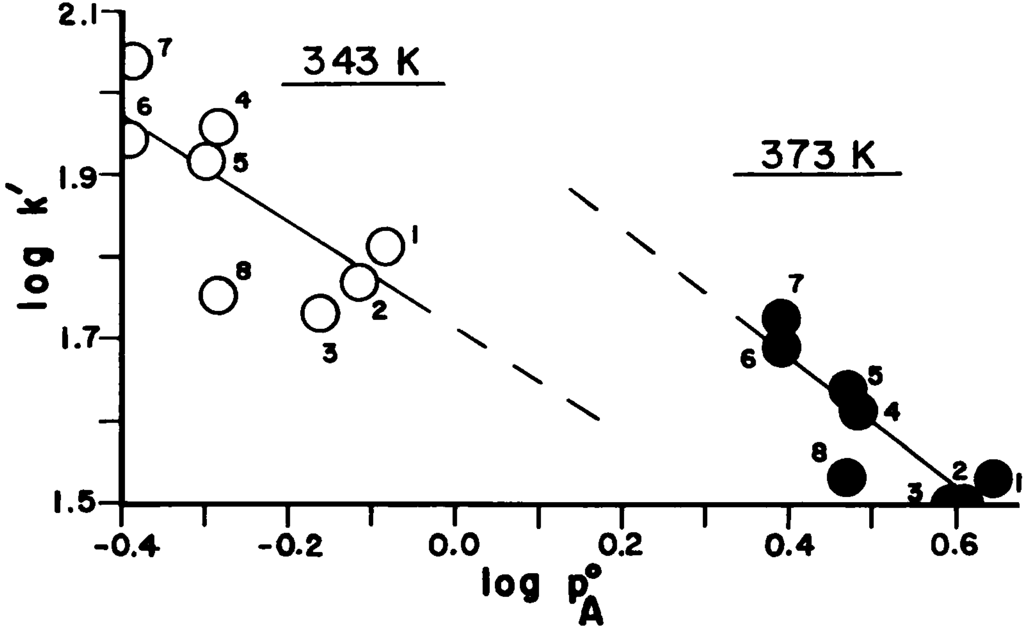

FIGURE 2. Plots of log k' against log p_A^o for solutes of Table I with MEPSIL $\underline{I}$ solvent at 343 K (nematic) and 373 K (isotropic). Symbol size reflects approximate experimental uncertainty on k'.

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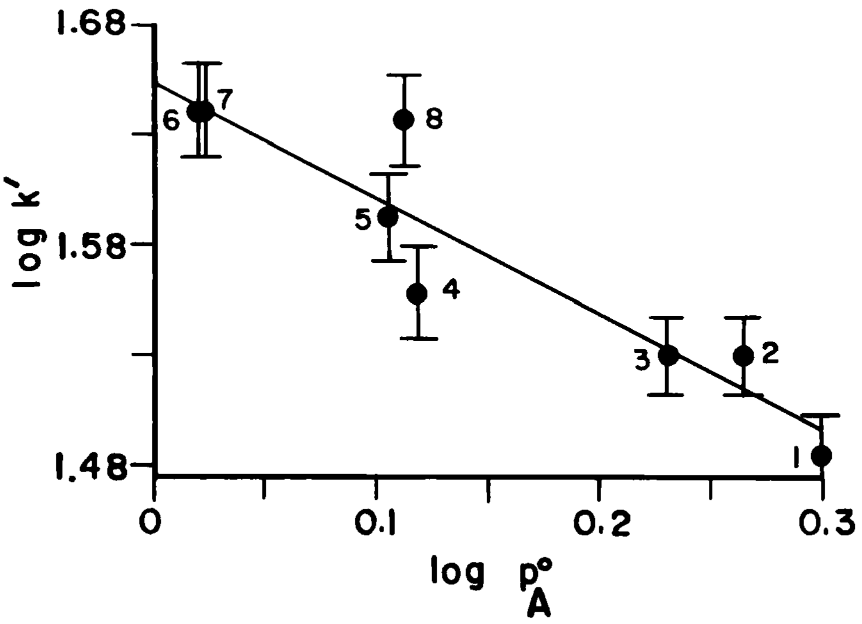

FIGURE 3. Plot of log k' against log P^{o}_{A} for solutes of Table I with SE-30 stationary phase at 358 K.

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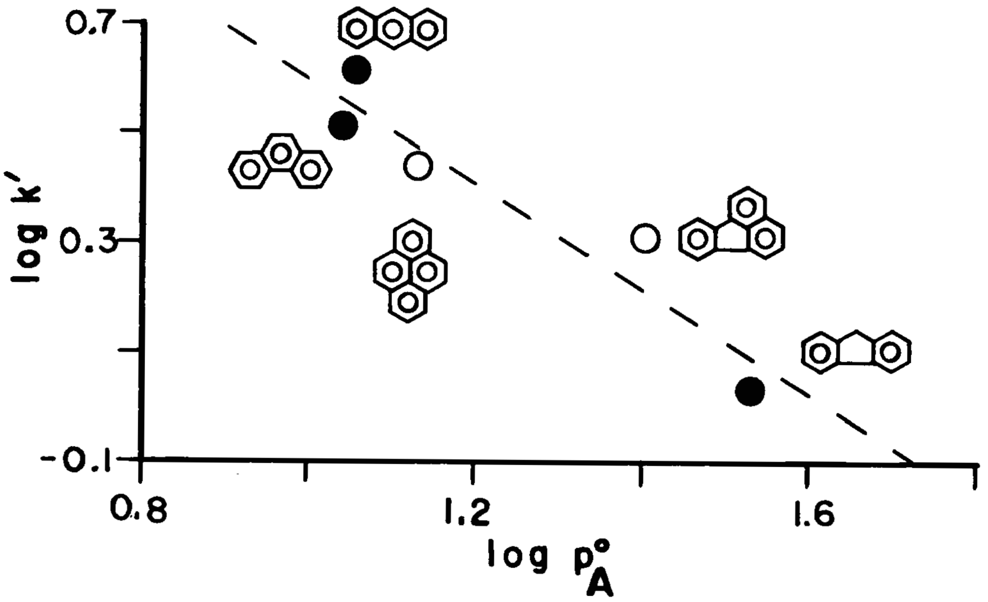

FIGURE 4. Plot of log k' against log p_A^o for solutes of Table II with MEPSIL II (nematic) stationary phase at 453 K (filled circles) and 508 K (open circles).

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We see in Figure 2, first, that there are two distinct lines for the solutes. That on the left corresponds to MEPSIL I in the nematic state, while the plot on the right refers to isotropic MEPSIL I stationary phase. The figure thus demonstrates, to the best of our knowledge for the first time, that retention diagrams of these kinds are discontinuous across phase transitions. The plots are comprised of only sixteen datum points at two temperatures, however, and so, further and comprehensive study of the capacity factors of a broader range of solutes is called for in order to establish, inter alia, whether pretransition effects might be detected by this form of graphical data reduction.

It would also be of interest to determine whether, and to what extent, classes of solutes exhibit homologous-series behavior with low molar-mass as well as polymeric liquid-crystalline phases. For example, sets of straight lines can usually be constructed for family series of solutes with a given stationary phase in two ways, first, from the elution of individual solutes at several temperatures; and, secondly, from the retentions of several homologs at an individual temperature. Further, when overlaid, the lines then form a hatched pattern, the so-called "grid" effect. However, whether this kind of retention behavior would be observed with liquid-crystalline phases in the isotropic state remains to be determined. (In view of the discontinuity shown in Figure 2, it is of course doubtful, although not inconceivable, that correlations of these kinds would be observed for solutes with mesomorphic solvents.)

The equation of the line on the right of Figure 2, that for the isotropic state of MEPSIL I, is: $\log k' = -0.769 \log p_A^o + 1.98$ (the symbol size corresponds to an approximate experimental error of ± 5%). The regression is improved substantially if the non-naphthalenic solutes biphenyl (no. 1) and diphenylmethane (no. 8) are not considered, the linear least-squares slope a and correlation coeffic-

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ient r then being -0.972 and 0.98. Also, the retentions were taken with an analytical gas chromatograph, that is, none of the usual precautions associated with high precision GC data acquisition were observed,[15] since it was the intent of the work at that time simply to test whether the phase would exhibit shape selectivity.

Figure 3 illustrates the goodness of linear regression of the naphthalene family of solutes with SE-30 poly(dimethylsiloxane) solvent (error bars of ± 5%), where the solutions are presumably nearly athermal. Despite some scatter, r = 0.96 for compounds 2-7, i.e., very nearly that found with MEPSIL I in the isotropic state. Moreover, the correlation coefficient drops only to 0.93 when solutes 1 and 8 are included in the regression.

In contrast, the retentions of the solutes with MEPSIL I in the nematic state (left-hand side of Figure 2) exhibit considerable scatter, as reflected by a decrease of the correlation coefficient to 0.92 for the napthalene solutes, i.e., considerably poorer than was observed for isotropic MEPSIL (0.96). In addition, r falls sharply when all solutes are considered, and is only 0.75 when the data for nos. 1 and 8 are included in the regression.

However, despite the differences in the extent of linearity of the two lines in Figure 2, the overall pattern of the data points appears to be similar from one to the other. We view this as a consequence of the combination of activity coefficient and vapor pressure effects, that is, while the activity coefficient of a given solute undoubtedly changes as the solvent passes from the isotropic to the nematic state, the solute vapor pressure nonetheless continues to play a substantial role in governing its retention. There can therefore be expected at least some residual family behavior of homologous series of solutes regardless of the solvent, although how prominent this might be e.g. with smectic stationary phases must for the present remain open to speculation pending further study and evaluation.

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Regression of the polycyclic aromatic hydrocarbon solutes with MEPSIL II at two temperatures, Figure 4, is reasonably good despite the use of an analytical gas chromatograph, there being obviously some experimental scatter as mentioned earlier. However, that there should be any correlation at all for these quite disparate compounds with a nematic liquid crystal, and then at two temperatures more than 50^{o} apart, is somewhat surprising. The solute vapor pressures must therefore exert considerable influence on the retentions, despite the strong shape selectivity of the liquid-crystalline stationary phase. Nevertheless, data of the relevant form are at present available only for the five compounds shown. Further testing of the regression with many more fused-ring solutes comprising several families is therefore required before any further generalities can be drawn.

We note in passing that plots such as those shown in Figures 2-4 are important from a purely analytical standpoint, since they can be used to predict retentions (hence, separations) of other family-member or related compounds. Also, homologous-series plots of high accuracy can usually be constructed by regression of the retentions of no more than four or five compounds.

In addition, the figures reveal that relatively small differences in the chemical characteristics of solute families (e.g., substituted naphthalenes, biphenyls, diphenylmethanes, and so forth) are sufficient to result in a different retention line for each. This suggests in turn that the retention/vapor pressure method of data reduction could be employed for qualitative analysis. Moreover, if retentions at several temperatures were available a grid plot could be constructed, which would then provide a kind of two-dimensioned confirmation of at least the chemical nature of an unknown (including any chirality provided that appropriate standards were used) and, in favorable cases, its identity as well.

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From the standpoint of physicochemical measurements, plots such as those shown in Figures 2-4 are also useful for the determination of vapor pressures and, recalling Eq. (12), heats of vaporization as well. Furthermore, the method will be particularly valuable in instances where the solutes are available only in minute quantities or are substantially impure. Each of these constraints ordinarily precludes bulk vapor-pressure measurements by conventional static procedures; however, the GC technique is of course ideally suited to just such situations. Thus, it should be possible to calculate vapor pressures of high accuracy for many compounds over a range of temperatures from the retention data obtained from just a few chromatographic runs. For example, Heath and Tumlinson[16] recently reported the use of what amount to log retention plots to determine the vapor pressures of trace acetate ester ingredients employed in pheromone formulations. The interesting feature of this work was that good correlations were obtained with a chiral-nematic stationary phase, cholesteryl p-chlorocinnamate.

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