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Characterization of Solvent Properties of Gas Chromatographic Liquid Phases

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I. Introduction

In simple terms separations take place in gas–liquid chromatography because the solutes have different volatilities and/or interact to different extents with the stationary liquid phase. The mobile phase provides the column transport mechanism and to a first approximation can be neglected as a source of retention differences. Failure of the mobile phase to behave in an ideal manner can influence retention in a solute-specific manner, but at the temperatures, sample sizes, and typical column pressure drops employed in analytical gas chromatography, errors will rarely exceed a few percent if ideality is assumed for the common carrier gases used and in many cases will be no greater than the general experimental error in determining retention volumes.[1,2] Therefore, this factor need not concern us here.

A thorough description of all the factors that influence retention is not possible at present because of deficiencies in our knowledge concerning the exact nature of solute–solvent interactions. The principal interactions that affect the solubility of a solute in a liquid phase, and therefore retention, are dispersion, induction, orientation, and donor–acceptor interactions, including hydrogen bonding.[3-6] Dispersion (or London) forces arise from the electric field generated by rapidly varying dipoles formed between nuclei and electrons at zero-point motion of the molecules, acting upon the polarizability of other molecules to produce induced dipoles in phase with the instantaneous dipoles forming them. Dispersion forces are universal and independent of temperature. Induction (or Debye) forces arise from the interaction of a permanent dipole with a polarizable molecule. Orientation (or Keesom) forces arise from the net attraction between molecules or portions of molecules possessing a permanent dipole moment. Induction and orientation forces decrease with increasing temperature and at a sufficiently high temperature disappear entirely as all orientations of the dipoles become equally probable. Complementing these physical interactions are donor–acceptor interactions of a chemical nature. Donor–acceptor complexes involve special chemical bonding interactions that arise from the partial transfer of electrons from a filled orbital on the donor to a vacant orbital on the acceptor molecule. Important examples in gas–liquid chromatography are hydrogen-bonding interactions and coordination forces between π-electron-rich systems and metal ions. These interactions are usually on the order of 1–3 kcal/mol for weak interactions and 3–8 kcal/mol for strong interactions. By comparison, the sum total of physical interactions is normally on the order of 1–10 kcal/mol.

It is not the purpose of this review to condense the physical–chemical description of the above-mentioned forces into a single article. Our approach will be to review the contribution made by chromatographers to a quantitative understanding of solute–solvent interactions with a view to characterizing the properties of solvents germane to their use in gas–liquid chromatography. These approaches are global and empirical in nature, resulting from the complexities of the systems studied, and are complementary to parallel efforts in physical chemistry that attempt to explain interactions, in generally simpler systems, starting from fundamental principles. These efforts can be divided into attempts to characterize gas chromatographic solvents in terms of their solvent strength (polarity), which we will define as the capacity of a solvent for various intermolecular interactions, and solvent selectivity, the relative capacity of compared solvents for a particular intermolecular interaction. Unlike other reviews that have dealt with the popular approaches, for example, the Rohrschneider/McReynolds phase constants,[5,7-18] sol-

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ubility parameters,[11,19,20] spectroscopic methods,[21,22] the solvent selectivity triangle,[23] and thermodynamic approaches,[24] this paper will critically review the principles and supporting experimental techniques for the various methods as well as update the information contained in these earlier articles. This will necessitate briefly reviewing the experimental techniques used to determine the solute retention mechanism and solute retention index values, as errors resulting from assumptions made in these measurements can lead to erroneous conclusions concerning the exact nature of solute–solvent interactions.

II. Retention Mechanisms in Gas–Liquid Chromatography

Early attempts to understand retention in gas–liquid chromatography were based on a partition model. Since the supports commonly used in packed columns were not entirely inert, it was realized, however, that adsorption at the support interface could also contribute to retention (although this was generally treated as an inconvenience and a source of peak asymmetry and poor sample recovery for polar molecules). Careful support deactivation can minimize the undesirable effects of peak tailing and irreversible sample adsorption, but the significance of adsorption at the support interface as a general contribution to retention cannot be entirely ignored. When Martin[25,26] first suggested that adsorption at the gas–liquid interface might make a substantial contribution to retention in gas–liquid chromatography, this was met with a great deal of skepticism. However, when a liquid is spread upon a support material of high surface area, the surface-to-volume ratio becomes very large, and any differences between the bulk liquid and surface concentration of the solute could be significant. Adsorption at the liquid interface will occur in those systems where formation of a solute film significantly reduces the free energy of the surface of the liquid phase and should be reflected in static measurements of the surface tension. Proof of the significance of adsorption at the gas–liquid interface as a retention mechanism comes from a large number of gas chromatographic studies, reviewed in ref 27–30, and from static measurements of solution surface tensions for a number of solutes in common liquid phases.[26,31–33]

Any model devised to explain retention in general terms must also take into account the distribution of the liquid phase on the support surface.[34] When the support is not readily wetted by the liquid phase, the liquid phase will be present in the form of individual droplets, located primarily in the outer grain surface with little penetration into the pores. At some point in the buildup of the liquid phase coalescence will occur from microdroplets to a continuous film. Coalescence was observed to occur for ethyl- and propylammonium nitrate on Chromosorb W at a phase loading of ca. 5.5%[35] and for squalane on a silanized diatomaceous earth support at ca. 7.15%.[36] Prior to coalescence the solute is exposed directly to a large support area and a very small liquid area, a situation that is reversed after coalescence.

For liquids with good wetting characteristics it is generally assumed that at low liquid-phase loadings the liquid phase is first adsorbed as a monomolecular and multimolecular layer over the entire support surface. As the phase loading is increased, the liquid phase collects initially in the fine pores and then progressively appears in large cavities at the same time as the adsorbed layer thickens up. For diatomaceous earth supports with typical surface areas of 1–3 m^2/g, a 0.01–2% (w/w) liquid-phase loading should be adequate to cover the support with a monolayer, depending on the orientation of the adsorbed molecules. Liquid-phase molecules near the support surface exist in a regular arrangement with an entropy of solution that is lower than that of the pure liquid. It is unlikely that surface influences become completely nonexistent beyond the

TABLE I. Relative Contribution (%) to the Net Retention Volume by Different Solute Interactions

			% liquid phase					
solute	phase	interaction[a]	1	2.9	4.7	9.1	13	17
octane	Apiezon M	V_LK_L	100	100	100	100	100	100
	Carbowax 4000	V_LK_L	58	81	88	93	95	97
		$A_{GL}K_{GL}$	42	19	12	7	5	3
benzene	Apiezon M	V_LK_L	100	100	100	100	100	100
	Carbowax 4000	V_SK_S	89	96	98	56	37.5	28.2
		V_LV_S				43	61.7	71.3
		$A_{GL}K_{GL}$	11	4	2	1	0.8	0.5
1-butanol	Apiezon M	V_LK_L	13	30	42	59	67	75
		$A_{LS}K_{GLS}$	87	70	58	41	33	25
	Carbowax 4000	V_SK_S	86	95	97	60	40	30
		V_LK_L				38	59	69
		$A_{GL}K_{GL}$	14	5	3	2	1	1
2-butanone	Apiezon M	V_LK_L	52	77	84	92	94	96
		$A_{LS}K_{GLS}$	48	23	16	8	6	4
	Carbowax 4000	V_SK_S	82	93	96	60	40	30
		V_LK_L				38	58	69
		$A_{GL}K_{GL}$	18	7	4	2	2	1
chlorobenzene	Apiezon M	V_LK_L	100	100	100	100	100	100
	Carbowax 4000	V_SK_S	96	99	99	62.8	41.8	31.4
		V_LK_L				36.8	57.9	68.4
		$A_{GL}K_{GL}$	4	1	1	0.4	0.3	0.2

[a] V_LK_L = contribution due to partition with the liquid phase; $A_{GL}K_{GL}$ = contribution due to adsorption at the gas–liquid interface; V_SK_S = contribution due to partition with the structured liquid-phase layer.

first monolayer or so, for although the forces themselves are of very short range, they can be transmitted by successive polarization of adjacent molecules to a considerable depth in the liquid. The propagation of these forces is opposed by the thermal motion of the molecules and so falls off with distance after the strongly attracted first monolayer. The structured layer adjacent to the support surface may, therefore, be of considerable thickness and will likely dominate the retention characteristics of the liquid phase at low phase loadings. Its retention characteristics will be different from those of the bulk liquid, which will dominate the retention properties of the liquid phase at high phase loadings. The characteristic properties of the liquid surface will be different for the two types of liquid films, structured and bulk, and the extent of the liquid surface area will change in a nonlinear manner with increasing phase loading until at high phase loadings it asymptotically approaches a limiting value approximately equivalent to the support surface area less the area of its narrow pores and channels.

Taking the above considerations into account, Nikolov[37] proposed a general model to describe retention in gas–liquid chromatography (eq 1). In eq 1 $V_N{}^*$ is the

$$V_N{}^* = V_LK_L + \delta V_L(K_S - K_L) + (1 - \delta)A_{LS}K_{DSL} + A_{GL}K_{GL} + A_{LS}K_{GLS} \quad (1)$$

net retention volume per gram of column packing, V_L is the volume of liquid phase per gram of packing, K_L is the gas–liquid partition coefficient, δ is a constant constrained to have values of 1 when the film thickness is less than or equal to the thickness of the structured layer (d_s) and zero when the film thickness exceeds the thickness of the structured layer, K_S is the gas–liquid partition coefficient for the structured liquid layer, A_{LS} is the liquid–solid interfacial area per gram of packing, $K_{DSL} = d_s(K_S - K_L)$, A_{GL} is the gas–liquid interfacial area per gram of packing, K_{GL} is the adsorption coefficient at the gas–liquid interface, A_{LS} is the liquid–solid interfacial area per gram of packing, and K_{GLS} is the coefficient for adsorption at the liquid–solid interface. Although eq 1 provides a general description of the retention process, it is rather unwieldly. Equation 1 is linear with five unknowns (K_L, K_S, K_{DSL}, K_{GL}, and K_{GLS}) and can be solved only by a system containing a minimum of five equations. This requires knowledge of the phase characteristics (V_L, A_{GL}, and A_{LS}) for a minimum of five column packings prepared from the same support at different liquid-phase loadings. There is generally no exact method of defining the thickness of the structured layer, and therefore δ, which must be set by intuition and trial and error. Nikolov applied eq 1 to the systems Apiezon M and Carbowax 4000 on Celite at phase loadings of 1–18% (w/w). An abbreviated summary of Nikolov's data is presented in Table I. Gas–solid adsorption of polar solutes contributes substantially to retention in the Apiezon–Celite system even for the most heavily loaded columns. By contrast, gas–solid adsorption is not significant for the Carbowax–Celite system, whereas liquid interfacial adsorption contributes moderately to the retention of all solutes, decreasing rapidly with increasing liquid-phase loading. The most pronounced retention effect is due to dissolution in the structured and/or the bulk liquid stationary phase layers.

The primary interest in using gas–liquid chromatography to study solution behavior is to derive an accurate value for the gas–liquid partition coefficient, K_L, from retention data that is independent of other concurrent retention mechanisms. Equation 1 can be simplified for this purpose by making all measurements at phase loadings where the contribution of the structured liquid phase layer can be neglected. Under these circumstances eq 2 would result, which after rearrangement

$$V_N{}^* = V_LK_L + A_{GL}K_{GL} + A_{LS}K_{GLS} \quad (2)$$

to eq 3 provides a direct experimental approach to the

$$V_N{}^*/V_L = K_L + (A_{GL}K_{GL} + A_{LS}K_{GLS})(1/V_L) \quad (3)$$

gas–liquid partition coefficient that requires only easily determined column parameters.[25–29,35,38,39] A plot of $V_N{}^*/V_L$ vs $1/V_L$ will be either a curve or straight line giving K_L as the intercept at $1/V_L = 0$. The shape of the plot is dependent on the relative importance of adsorption at the gas–liquid and gas–solid interfaces. Generally, one of these terms will tend to dominate, and in most cases a linear extrapolation can be used. For solutes retained solely by gas–liquid partitioning, eq 3 predicts a zero slope.

There are other constraints on eq 1 and 3 that should not be overlooked. It is assumed that the individual retention mechanisms are independent and additive. This will only be true under conditions where the infinite dilution and zero surface coverage approximations apply or alternatively at a constant concentration with respect to the ratio of sample size to amount of liquid phase. The infinite dilution/zero surface coverage approximation will apply to very small sample sizes where the linearity of the various adsorption and partition isotherms is unperturbed and solute–solute interactions are negligible. These conditions can generally be met in gas–liquid chromatography by using sensitive detectors such as the flame ionization detector. The constancy of the solute retention volume with variation of the sample size at low sample sizes and the propagation of symmetrical peaks are a reasonable indication that the above conditions have been met. For asymmetric peaks, however, the constant-concentration method of Conder and Purnell must be employed if reliable gas–liquid partition coefficients are to be isolated.[40–43]

In some instances where the resistance to mass transfer prevents equilibrium conditions from being approached, for example in the case of high-molecular-weight viscous polymers, it may be necessary to extrapolate V_N^* to zero flow rate to obtain a true equilibrium value for V_N^*.[44] Equation 3 can only be used in place of eq 1 if contributions to retention from the structured liquid phase layer can be neglected. At precisely what phase loading this is true will depend on the surface area of the support, the liquid phase support wetting characteristics, and possibly the column temperature.[34,45–48] For any set of experimental conditions the properties of the stationary phase will resemble those of the bulk liquid at high phase loadings. Occasionally this will be true for phase loadings below 5% (w/w) on typical diatomaceous earth supports but is more likely to be generally true at phase loadings exceeding 10% (w/w). The most convincing final proof that bulk liquid properties can be determined from gas–liquid chromatographic experiments is the excellent agreement between the solution thermodynamic properties measured chromatographically and those determined by conventional static and calorimetric methods.[1,2,48]

Equation 3 also permits the measurement of the gas–liquid adsorption coefficient if the liquid-phase surface area is known for each column packing. Equation 3 is usually rearranged to eq 4 for this purpose

$$V_N^*/A_{GL} = K_{GL} + (V_L K_L)(1/A_{GL}) \qquad (4)$$

and is most useful for polar phases, where it can be reasonably assumed that solute–support interactions are negligible. Liquid surface areas have been measured by the BET method, the continuous-flow method, and the thin-film method.[1,2,46,50–52] None of these methods is free of potential errors because of the approximations made in the model used to interpret the experimental data and because of cracking of the film upon abrupt freezing in the BET and continuous-flow methods. Under these conditions the liquid phase is solidified and there is no assurance that the frozen surface can be distinguished from that of any uncoated solid that may be present. In addition, the surface areas measured by a nitrogen molecule may be larger than those measured by a larger molecule, such as acetone, which might not fit into the smaller micropores and cracks.[53] The chromatographic/tensiometer values of Martire et al.,[31] determined for thiodipropionitrile on Chromosorb W and P at different phase loadings, have frequently been adopted as a reasonable approximation for the liquid surface area for any phase of interest. However, the question of how to interpret liquid surface areas obtained in different ways clearly remains open, and published values for gas–liquid adsorption coefficients should, generally, not be considered absolute.

Contemporary studies on popular liquid phases provide accurate data for the gas–liquid partition coefficient and a qualitative indication of the importance of interfacial adsorption as a retention mechanism. Most nonpolar solutes on squalane are retained by partitioning while polar solutes, particularly those capable of hydrogen bonding, show substantial gas–liquid and/or gas–solid interactions.[35,41,54–56] Saturated hydrocarbons are retained solely by interfacial adsorption on water while for aromatic hydrocarbons partitioning and interfacial adsorption are both important retention mechanisms.[57–60] Interfacial adsorption is an important retention mechanism for saturated hydrocarbons on glycerol and for ethylene and propylene glycols which decreases in magnitude as the alkyl portion of the molecule is extended.[33,61–65] Partitioning is the most important mechanism for polar solutes. Liquid organic salts show a wide diversity of properties with respect to the retention of individual solutes that are a function of the intrinsic properties of the anion and cation.[28,35,55,56,65–77] Saturated hydrocarbons are retained largely by interfacial adsorption for low-molecular-weight salts. For alkylammonium and alkylphosphonium salts the importance of partitioning increases with the chain length of the alkyl group attached to the cation. The tendency for hydrogen-bonding solutes such as alcohols to show significant interfacial adsorption is greater than that of other polar molecules on many salts. The retention of polar solutes is generally governed by a mixed retention mechanism, but several examples of purely partitioning systems are known. Polymeric, highly fluorinated stationary phases partition with most solutes but provide relatively weak shielding of active sites on the support, which contribute substantially to the retention of polar solutes.[78]

Thus the body of experimental evidence supports the observations that interfacial adsorption seems to be most significant for saturated hydrocarbons and that this retention mechanism increases in importance as the polarity of the liquid phase increases. For polar solutes on nonpolar liquid phases solute–support interactions can be significant. Their importance as a retention mechanism tends to decline with increasing liquid-phase polarity at moderate phase loadings, and for polar phases they are not generally significant. Partitioning seems to be an important mechanism for the retention of polar molecules on all phases but not to the total exclusion of interfacial adsorption, which must be accounted for on an individual basis. Although the evidence is qualitative (surprisingly no quantitative studies exist), when solutes are retained by a mixed retention mechanism, increasing the temperature tends to diminish the importance of the contribution from adsorption relative to partitioning.

III. Retention Index System

The retention index, originally proposed by Kovats, as a method of substance identification is widely used in studies of liquid-phase characterization.[13,18,79,80] Only the latter application will be discussed here. The retention index of a substance is equivalent to 100 times the carbon number of a hypothetical *n*-alkane with the same adjusted retention time, adjusted retention volume, specific retention volume, etc. The retention index values for the *n*-alkanes, used as the fixed points on the retention index scale, are defined as 100 times the carbon number of the *n*-alkane on all phases. Consequently, the retention index of any substance X is calculated from eq 5 by coinjection of X with two

$$I = 100n + 100\frac{\log R_X - \log R_n}{\log R_{n+1} - \log R_n} \qquad (5)$$

bracketing *n*-alkanes usually differing by one carbon number.[81,82] In eq 5 R is the adjusted retention time (or adjusted retention volume, specific retention volume, etc.), n is the carbon number of the *n*-alkane eluting before substance X, and $n + 1$ is the carbon number of the *n*-alkane that elutes directly after substance X. In theory the retention index of a substance depends only on the identity of the stationary phase and the column temperature and should be independent of other chromatographic variables. In essence, this simple picture is untrue in many cases, and the retention index may be subject to systematic errors. From the retention model described by eq 2 the retention index will only be independent of the column variables when the *n*-alkanes and substance of interest are retained by a single retention mechanism, partitioning. Substantial retention index differences, exceeding 100 index units in extreme cases, have been observed for polar solutes on nonpolar phases due to support interactions.[83-90] Different retention index values for the same substance and stationary phase have been observed on supports of different surface activity. Retention index values of various substances on polar phases show an equally wide variation due to significant liquid-phase adsorption of the *n*-alkanes mainly, but also because of surface adsorption of test solutes.[79,84-87] The retention index values in this case vary with the sample size, particularly the concentration ratio of the test substance to the *n*-alkanes, and with the phase loading since the available liquid surface area declines in a nonlinear manner with increasing phase loading. Instead of treating these observations as exceptional, as has frequently been done in the literature, they can be seen to be a general consequence of the general retention model discussed in section II. For polar phases the *n*-alkanes are an unfortunate choice of retention index standards since their retention is a function of the surface area of the liquid phase, which in turn depends on the support structure. Alternative homologous series such as 2-alkanones, fatty acid methyl esters, 1-bromoalkanes, etc. are a better choice since they show a greater preference for retention by partitioning on the full polarity range of liquid phases.[13,55,56,91,92]

Equation 3 provides an option to calculate retention indices that are invariant of the chromatographic conditions, at least for those substances exhibiting significant retention by partitioning.[55,56,93] The adjusted retention time in eq 5 can be replaced by the gas–liquid partition coefficient calculated from eq 3. Even this approach is limited for polar phases by a lack of significant solubility of the *n*-alkanes.

A great many of the liquid phases currently in use are poorly characterized polymers that are subject to batch-to-batch nonuniformity in their production. Compositional changes can occur in use due to oxidation or chemical reaction with the support or catalyzed by the support and through loss of volatile prepolymers, cosolvents, etc. embedded in the original stationary phase. Molecular weight differences between fractions of the same polymer can cause significant changes in the retention index values.[90,94-98] At least part of these changes can be explained by differences in the entropic contribution to the solute solution.

IV. Rohrschneider/McReynolds Phase Constants

The most widely used method for stationary-phase characterization was first proposed by Rohrschneider[7,8,99,100] and later modified by McReynolds.[101] Vendors of stationary phases commonly publish compilations of McReynolds constants to aid phase selection for a particular problem, and researchers generally determine the same constants as proof of the unique properties of new phases. At the time McReynolds published his results for more than 200 phases, its most immediate impact was to demonstrate the great similarity that existed in the solvent properties of liquid phases in common use, bringing to an end a period of stationary-phase pollution. These data combined with various statistical techniques were used to select a much smaller group of "preferred stationary phases" that could adequately represent the full selectivity range of the original data collection.[102-106] These preferred phases, or recently improved analogues, tend to dominate the marketplace even today. Notwithstanding the wide acceptance and use of the Rohrschneider–McReynolds system, it is the purpose of this section to demonstrate the erroneous nature of the approach by the preponderance of available evidence. However, first an outline of the theoretical background to the Rohrschneider–McReynolds system will be presented.

The founding principle of the method proposed by Rohrschneider is that intermolecular forces are additive and their individual contributions to retention can be evaluated from the difference in retention index values of a series of test probes measured on the liquid phase to be characterized and on squalane, used as a nonpolar reference phase. The general approach is illustrated in Figure 1, which is a plot of the logarithm of the gas–liquid partition coefficient for a series of *n*-alkanes against their carbon number for squalane, the nonpolar reference phase, and Carbowax 20M as an example of a selective phase. In both cases an approximately linear relationship exists, conforming to the general equation

$$\log K_L^n = A + B(n) \qquad (6)$$

where K_L^n is the gas–liquid partition coefficient for an

TABLE II. Interactions Characterized by McReynolds Probes (Rohrschneider Probes in Parentheses)

symbol	test substance	interactions measured	characteristic substance group
X′	benzene	primarily dispersion with some weak proton-acceptor properties	aromatics, olefins
Y′	butanol (ethanol)	orientation properties with both proton-donor and proton-acceptor	alcohols, nitriles, acids
Z′	2-pentanone (2-butanone)	orientation properties with proton acceptor but not proton donor	ketones, ethers, aldehydes, esters, epoxides, dimethylamino derivatives
U′	nitropropane (nitromethane)	dipole orientation properties; weak proton acceptor	nitro and nitriles
S′	pyridine	weak dipole orientation with strong proton-acceptor capabilities; proton-donor properties are absent	aromatic bases
H′	2-methyl-2-pentanol		branched-chain compounds, particularly alcohols
J′	iodobutane		halogenated compounds
K′	2-octyne		
L′	1,4-dioxane	proton-acceptor but not proton-donor capabilities; weak orientation properties	
M′	*cis*-hydrindan		

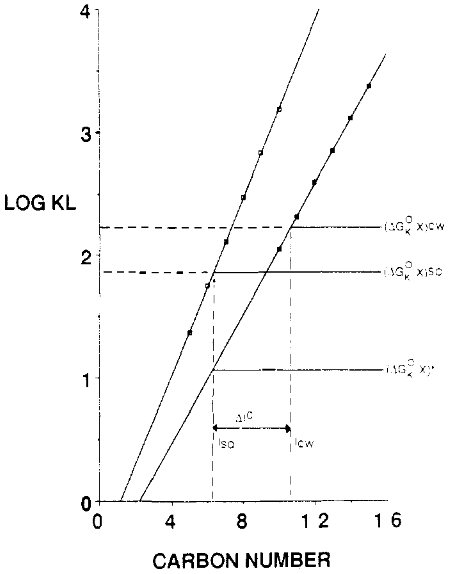

Figure 1. Definition of ΔI^c (ΔI corrected for interfacial adsorption) according to Rohrschneider (100 × carbon number). Other terms are defined in eq 8. Open squares (top line) are for *n*-alkanes on squalane, and closed squares are for *n*-alkanes on Carbowax 20M. The solute X is dioxane in this example.

n-alkane with *n* carbon atoms. If dioxane is selected as a probe of proton-donor capacity, it will elute from Carbowax 20M with an index value corresponding to I_{CW}^{DIOX} and from squalane with a value of I_{SQ}^{DIOX}. Rohrschneider assumed that the retention index of a substance on a nonpolar phase, such as squalane, is determined solely by dispersive forces and that any difference in the retention index values for a polar phase and a nonpolar phase was due to polar interactions and could be expressed by eq 7, where ΔI is the retention

$$I_{CW}^{DIOX} = I_{SQ}^{DIOX} + \Delta I \qquad (7)$$

index difference resulting from the polar interactions. A thermodynamic definition of ΔI was also provided by Rohrschneider. Using Figure 1 again, the partial molar Gibbs free energy of solution for dioxane is corrected for the contribution made by dispersion to its retention on Carbowax 20M by subtraction of the Gibbs free energy corresponding to a hypothetical *n*-alkane having an identical number of carbon atoms as that determined for dioxane on squalane. This resulted in the semiempirical equation

$$\Delta I(X) = 100\frac{(\Delta G^\circ_K(X))^{CW} - (\Delta G^\circ_K(X))^*}{(\Delta G^\circ_K(CH_2))^{CW}} \qquad (8)$$

where $(\Delta G^\circ_K(X))^{CW}$ is the partial molar Gibbs free energy of solution for dioxane in Carbowax 20M, $(\Delta G^\circ_K(X))^*$ is equivalent to the partial molar Gibbs free energy of solution determined on Carbowax 20M for a hypothetical *n*-alkane coeluting with dioxane on squalane (I_{SQ}^{DIOX} value reflected onto the Carbowax 20M plot in Figure 1), and $(\Delta G^\circ_K(CH_2))^{CW}$ is the partial molar Gibbs free energy of solution for a methylene group. Fundamental to the development of eq 8 is the equivalence between the free energy of the probe and the hypothetical *n*-alkane having the same retention properties (at a constant temperature). Rohrschneider then divided the free energy of solution into a series of terms representing the individual contributions of molecular interactions, which were assumed to be additive and composed of two terms, a solute-specific term *a*, ---, *e* and a stationary-phase characteristic term *x*, ---, *s*, allowing the retention dispersion to be written as

$$\Delta I = ax + by + cz + du + es \qquad (9)$$

Rohrschneider first attempted to describe ΔI in terms of the first three product terms but found it necessary to consider five terms, which explains the lack of sequence of the solvent terms. The set of test solutes must adequately characterize the principal interactions responsible for retention in gas chromatography: dispersion, orientation, induction, and donor–acceptor complexation. Rohrschneider suggested that benzene, ethanol, 2-butanone, nitromethane, and pyridine be used for this purpose (Table II). To evaluate the phase constants Rohrschneider assigned values of 100 for each of the solute constants in turn. For example, for benzene, $a = 100$, $b = 0$, $c = 0$, $d = 0$, $e = 0$, and, therefore, *x* is determined from eq 10. By repetition

$$x = \Delta I(\text{benzene})/100 \qquad (10)$$

of the above process for each probe in turn, all the stationary-phase constants *x*, ---, *s* can be determined. Experimentally, this requires the determination of the retention indices of the five test probes on the phase to be characterized and on a squalane column under identical experimental conditions. The stationary-phase selectivity constants are then tabulated in terms of their *x*, *y*, *z*, *u*, and *s* values. Rohrschneider's system also allows the prediction of retention index values of a solute of known solute constants, *a*, ---, *e*. These are determined from the ΔI values for the solute on at least five phases of known phase constants and solving the series of linear equations.[99,107,108] Once these values are known, the retention index of the solute on any phase of known x, ---, s values can be calculated by using eq 9. The prediction of retention index values within reasonable error limits using eq 9 has been taken as providing strong support for the correctness of the model. Rohrschneider obtained a mean error of 6 index units for 25 solutes on 22 different stationary phases compared to an average experimental difference between duplicates of 3.5 index units.[99]

McReynolds improved the applicability of the Rohrschneider method by making the following changes:

(1) Three of the probes suggested by Rohrschneider (ethanol, nitromethane, and 2-butanone) have low retention on many phases, frequently requiring gaseous hydrocarbons as bracketing standards for calculating retention indices.

(2) McReynolds replaced these with the less volatile solutes butanol, nitropropane, and 2-pentanone, thus making the determination of the retention indices more convenient.

(3) McReynolds increased the number of test solutes from 5 used by Rohrschneider to 10 so as to better characterize the liquid-phase interactions.

(4) McReynolds used ΔI rather than $\Delta I/100$ values to measure the phase constants. Thus tabulated values of McReynolds phase constants are 100 times larger than those of Rohrschneider.

(5) McReynolds used 120 instead of 100 °C for all experimental measurements. At this point we will look at some of the deficiencies in the above model as they relate to sections II and III and some additional considerations. We will try to be comprehensive in our treatment, although some points can be seen to be minor and could be dismissed as trivial while others must be considered catastrophic.

A. Questions Related to the Choice of Squalane as the Nonpolar Reference Phase

Rohrschneider and McReynolds employed squalane as the nonpolar reference phase. This imposes some unnecessary restrictions on the method due to the modest column temperature limit of squalane, 120 °C, poor oxidative stability, and poor support deactivating characteristics. Because of the low temperature limit for squalane, the method provides no information about changes in phase polarity with increasing temperature above 120 °C. Also, the method provides no means of determining the selectivity of phases with melting points or glass transition temperatures above 120 °C. Various suggestions have been forthcoming to eliminate the temperature limitation, for example the selection of a more thermally stable nonpolar reference phase such as Apiezon MH, Apolane-87 (24,24-diethyl-19,29-dioctadecylheptatetracontane), or SE-30 (poly[dimethylsiloxane]) to replace squalane. From theoretical considerations Kovats has shown that a hydrocarbon should have a molecular weight of ~2000 for use as a stationary phase in order to reproduce retention index values to ±0.2 index unit and at the same time have good thermal stability (~300 °C) and a low melting point.[95,109] Apolane-87, molecular weight 1222, is a reasonable approximation for this condition; it has a liquid range of 30–280 °C, has a clearly defined chemical structure, and is commercially available.[110-113] Apiezon greases have a sufficiently high molecular weight to ensure thermal stability, but their high degree of unsaturation will mean that retention parameters on Apiezon columns will depend upon the origin of the stationary phase. Commercial sources of Apiezon greases, which are prepared by the high-temperature treatment and molecular distillation of lubricating oils, may also contain residual carbonyl and carboxylic acid groups, which have to be removed by chromatography over alumina.[114] Exhaustive hydrogenation of Apiezon produces a new product, Apiezon MH, with <3% residual unsaturation, an approximate molecular weight of 2680 by vapor-phase osmometry[115] (but much lower by size-exclusion chromatography (~950[113])), and a liquid range of 40–200 °C. Retention index values on Apiezon MH and Apolane-87 are virtually identical and, in both instances, slightly larger than on squalane; this difference (Table III) is attributed to the molecular weight difference between the thermally stable hydrocarbon phases and squalane. This is predictable from the results of Kovats,[105] who demonstrated that the retention index values of the McReynolds test solutes will increase approximately linearly with the molecular weight of the hydrocarbon phase. The retention index values of the test solutes at infinite molecular weight are also recorded in Table III. Apolane-87 and Apiezon MH are closer to the theoretical value, indicating the inadequacy of squalane as a nonpolar reference phase due to its low molecular weight. However, it should be noted that obtaining reproducible retention indices on squalane for polar solutes is notoriously difficult, possibly because of film disruption due to the fact that the squalane columns are operated at their maximum allowable temperature.[112] There is thus a fairly large spread in the literature values for the squalane retention index values, which may also account for some of the differences observed in Table III.

TABLE III. Retention Index Values for McReynolds Test Solutes on Candidate Nonpolar Reference Phases[109,112,113]

stationary phases	retention index at 120 °C				
	benzene	butanol	2-pentanone	nitropropane	pyridine
squalane	653	590	627	622	699
Apiezon M	686	627	651	698	767
Apiezon MH	671	599	632	667	736
Apolane-87	674	600	630	664	724
SE-30	668	643	672	716	740
infinite molecular weight hydrocarbon	684	602	635	669	736

The retention index values for SE-30 are larger than those of the hydrocarbon phases and of the infinite molecular weight limit, indicating a greater capacity for selective interactions than the hydrocarbon phases (at least according to the general interpretation of McReynolds constants). This would be undesirable for a nonpolar reference phase supposedly exhibiting minimum selectivity. Also, both Apiezon MH and SE-30 are industrial products of somewhat indefinite composition, accounting for the reluctance to rely on these products for use as reference phases. This would not apply to Apolane-87, however, which is a well-characterized synthetic product and a logical choice for a reference phase, providing a much larger operating temperature range than squalane.

TABLE IV. Physical Properties of McReynolds Test Solutes

test solute	bp, °C	dipole moment, D	solubility parameters[b] S_T	δ_d	δ_{in}	δ_o	δ_a	δ_b
benzene	80.1	0.03-0.1	9.2	9.2	0	0	0	0.6
butanol	117.5	1.75	9.8	7.4		2.2	4.0	4.0
2-pentanone	102	2.82	9.0	7.0		2.3	0	1.5
nitropropane	103.5	3.59	10.4	7.0		5.0	0	1.0
pyridine	115.5	2.37	10.6	9.0	1.0	3.8	0	4.9
2-methyl-2-pentanol	121.5							
iodobutane	130	1.81						
2-octyne	125							
dioxane	101	0.45	10.1	7.8	5.2	1.0	0	4.6
cis-hydrindan[a]	159							

[a] Boiling point is given for the trans isomer. [b] See section VI for details.

The available chemical purity and stability of squalane can also be questioned. Although its chemical structure is well-known, it should be noted that it is a natural product prepared by the hydrogenation of squalene, isolated from shark liver oil. Commercial samples of squalane may contain many impurities, of which squalene and batyl alcohol are the most common.[12] Purification by chromatography over alumina and carbon is recommended to obtain consistent chromatographic properties from batch to batch.[115] All hydrocarbon phases are susceptible to oxidation, which alters their chromatographic property by the introduction of polar, oxygenated functional groups.[116-119] Oxidation of squalane, which is fully hydrogenated, arises from the presence of tertiary hydrogen atoms that react with oxygen to form thermally unstable hydroperoxides that in turn yield hydroxylic and carbonyl derivatives. Apolane-87 has a much lower concentration of tertiary hydrogens and is therefore more resistant to oxidation.[117] The properties of Apolane-87 are thus less likely to change in use than those of squalane.[112]

On theoretical and practical grounds a nonpolar reference phase may not be needed. Ashes et al.[120] have shown theoretically and demonstrated experimentally that Rohrschneider-type schemes are based on the difference in intermolecular interactions between a solute and each of two stationary phases, rather than on polar interactions alone as originally postulated. Phase constants change in magnitude when a different reference phase is used, but the numerical difference between the new phase constants is identical with that determined based on squalane. Evans et al.[121,122] proposed characterizing stationary-phase interactions in terms of selectivity indices, which are, in effect, an extension of the McReynolds system without use of a reference phase. In this scheme it is assumed that the *n*-alkanes interact exclusively by dispersion forces in all phases and that these forces increase in proportion to the molecular weight. The retention index can then be expressed in the form

$$I = I_M + I^*$$

I_M is defined as the retention index of a hypothetical *n*-alkane having the same molecular weight as the analyte and determined by the relationship $I_M = (M - 2.016)/0.14026$. I^* is the selectivity index determined by the combined effects of molecular shape and polar interactions. I^* values for the McReynolds test solutes for different stationary phases then provide a ranking of the capacity of the individual stationary phases for a particular interaction.[122]

B. Questions Related to the Type and Number of Test Solutes Required for Stationary-Phase Characterization

A sufficient number of test solutes are required to adequately characterize the principal intermolecular interactions of dispersion, induction, orientation, and donor–acceptor complexation, including hydrogen bonding. Unfortunately, no solutes interact by a single interaction, excepting the limited case of the solubility of one alkane in another. In all other cases multiple interactions are involved. For example, even *n*-alkanes in polar liquids experience induction as well as dispersive interactions. The selection of test solutes involves a combination of intuition and experiment with the additional constraint that their volatility characteristics must permit the convenient determination of retention time on a wide range of liquid phases, being neither too short nor too excessive. As stated previously, Rohrschneider used five substances for this purpose that were later extended by McReynolds to 10 selected from a total of 68 test compounds (see Table II). 2-Methyl-2-pentanol and 1-iodobutane were added to improve the prediction of branched-chain compounds and halogen derivatives, respectively. The addition of 2-octyne, dioxane, and *cis*-hydrindan gave only a small increase in predictive accuracy compared to the use of seven probes. Some physical properties of McReynolds test solutes are summarized in Table IV.[11,20,123,124] This is the physical interpretation of the observations presented in Table II and confirms that the selection of test solutes is correct in terms of sense although duplicates for certain interactions exist. This is because the data analysis used by Rohrschneider and McReynolds was based on the number of probes required to accurately predict retention, which may exceed the number of probes required to characterize the magnitude of solvent interactions. Different statistical techniques when applied to the data of Rohrschneider and McReynolds do not provide a definite answer. Hartkopf et al.[125] found that with four test solutes [benzene, nitroethane, 1-propanol (or chloroform), and dioxane] they could reproduce Rohrschneider's results with similar accuracy to the five test solutes Rohrschneider used. Lowry et al.,[126] using a nearest-neighbor technique, showed that two sets of three probes and several sets of four probes gave results similar to those obtained with the first five of the test probes evaluated by McReynolds. Factor analysis has been used to indicate how many of the original ten McReynolds probes could be eliminated for the accurate prediction of retention.[127]

TABLE V. Capacity Factor Values for Some McReynolds Test Solutes on Different Stationary Phases[a]

	capacity factor					
stationary phase	benzene	butanol	2-pentanone	nitropropane	2-octyne	dioxane
squalane	4.6	2.8	3.8	4.6	23.9	4.7
QF-1	1.3	1.5	3.8	7.6	2.8	2.9
OV-225	3.0	5.7	5.4	16.0	7.0	6.3
Carbowax 20M	4.0	12.2	4.8	20.0	7.7	8.3
DEGS	1.5	6.2	2.6	9.6	2.0	6.1
OV-275	1.2	3.6	2.2	9.5	1.0	3.8

It was concluded that seven probes were necessary to reproduce the retention indices, but the identity was less important than the actual number. Other applications of factor analysis to the McReynolds data set provide some insight into the number of factors required to describe the data but do not lead to the identification of individual test solutes of value for phase characterization.[128,129] Common practice dictates that the first five McReynolds probes are used for stationary-phase characterization. Neither theoretical nor practical considerations indicate that these probes are inadequate for this purpose. It would seem reasonable that alternative solutes could be substituted for some of the McReynolds solutes without changing the effectiveness of the classification scheme, but there has been little impetus to do this. However, it is important to establish that the test solutes are retained by partitioning on phases covering a wide range of polarity and that they exhibit reasonable retention characteristics so that accurate retention values can be determined. The first point seems to be largely true for the McReynolds test solutes on a wide range of stationary phases.[35,55,56,71,72] However, the retention requirement may not be adequately met in general practice (Table V).[55] The capacity factor values in Table V, which were measured at 80.8 °C (approximately 40 °C below the temperature recommended by McReynolds), indicate that on many phases the test solutes, particularly benzene and 2-octyne, are insufficiently retained for their intended purpose. In other cases some probes such as butanol have good retention characteristics on some phases but are only poorly retained on squalane and QF-1.

Thus the character of the test solutes selected by McReynolds would seem to be adequate but their volatility range is inadequate. In future studies consideration should be given to the development of a new set of test solutes better matching the capacity factor requirements for a wide range of phases of different solvent strength. The number of new probes required to adequately characterize selectivity cannot be stated exactly but will probably be a lot less than the ten that were selected by McReynolds.

C. Questions Related to the Use of *n*-Alkanes as Retention Index Standards

The retention index concept has been widely adopted in gas chromatography almost since its introduction over 25 years ago.[12,13,18] When the conditions are most favorable it provides an accurate method of determining the retention volume of a solute relative to two internal standards and is largely independent of the measurement conditions except for temperature. It is a matter of record that retention index values can be determined more precisely than absolute retention volumes since the latter are influenced by the experimental conditions, which must be determined and controlled to a high degree of accuracy.[130,131] It was, therefore, natural that retention index values were selected as the basis for the stationary phase characterization method of Rohrschneider and McReynolds. The retention index system, however, is at the heart of the flaw in the Rohrschneider–McReynolds method of phase characterization.

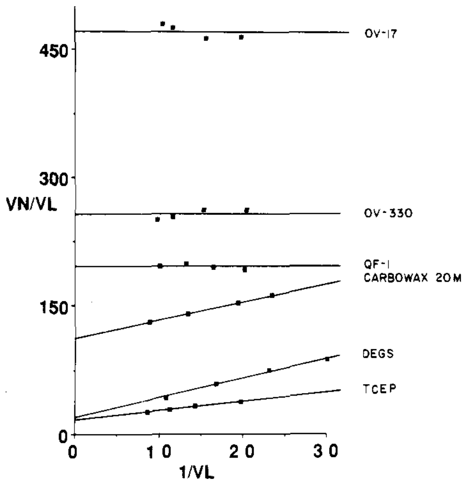

Figure 2. Plot of V_N^*/V_L vs $1/V_L$ for *n*-decane on a series of stationary phases of different polarity. Stationary phases are identified in Table VI.

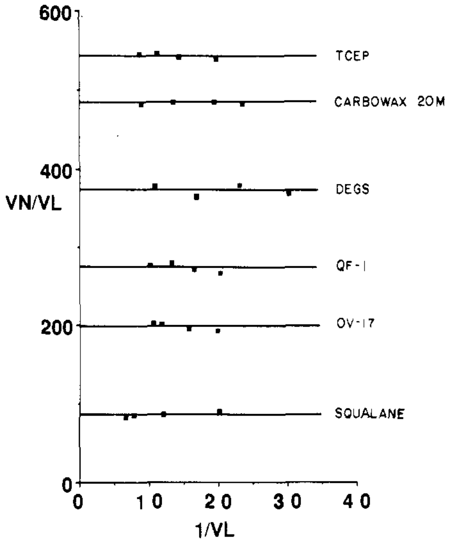

Figure 3. Plot of V_N^*/V_L vs $1/V_L$ for 1-nitropropane on a series of stationary phases of different polarity. Stationary phases are identified in Table VI.

The determination of McReynolds phase constants is based on an assumed partition model for both the *n*-alkanes and test solutes in squalane and the polar stationary phase to be characterized. Data are presented in the form of eq 3 for the hydrocarbon *n*-decane (Figure 2) and the test solutes 1-nitropropane (Figure 3) and dioxane (Figure 4) for some common stationary

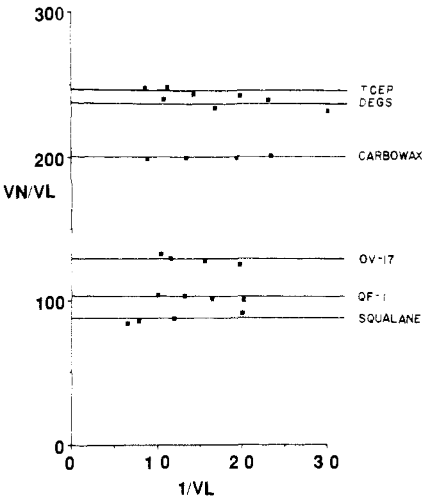

Figure 4. Plot of V_N^*/V_L vs $1/V_L$ for dioxane on a series of stationary phases of different polarity. Stationary phases are identified in Table VI.

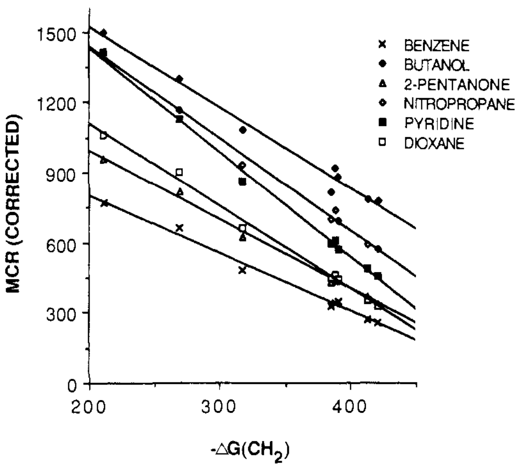

Figure 5. Plot of McReynolds phase constants (corrected for interfacial adsorption) against the partial molar Gibbs free energy for a methylene group for eight liquid organic salts (data recalculated from ref 76).

phases spanning a wide polarity range.[55,56,132] The dominant retention mechanism for 1-nitropropane and dioxane is partitioning on all phases as indicated by the zero gradient. In the case of *n*-decane, partitioning dominates for the nonpolar phases but with increasing polarity, interfacial adsorption becomes significant, for example Carbowax 20M, and eventually becomes dominant as indicated by DEGS and TCEP. In the latter instance the partition coefficients are very small and show no regular increase with increasing number of methylene groups. Using retention index values corrected for interfacial adsorption, Poole and co-workers[35,55,56,72,76] have indicated the relative magnitude of the errors that exist in calculating McReynolds phase constants under the conditions proposed by McReynolds. These errors varied from 0 to 40% for liquid phases behaving ideally and exhibiting a mixed retention mechanism. These same authors indicated that it was not possible to determine meaningful McReynolds constants for the most polar phases such as poly[(dicyanoallyl)siloxane] (OV-275), poly(diethylene glycol succinate) (DEGS), and 1,2,3-tris(2-cyanoethoxy)propane (TCEP) and the liquid organic salts ethylammonium and propylammonium nitrate. This is a very serious consideration because these are some of the most selective solvents in use in gas chromatography and any method that is unable to characterize their properties, or, even worse, misclassifies them, is of limited value and potentially dangerous as it leads to the perpetuation of false assumptions. The choice of the *n*-alkanes as standards for measuring retention index differences can therefore be seen to be a poor choice since on most polar phases it cannot be assumed that their retention is not caused by mechanisms other than gas–liquid partitioning.

The retention index values could be determined by using standards that are retained by gas–liquid partitioning on most, if not all, phases.[55,56] The homologous series of 2-alkanones and fatty acid methyl esters usually meet this requirement. Where a comparison of phase constants was possible, there was only poor agreement in the ranking of phases for a particular interaction. It was concluded that the type of standards used to determine the retention index values can influence the retention differences for compared phases and that the retention index differences themselves are composite parameters determined by a contribution from the test probe and the retention index markers. In fact, on the basis of largely philosophical grounds, Aue and Paramasigamani[133] concluded that the magnitude of the McReynolds phase constants was determined largely by the solubility of the *n*-alkanes in the stationary phase and only to a much smaller extent by specific interactions of the test solutes. Roth and Novak[134] demonstrated a general correlation between the ΔI values of McReynolds for seven test solutes and the partial molar Gibbs free energy of solution per methylene group on 55 phases. Correlation coefficients, r = 0.7–0.9, were only moderate due to the fact that no allowance was made for interfacial adsorption on the phases studied. Using corrected retention indices, Poole et al.[76,135] demonstrated a fairly general correlation for corrected McReynolds phase constants and the partial molar Gibbs free energy of solution for a methylene group on many phases. In all cases correlation coefficients (r^2) exceeded 0.9 and in most cases exceeded 0.95. Figure 5 illustrates some typical data for six McReynolds test solutes on eight liquid organic salt phases. Confirming the importance of the *n*-alkanes in determining the magnitude of the McReynolds phase constants, these authors pointed out that there was no correlation between the partial molar Gibbs free energy of solution for the test solutes and the partial molar Gibbs free energy of solution per methylene group for the *n*-alkanes on the same group of phases, thus establishing the dominant role of the solubility of the *n*-alkanes in controlling the magnitude of the McReynolds phase constants rather than the intended selective interaction anticipated for the test solutes.

In thermodynamic terms Rohrschneider identified ΔI(X) with the difference in the partial molar Gibbs free energy of solution of solute X on the polar phase and squalane as a nonpolar reference phase according to eq 8.[99] Based on earlier studies of Golovnya et al.,[24,137–140] who derived several relationships between the retention index and the thermodynamic properties of the retention index standards and test solutes, a new equation was derived relating the partial molar Gibbs free energy of solution for any solute to the retention index values of the test solutes on two phases[132,136]

$$\delta(\Delta G^\circ{}_K(X))^P_{SQ} = \frac{2.3RT}{100}(I^X_{SQ}B_{SQ} - I^X_P B_P) + 2.3RT(A_{SQ} - A_P) \quad (11)$$

where $\delta(\Delta G^\circ{}_K(X)^P_{SQ}$ is the difference in the partial molar Gibbs free energy of solution for solute X in the polar phase P and the nonpolar reference phase squalane (SQ). Equation 11 was shown to predict values of Gibbs free energies with a high degree of accuracy and is a general relationship, being equally applicable to retention index values measured on any pair of phases and for any homologous series used as retention index standards. It reveals the complex relationship between stationary-phase selectivity schemes based on $\delta(\Delta G^\circ{}_K(X)^P_{SQ}$ and McReynolds phase constants ($I^X_P - I^X_{SQ}$) (section VIII).

D. Questions Related to the Selection of the Measurement Temperature

The standard temperature for the determination of Rohrschneider constants is 100 °C and for McReynolds constants 120 °C. This limitation arises from the use of squalane as a standard nonpolar reference phase and was discussed in section III.A. Replacing squalane by another phase with a higher operating temperature limit would only provide half a solution to the problem of characterizing stationary phases at temperatures higher than those available with squalane. The test solutes suggested by McReynolds are not sufficiently retained at high temperatures on most phases to provide meaningful data. Vernon and Gopal[141] suggested replacing the first five McReynolds probes by *n*-butylbenzene, octanol, 2-octanone, 1-nitrohexane, and collidine for determining phase constants at 180 °C using a calculation method otherwise identical with that of McReynolds. Other probe sets discussed in the literature have been applied qualitatively for comparing the properties of a limited number of phases. These include monofunctional benzene derivatives (*n*-butylbenzene, benzyl alcohol, acetophenone, nitrobenzene, and aniline),[68,70,77,115] monofunctional naphthalene derivatives,[67,70] monofunctional biphenyl derivatives (biphenyl, 4-phenylpyridine, 4-hydroxybiphenyl, and 4-aminobiphenyl),[142] a mixture comprised of *n*-decane, naphthalene, dipyridyl, and benzil,[143] and linalool, estragole, and carvone.[144] Clearly, there is a need for standardization of both the test solutes and methods to be used to characterize stationary-phase selectivity at temperatures above 120 °C.

Temperature as a general parameter affecting the strength of solute–solvent interactions is in need of quantitative studies. Except for dispersive interactions the principal intermolecular forces between solute and liquid phase are temperature dependent and unlikely to change in an identical manner with temperature for all phases. The selectivity ranking of liquid phases at different temperatures may not be the same and at high temperatures could well be different from their ranking at 120 °C. Vernon and Gopal noted reasonable agreement between the ranking order of six stationary phases at 120 and 180 °C using two different probe sets.[141] However, it is difficult to interpret their data in terms of the effect of temperature on selectivity. Ashes and Haken[145] studied the influence of temperature over the range 90–150 °C on McReynolds phase constants for four stationary phases. They observed, in general, a small linear increase in the value of the phase constants or no significant change as a function of temperature, which also depended on both the identity of the solute and the stationary phase. An interpretation, however, in terms of selectivity changes is difficult because the phase constants, as shown in the previous section, are a relative value that depends on both the solubility of the *n*-alkane retention index standards and test solutes in the compared phases. Also the phase constants were not corrected for contributions from interfacial adsorption, and the results may not be interpretable in terms of a simple partition model. In the future the influence of temperature on stationary-phase selectivity will have to be tackled in a serious and quantitative manner.

E. Questions Related to the Reliability of the Experimental Data of Rohrschneider and McReynolds

Most stationary-phase classification schemes and models to predict retention as a function of sample properties are based on the original experimental data published by McReynolds[107,149] and to a lesser extent those of Rohrschneider[99,100] or Rohrschneider parameters determined by Supina.[9,10] The McReynolds constants published in many handbooks and supply house catalogues are taken from the original data of McReynolds and have not been redetermined except for phases that were not in existence at the time that McReynolds published his compilation of selectivity constants for over 200 phases. Surprisingly, McReynolds' paper contains scant information concerning the experimental conditions used to determine the phase constants beyond the fact that all data were collected at 120 °C.[101] However, McReynolds authored an earlier compilation of retention data for over 60 phases that was probably incorporated into his later work.[146] In this compilation the stationary-phase loading is stated to be between 20 and 25% (w/w), the support is Celite 545, the sample size is 0.5 μL except for some columns where a smaller size was used to avoid skewed peaks, and a wetting agent, Poly-tergent J-300, was added to each column at ca. 0.5% (w/w) to reduce tailing of polar compounds and to give more efficient columns. The weight of the liquid phase was assumed to be the same as that placed on the column and was not corrected for phase lost in the coating process or light ends removed during conditioning or data collection. It was also noted that on several columns the retention index values were determined retrospectively using the indirect method (i.e., bracketing hydrocarbons were not injected simultaneously with each test solute). The retention time of *n*-alkanes less than butane and greater than docosane were estimated by extrapolation. Columns of lengths of 4, 12, or 25 ft were used for the same phase depending on the volatility of the test solutes. Supina used a temperature of 100 °C, 20% (w/w) phase loading on Chromosorb W-AW, 0.1% (w/w) of Alkertage T as a wetting agent to minimize tailing, and 20-ft columns. Large sample sizes were used when retention indices were found to vary as a function of sample size.

As best we can judge from the above summary of the experimental conditions, the probability of large errors in the data compilations is very great. First of all, the

TABLE VI. Gas-Liquid Partition Coefficients for McReynolds Test Solutes on Some Representative Stationary Phases at 80.8 °C

	McReynolds test solutes[b]									
stationary phase[a]	X′	Y′	Z′	U′	S′	H′	J′	K′	L′	M′
squalane	80.8	47.8	67.2	80.6	114.7	111.9	310.8	420.1	81.4	1394.1
OV-17	77.6	69.6	94.8	198.4	196.9	104.9	258.2	312.4	129.2	668.8
OV-105	61.5	87.0	78.9	126.3	118.9	110.1	186.2	256.9	84.7	575.0
OV-330	88.9	199.5	111.9	350.4	291.2	197.2	247.3	245.2	161.0	432.9
OV-225	70.5	133.7	129.6	378.6	256.7	152.2	197.4	167.2	148.1	320.4
QF-1	45.6	52.4	136.8	274.1	146.9	85.3	118.4	100.2	101.6	228.0
Carbowax 20M	99.1	292.1	114.2	483.6	401.2	212.9	204.3	180.3	199.6	264.1
DPAT	77.5	583.3	177.0	479.2		425.0	143.4	74.8	229.8	130.8
DEGS	58.2	240.2	97.9	372.8		186.9	89.9	68.7	236.1	86.1
BAT	37.6	658.4	203.6	304.7		476.7	74.2	38.2	406.3	79.0
sBAT	38.3	795.8	249.1	355.8		553.9	74.4	38.7	505.2	65.2
TCEP	62.4	205.0	133.7	543.1	424.9	139.7	92.3	62.6	245.9	68.1
OV-275	40.9	110.6	67.7	313.1	225.5		49.6	25.5	126.4	37.6

[a] Squalane = 2,6,10,15,19,23-hexamethyltetracosane, OV-17 = poly(phenylmethylsiloxane), OV-105 = poly[(cyanopropyl)methylphenylmethylsiloxane], OV-330 = dimethylsilicone/Carbowax copolymer, QF-1 = poly[(trifluoropropyl)methylsiloxane], Carbowax 20M = poly(ethylene glycol), DPAT = di-*n*-propylammonium thiocyanate, DEGS = poly(diethylene glycol succinate), BAT = *n*-butylammonium thiocyanate, sBAT = *sec*-butylammonium thiocyanate, TCEP = 1,2,3-tris[(2-cyanoethoxy)propane], and OV-275 = poly[bis(cyanoallyl)siloxane]. [b] See Table II for solute identification.

addition of a polar wetting agent to all phases must have modified the retention properties of some phases, particularly those of low polarity.[147] The use of highly active supports may also have influenced the retention indices as discussed earlier (this may have been masked to some extent by the properties of the wetting agent). The use of large sample sizes would tend to indicate that the condition of infinite dilution and/or zero coverage was not met in all cases. Neither data collection takes into account the influence of interfacial adsorption on retention, and clearly, from the earlier discussion in section II, the retention index differences cannot be assumed to accurately describe the solution properties of the solute in the stationary phase. Of all classes of organic compounds the *n*-alkanes are the most prone to interfacial adsorption and, therefore, the least likely to provide accurate values for the retention index on a variety of phases spanning a wide polarity range.

For future studies of solvent interactions in gas-liquid chromatography new data compilations of accurate retention indices or gas-liquid partition coefficients corrected for interfacial adsorption and for solutes that are better retained than those suggested by Rohrschneider and McReynolds are needed. The onerous task of characterizing the properties of several hundred phases is no longer needed as many of the phases characterized by McReynolds were industrial products of poorly defined composition and have long since passed into disuse, at least in the chromatographic sense. A much smaller group of preferred phases that the various manufacturers of liquid phases would agree to maintain within tight, widely publicized, specifications would suffice for most analysts and theoreticians. Until more reliable data are available the self-serving analysis of the data set of McReynolds should be seen for what it is. Most models of various kinds based on this data set have been trained to reproduce the data set, and the conclusions reached from them may be divorced from reality as far as solution properties and solvent selectivity characteristics are concerned. A small number of accurately determined gas-liquid partition coefficients for McReynolds test solutes on a limited selection of selective phases is given in Table VI and will have to suffice for studying solution characteristics until a larger standardized collection of data for preferred liquid phases becomes available.

V. Solvent Selectivity Triangle

Snyder proposed the characterization of chromatographic solvents by the relative strength of hydrogen-bonding interactions (proton donor-acceptor) and orientation interactions.[148,149] The test solutes ethanol, dioxane, and nitromethane were selected to measure the relative strength of the three intermolecular forces determined as the retention index difference of the test solute on a polar phase and on squalane as a nonpolar reference phase in a manner similar to that of Rohrschneider. The selectivity coefficients, x_i, are then calculated and plotted on the face of the selectivity triangle by using eq 12, where x_e is the selectivity parameter for proton-acceptor interactions with a retention index difference of ΔI_e, x_d is the selectivity parameter for proton-donor interactions with a retention index difference of ΔI_d, and x_n is the selectivity parameter for orientation interactions with a retention index difference of ΔI_n. The denominator of eq 12 reflects the excess retention index due to polar interactions; the larger the value of $\sum \Delta I_i$, the more significant the polar contribution of the stationary phase to the retention of a solute. The most selective stationary phases will have a large value of $\sum \Delta I_i$ and a large value of one of the x_i coefficients. Nonselective phases have small values of $\sum \Delta I_i$ and x_i values close to 0.3 (that is located at the center of the triangle). Klee et al.[150] and Poole and Kersten[56] have classified several commonly used stationary phases by using the procedure outlined by Snyder. Na and Rogers[151] noted that the position of a solvent within the selectivity triangle varied with the selection of the test solutes, including the use of homologues of the original test solutes used by Snyder. Betts suggested that 2-octyne, 1-butanol, and pyridine were more appropriate probes than those suggested by Snyder for estimating polar interactions.[152] Betts also used the absolute retention index value on each phase to calculate the selectivity indices without subtracting the value for the test solutes on squalane. However, it is not clear what advantage was gained by the change

$$x_i = \Delta I_i / \sum \Delta I_i \quad \text{for i = e, d, or n} \qquad (12)$$

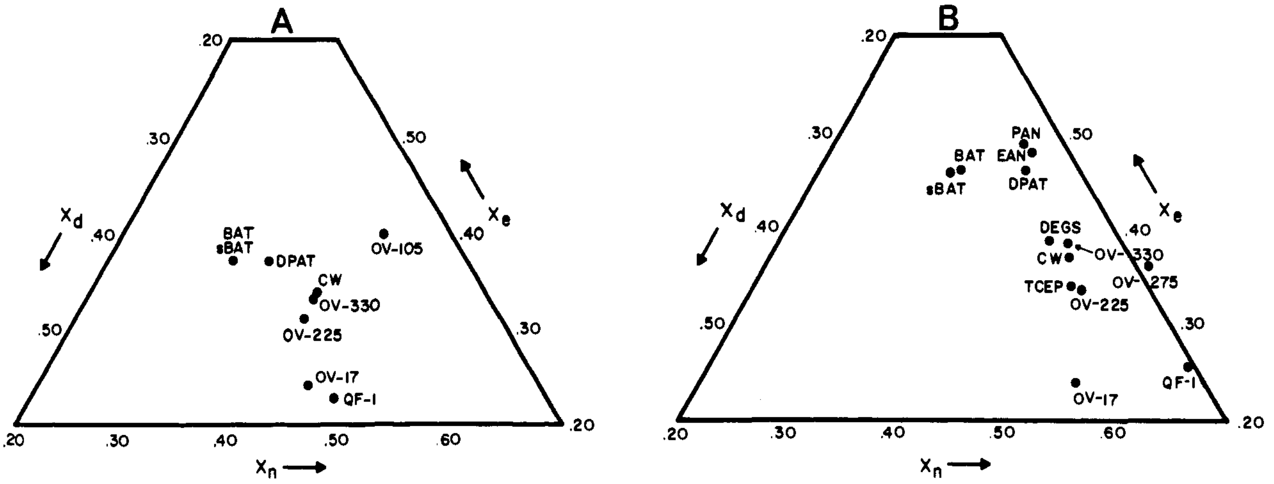

Figure 6. Representation of stationary-phase selectivity using the Snyder triangle method. Triangle A was plotted according to eq 12, and triangle B according to eq 14.

in calculation method and test solutes. Essentially, the new probe 2-octyne measures mainly dispersive interactions so that the nature of the interactions encompassed within the boundaries of the triangle is changed. This approach is related to earlier studies by Brown,[153] who used the retention volumes of various test solutes on different stationary phases plotted as triangular coordinates to indicate selective stationary-phase interactions. Plotting retention data in triangular form has strong visual impact, which is lost as additional dimensions are added. It is thus most useful for plotting systems with three variables, and as far as solvent selectivity factors are concerned, the original choice of axes for proton donor–acceptor and orientation interactions by Snyder is quite reasonable.

Since retention index differences are used to calculate selectivity indices, much of the previous discussion of the Rohrschneider–McReynolds system is also applicable here. The quantitative accuracy of published indices is compromised by a failure to account for the influence of interfacial adsorption as a retention mechanism and by the low retention of the test solutes on some phases.[56] Retention index values cannot be determined for some of the most selective phases since the n-alkane retention index standards do not show any significant partitioning with these phases. To eliminate the inconsistencies in Snyder's approach resulting from the use of the n-alkane retention index system, the selectivity parameters were redefined by Kersten and Poole[56] in thermodynamic terms using eq 13–15, where

$$\delta(\Delta G^\circ_K(i))^P_{SQ} = (\Delta G^\circ_K(i))^P - (\Delta G^\circ_K(i))^{SQ} \quad (13)$$

$$x_i = \delta(\Delta G^\circ_K(i))^P_{SQ} / \sum \delta(\Delta G^\circ_K(i))^P_{SQ} \quad (14)$$

$$\sum \delta(\Delta G^\circ_K(i))^P_{SQ} = \delta(\Delta G^\circ_K(e))^P_{SQ} + \delta(\Delta G^\circ_K(n))^P_{SQ} + \delta(\Delta G^\circ_K(d))^P_{SQ} \quad (15)$$

$(\Delta G^\circ_K(i))$ is the partial molar Gibbs free energy of solution of solute i, $\delta(\Delta G^\circ_K(i))^P_{SQ}$ is the difference in the partial molar Gibbs free energy of solution for solute i in the polar phase P and the nonpolar reference phase squalane (SQ), and e, n, and d refer to the test solutes ethanol, nitromethane, and dioxane. The position of individual phases in selectivity groups is similar for selectivity parameters calculated by using either corrected retention indices or differences in the partial molar Gibbs free energy of solution except that all phases are displaced to the right in the triangle constructed by using the Gibbs free energy differences (Figure 6). This shift results from the weak interactions for the stationary phases with the proton-acceptor solute dioxane. This clearly indicates a deficiency of thermally stable proton-donor phases for gas chromatography and the need for new phases with strong proton-donor properties. In agreement with other authors,[150,151] it was also found that the position of a phase within the selectivity triangle is a function of the test solutes used for the species. This is not too surprising since the test solutes do not characterize a single intermolecular interaction but a composite range of interactions and the nature of the selectivity space bounded by the triangle is changed when different test solutes are used.

VI. Solubility Parameters

The Hildebrand solubility parameter approach to solution behavior offers a starting point for a general treatment of stationary-phase selectivity.[19,29] The major limitation of the classical approach is that it applies only to interactions in nonpolar systems. Several workers have extended the concept to polar systems by assuming that the various interaction energies in solution are additive. Karger et al.,[154,155] Tijssen et al.,[156] Laffort,[157] and Poole et al.[158] have employed the extended solubility parameter approach to liquid-phase characterization based on eq 16, where δ_T is the total

$$\delta_T^2 = \delta_d^2 + 2\delta_{in}\delta_d + \delta_o^2 + 2\delta_a\delta_b \quad (16)$$

solubility parameter, δ_d is a measure of the ability of a substance to participate in dispersive interactions, δ_o is a measure of the ability of a substance to participate in orientation interactions, δ_{in} is a measure of the ability of a substance to induce a dipole moment in surrounding molecules, and δ_a and δ_b are measures of the ability of a substance to function as a proton donor or acceptor, respectively. The total solubility parameter, δ_T, is roughly equivalent to the polarity of a substance, and the partial solubility parameters δ_d, δ_o, δ_{in}, δ_a, and δ_b are measures of the ability of that substance to enter into selective interactions. The larger the value of the solubility parameter, the stronger the interaction measured by that parameter. The solubility parameters

TABLE VII. Solubility Parameters for Some Representative Stationary Phases and Test Solutes[a]

solvent	S_T	δ_d	δ_{in}	δ_o	δ_a	δ_b
SE-30 [poly(dimethylsiloxane)]		7.6	0	0	0	0
OV-7 [poly(methylphenylsiloxane) (contains 20% phenyl)]		8.6	0.1	0.35	0	0.1
OV-25 [poly(methylphenylsiloxane) (contains 75% phenyl)]		10.2	0.8	0.6	0	0.3
XE-60 [poly[(cyanoethyl)methylsiloxane] (contains 25% cyanoethyl)]		7.8	2.3	1.6	0	0.3
OV-225 [poly[(cyanoethyl)methylphenylsiloxane] (contains 25% cyanoethyl, 25% phenyl)]		9.2	1.9	1.4	0	0.3
Silar 5CP [poly[(cyanoethyl)phenylsiloxane] (contains 50% cyanoethyl)]		9.6	3.4	2.0	0	0.3
ethanol	12.7	6.8	0.5	3.4	6.9	6.9
2-pentanone	9.0	7.0	*b*	2.3		1.5
nitromethane	12.9	7.3	3.0	8.3		1.2
hexane	7.3	7.3				
triethylamine	7.5	7.5				4.5
chloroform	9.3	8.1	3.0	0.5	6.5	0.5
tetrahydofuran	9.1	7.6	3.5	0.8		3.7
acetone	9.6	6.8	5.1	1.5		3.0
acetonitrile	12.1	6.5	8.2	2.8		3.8
water	23.4	6.3	*b*	*b*	large	large

[a] Units are $(\mathrm{cal/mol})^{1/2}$. [b] Not determined.

can be calculated from the physical properties of the pure substances, although disagreement exists as to the best method and is reflected in the discordance between quoted values for the same solubility parameter. This and the fact that the model is only an approximation for polar substances (particularly for those capable of strong association) has contributed to the diminished interest in this approach to stationary-phase characterization. Some typical values of the solubility parameters for common phases and test solutes used in selectivity characterization in gas chromatography are summarized in Tables IV and VII.

VII. Spectroscopic Methods

Numerous spectroscopic methods have been discussed for determining the polarity and/or selectivity of low-molecular-weight and low-viscosity solvents.[21,22,158-160] Similar techniques have rarely been applied to characterize polymeric materials similar to those most frequently employed in gas chromatography. From the chromatographic point of view, the Kamlet–Taft solvatochromic approach developed by Carr and co-workers[161-163] and the development of selectivity indices from the correlation of gas chromatographic retention data with spectroscopic data by Hawkes and co-workers[164,165] are the most complete and useful studies.

Hawkes and co-workers made direct measurement of dispersion, orientation, acidity, and basicity from refractive indices and infrared, ultraviolet, and nuclear magnetic resonance spectroscopy. The spectroscopic data were compared with results obtained from gas chromatography to select a series of test solutes suitable for evaluating the selectivity of stationary phases by a simple, reliable gas chromatographic technique. Dispersion interactions were measured from refractive indices.[164] Orientation interactions were determined from the wavelength shift of the band at 650 ± 10 cm^{-1} in the infrared spectra of 1-chlorohexane dissolved in the stationary phase and squalane as a reference phase. The frequency shift was correlated with the relative retention of 1-octene to *n*-octane corrected for dispersion forces using either eq 17 or a second method based

$$P = [RT \ln (k_2/k_1) + 3\delta_d^2 - 14\delta_d]/100 \qquad (17)$$

on the use of principal component analysis.[165,166] In eq 17 P is the polarity index, k_2 is the capacity factor for 1-octene, k_1 is the capacity factor for *n*-octane, R is the universal gas constant, and δ_d is the solubility parameter characteristic of dispersion. Here, it is assumed that the separation of the alkene from the alkane is caused solely by the induced dipole impressed on the π-bond of the alkene. The acidity index was based on the equilibrium constant for the interaction between chloroform (used as an acid) and the liquid phase determined by NMR proton shifts. The spectroscopic data were found to correlate well with the relative retention of *n*-butylamine and chlorobutane, which were selected because their retention characteristics should differ only because they interact differently with the acid groups of the stationary phase. The two test solutes have similar refractive indices, indicating a similar potential for dispersive interactions. The differences in molecular volumes can be offset by referring data to the nonacidic reference stationary phase squalane, eq 18, where R_{ac}

$$\text{acidity} = 4(\log R_{ac(P)} - \log R_{ac(SQ)}) \qquad (18)$$

is the relative retention of *n*-butylamine/chlorobutane on the polar phase, P, and squalane, SQ. The basicity of the stationary phases was determined by the position of the visible absorption band for iodine (450–520 nm) when dissolved in the stationary phase. The position of the absorption band was found to correlate strongly with the relative retention ratio of chloroform to carbon tetrachloride, again corrected for dispersion forces by referring the data to that obtained on squalane, eq 19,

$$\text{basicity} = 10(\log R_{ba(P)} - \log R_{ba(SQ)}) \qquad (19)$$

where R_{ba} is the relative retention of chloroform/carbon tetrachloride on the polar phase, P, and on squalane, SQ. Chloroform contains an acidic proton, which is replaced by an unreplaceable group in carbon tetrachloride, and the two solutes together are thus capable of probing the basicity of the phase to be characterized.

Some indices measured for common stationary phases are summarized in Table VIII.[167] As a number of assumptions have been made in developing these indices, they should be considered as qualitatively reliable and as a useful approach to the gross ranking of phases by their ability to enter into a specific intermolecular interactions.

Kamlet, Taft, and co-workers have used linear solvation energy relationships and solvatochromic indi-

TABLE VIII. Dispersion, Orientation, Basicity, and Acidity Indices for Some Common Phases according to Hawkes[a]

stationary phase	solubility parameter for dispersion (δ_d)	polarity index	basicity index	acidity index
squalane	8.5	0	0	0
poly(diethylene glycol succinate)	8.5	4	5	1
poly(ethylene glycol)	8.6	3	5	1
poly[(3,3,3-trifluoropropyl)-methylsiloxane]	8.6	2	1	2
poly(dimethylsiloxane)	9.0	0	0	0
poly(phenyl ether)	10.1	2	2	0
poly(phenyl-methylsiloxane)	11.6	1	2	0
poly[(3-cyanopropyl)-methylsiloxane]	10.4	4	?	1

[a] Normal range for δ_d = 7.0–11.6; normal range for polarity index = 0–6; normal range for basicity index = 0–7; normal range for acidity index = 0–6.

cator compounds to characterize the properties of numerous solvents used in organic chemistry.[21,168] Using their nomenclature, the observed property of a solvatochromic indicator XYZ in a solvent is comprised of a contribution from the indicator in a chosen reference solvent XYZ_0 and additional contributions that depend on the solvent dipolarity/polarizability (π^*) and the hydrogen bond donor (α) and hydrogen bond acceptor (β) properties of the solvent (eq 20). The coefficients

$$XYZ = XYZ_0 + s(\pi^* + d\delta) + a\alpha + b\beta \qquad (20)$$

s, a, d, and b are a measure of the susceptibility of the indicator for a particular interaction, and δ is the polarizability correction term. By selecting indicators for which a, b, and d are assumed to be approximately zero and/or δ is zero, one may simplify eq 20. For stationary-phase characterization π^*, α, and β values have been determined for six liquid organic salts,[158] and π^* values have been determined for a series of methylphenylsiloxane phases.[163] In the latter study the average π^* value was found to correlate with the mole percent of phenyl groups in the methylphenylsiloxane polymer. In this case it was argued that the increase in the π^* value was due to the increase in polarizability of the methylphenylsiloxane phases as successive methyl groups were replaced by phenyl. As the solvatochromic approach has a sound basis in theory and has enjoyed unparalleled success in describing solvent properties in organic chemistry, further extensions of the method to gas chromatography can be anticipated. Applications to liquid chromatography have already borne fruit in explaining mobile-phase selectivity characteristics.[169–171]

VIII. Thermodynamic Approaches

Thermodynamic approaches to the measurement of selectivity are based on the determination of the partial molar Gibbs free energy of solution of either functional groups[172] or specific test solutes, such as the first five probes suggested by McReynolds.[24] Early studies using solution free energy differences to characterize stationary-phase interactions employed the specific retention volume of the test solutes corrected for interfacial adsorption.[55,56,173] The exact molecular weight of many polymeric solvents used in gas chromatography is generally unknown and/or poorly defined, indicating that for a refined theory the molal standard state may be more appropriate than the molar standard state.[174,175] Some representative values for the partial molar Gibbs free energy of solution for McReynolds test solutes on some common stationary phases are given in Table IX.[132] Interpretation of the data in Table IX requires that equal weight be given to the sign as well as the magnitude of the number. For example, many of the entries for benzene are positive, indicating that squalane is a more selective phase for the retention of benzene than are most of the polar phases, which, although opposite to conclusions based on McReynolds constants, is in agreement with intuition, benzene being essentially nonpolar with some weak induction and proton-acceptor capacity. All the phases retain butanol better than squalane—thus the negative sign. Carbowax 20M is the most selective phase for proton-donor solutes of those studied. Several phases in Table IX also show strong orientation interactions, largely in agreement with expectations, but it is particularly notable that these phases also show the strongest proton-donor interactions. Since the proton-acceptor test solutes also have considerable orientation properties, it is reasonable to conclude that there are very few thermally stable phases with strong proton-donor properties. This is again in general agreement with the common consensus among chromatographers but is at odds with predictions based on the McReynolds phase constants.

Risby et al.[176,177] proposed that the selectivity of a stationary phase be defined in terms of the partial molar enthalpy of solution of a number of common functional groups, determined from the temperature dependence of the specific retention volume of the test substances. However, an evaluation of the capacity of a stationary phase to retain polar solutes without taking into account the accompanying changes in entropy is not rigorous and can lead to erroneous conclusions. In

TABLE IX. Stationary-Phase Selectivity Determined as the Difference in the Partial Molar Gibbs Free Energy of Solution for Some McReynolds Test Solutes Using Squalane as a Reference Phase at 80.8 °C

	difference in partial molar Gibbs free energy of solution (cal/mol)					
stationary phase	benzene	1-butanol	2-pentanone	1-nitropropane	pyridine	dioxane
squalane	0	0	0	0	0	0
OV-17	30	-260	-250	-640	-380	-340
OV-105	190	-420	-110	-310	-30	-30
OV-330	-70	-1100	-360	-1030	-660	-490
OV-225	100	-740	-470	-1090	-580	-440
QF-1	-410	-750	-500	-860	-180	-160
Carbowax 20M	-150	-1270	-370	-1260	-880	-640
DEGS	240	-1140		-1070		-750
TCEP	190	-1020	-480	-1330	-920	-780
OV-275	480	-590	-50	-950	-480	-310

later work these authors recognized the above criticism and used the partial molal Gibbs free energy of solution for the functional groups OH, CHO, >CO, OC(O)H, $OC(O)CH_3$, and O to characterize stationary-phase interactions.[172,178] Earlier data published by McReynolds[146] and Rohrschneider[99] were used for the calculations, and as discussed previously in section IV.E, the reliability of these data is suspect for modeling solute–solvent interactions. These authors also assumed that the free energy contribution of the functional group is independent of its position in the molecule, which is unlikely to be true in all cases and needs to be rigorously tested. There is some evidence that even for monofunctional compounds, the fractional contribution to the total free energy of a functional group or heteroatom is position dependent within an alkyl chain.[179,180] The correlation between stationary-phase selectivity and suitably chosen test solutes, for example the McReynolds test solutes, was equally as good as that for the individual functional groups and, therefore, the McReynolds approach has been the one most generally adopted.

According to Golovnya and co-workers,[24,137,139] the selectivity of two compared liquid phases for a particular solute can quantitatively be expressed as the difference in excess mixing energies. The larger this difference, the greater the selectivity difference between the two phases for the tested interaction. To quantify these interactions these authors selected the first five McReynolds test solutes, using eq 21 to calculate the

$$\Delta G^{\circ}_{K} + 2.3RT \log \rho = -2.3RT\frac{I^{X} - 100n}{100}B + \log \frac{V^{\circ}_{gn}T}{273} \qquad (21)$$

partial molar Gibbs free energy of solution from the specific retention volumes and retention index values reported by McReynolds. In eq 21 ρ is the density of the liquid phase at the column temperature T, I^X is the retention index of the test solute, $B = \log V^{\circ}_{gn+1} - \log V^{\circ}_{gn}$, V°_{gn} is the specific retention volume of a normal hydrocarbon with n carbon atoms, used to calculate I^X, and V°_{gn+1} is the specific retention volume of a normal hydrocarbon with $n + 1$ carbon atoms. Since the densities of many of the phases characterized by McReynolds are unknown, these authors used the quotient on the left-hand side of eq 21 to rank individual phases in terms of their interactions with the test solutes. The error in the free energies due to a lack of knowledge of the liquid phase density is unlikely to exceed 10% and will generally be less.[24,55,56,173] Equation 21 is theoretically correct but its use is compromised by the inexact nature of the data collected by McReynolds (see section IV.E). The approach, however, is sound, and the determination of selectivity as free energy differences for a test solute on compared phases is the most logical approach to the general problem of a standardized scheme for evaluating selectivity differences (see section IV.C).

IX. Polarity Scales

The strength of interactions between a solute and a liquid phase depends on the properties of both the solute and the phase. The characteristics of the phase of importance are its solvent strength (or polarity) and its selectivity. The polarity of a liquid phase is the least satisfactory measure of the properties of a phase. Although most chemists have a reasonable idea of the meaning of polarity and have no difficulty in recognizing water as a polar solvent and hexane as a nonpolar one, the use of the term is still subject to considerable misunderstanding. Polarity is frequently used where selectivity is meant; at other times, polarity is taken to be the sum of induction and orientation interactions only. In thermodynamic terms, polarity can be defined as the capacity of a solvent for various intermolecular interactions corresponding to the partial molar Gibbs free energy of solution. In practice, a suitable probe must be selected to determine the polarity of a liquid phase and to enable phases to be ranked in order of polarity. Since polarity is not a unique property of a molecule but a composite expression for several different interactions, there is no single substance that can be defined as polar. Several ways around this problem have been suggested and are reviewed below.

TABLE X. Comparison of Polarity Scales for Some Common Stationary Phases[55,56] (T = 80.8 °C)

stationary phase	$\Delta G_K^{\circ}(CH_2)$, cal/mol	$\sum_{i=1}^{5}\Delta I^{a}$	P'^{b}	$\sum\delta(\Delta G_K^{\circ}(i))^{P}_{SQ}$
squalane	-579	0	1.20	0
OV-17	-513	867	3.10	-1.66
OV-105	-503	495	2.76	-1.24
OV-330	-482	1590	4.79	-3.36
OV-225	-459	1733	4.78	-3.02
QF-1	-437	1305	3.51	-1.87
Carbowax 20M	-428	2409	5.84	-4.42
DEGS	-352			-4.47
TCEP	-322			-4.61
OV-275	-291			-3.41

[a] $\sum_{i=1}^{5}\Delta I$ = sum of first five ΔI values for McReynolds test solutes. [b] P' defined in eq 23 [c] $\sum\delta(\Delta G_K^{\circ}(i))^{P}_{SQ}$ defined in eq 15.

In one of the earliest standardized scales of polarity Rohrschneider defined the polarity of a liquid phase in terms of the observed relative retention of butane and butadiene.[181] These values for different phases were scaled to represent a fraction of the value between squalane (assigned a polarity of zero) and β,β'-oxydipropionitrile, having a polarity of 100. Schomburg[182] suggested that the polarity of a liquid phase could be defined as the difference in the retention index differences for benzene and cyclohexane on the polar phase with respect to those on squalane

$$P = \Delta I^{\text{benzene}} - \Delta I^{\text{cyclohexane}} \qquad (22)$$

where P is the polarity of the polar phase. Following the suggestion of McReynolds[101] the average polarity of a stationary phase has been assumed to be equal to the sum of the ΔI values on the polar phase and squalane for the test solutes benzene, butanol, 2-pentanone, nitropropane, and pyridine (Table X). Lee et al.[142] suggested that the polarity of a stationary phase could be determined by the retention index of an easily polarizable substance such as biphenyl, similar to an earlier suggestion of Rohrschneider, who used benzene as the test solute.[7] Snyder used the solvent polarity parameter, P', determined according to eq 23, where

$$P' = 1.2 + \sum\Delta I_{i}\frac{B}{100} \qquad (23)$$

$\sum\Delta I_i$ is defined in eq 12 and B according to eq 21. Another approach that has been widely used is to equate the polarity of a stationary phase with its reluctance to retain a nonpolar solute such as a hydrocarbon.[6,28,134,183-187] The polarity criterion is usually based on the relative retention of neighboring hydrocarbons or the partial molar Gibbs free energy of solution for a methylene group. Expressed in terms of the free energy per methylene group, other homologous standards besides the *n*-alkanes can be used as the test solutes, which extends the applicability of the method to polar phases on which the *n*-alkanes are retained by interfacial adsorption or have asymmetric peak shapes.[55,56,184] For other less standardized or narrowly used techniques for assessing stationary-phase polarity earlier reviews are recommended.[5-8,12,13]

Because of the arbitrary nature with which polarity is generally defined, it is perhaps not very surprising that little attempt has been made to correlate the various polarity scales with each other. The polarity scale derived from summing the ΔI values for the first five McReynolds constants did not correlate with the partial molar Gibbs free energy of solution for a methylene group using retention index values corrected for interfacial adsorption.[55] A good correlation was found between Snyder's P' polarity scale and the partial molar Gibbs free energy of solution per methylene group for liquid phases that retained *n*-alkanes, at least in part, by partitioning[56]

$$P' = 16.115 + 0.0251[\Delta G^\circ{}_{\mathrm{K}}(\mathrm{CH_2})] \tag{24}$$

$$n = 8 \qquad r^2 = 0.966$$

and also between the sum of the difference in the partial molar Gibbs free energy of solution for ethanol, nitromethane, and dioxane on the polar phase and squalane

$$P' = 0.461 - 0.791[\textstyle\sum\delta(\Delta G^\circ{}_{\mathrm{K}}(\mathrm{i}))^{\mathrm{P}}_{\mathrm{SQ}}] \tag{25}$$

$$n = 9 \qquad r^2 = 0.973$$

It should be noted that in deriving the expression for P' (eq 25), Snyder determined the reference value for squalane to be 1.2; in a later study Poppe and Slats[188] proposed a different method to account for the influence of the molecular size of the solvents on the polarity scale and selectivity indices and proposed a reference value of −0.03 for squalane. Changing the reference value, however, only changes the numerical value of P' for each phase and not the polarity difference between phases. Lowry et al.[189] compared seven measures of polarity for the original data set of ΔI values for 10 compounds on 226 liquid phases published by McReynolds. Polarity was determined as the retention index difference for benzene and nitropropane, the sum of the retention index differences for the first five McReynolds test solutes, the sum of the retention index differences for butanol, 1-nitropropane, and pyridine, and three mathematical expressions using either factor analysis or principal component analysis. On the basis of correlation analysis these authors concluded that all seven methods for determining polarity yield quite similar results. Interestingly, the principal component analysis methods identified 97.0% of the variance with a single axis associated with polarity.[128,129,166,167] Unfortunately, these methods of analysis do not lead to a thermodynamic definition of the term "polarity" but strongly support the view that the overall capacity of a liquid phase to enter into selective interactions is an important term that controls relative retention. Again we must caution that the McReynolds data set used in these studies may contain substantial errors (see section IV.E) that must be reflected in the conclusions based on its mathematical analysis.

X. Conclusions

Two characteristics are of interest to chromatographers for determining the quantitative characteristics of solute–solvent interactions in liquid phases. The least perfect of these parameters is the solvent strength or polarity, which is related to the capacity of a solvent to enter into all solute–solvent interactions. There is no single characteristic test solute that can be used to determine polarity, and, consequently, we must rely on indirect methods and intuition. On the basis of these considerations the partial molar Gibbs free energy of solution for a methylene group seems to correlate most closely with general expectations, and extensive collections of this parameter are now available for many common phases.[24,28,35,55,56,132,136,139,173]

Solvent selectivity is a measure of the capacity of a solvent to enter into specific solute–solvent interactions characterized as dispersion, induction, orientation, and complexation interactions. These forces are probably best characterized by differences in the partial molar or molal Gibbs free energy of solution for a series of test solutes on two phases, one of which is a reference phase, generally taken to be a nonpolar phase. The test solutes suggested by McReynolds seem to possess the correct character for the above purpose but are not well matched with the volatility requirements needed to yield accurate retention data on a wide range of phases of different polarity. Since polarity and selectivity characteristics are temperature dependent, future studies should be aimed at a quantitative description of the influence of temperature on these terms. It is highly probable that the large compilations of selectivity indices determined by Rohrschneider and McReynolds contain substantial errors, which inhibits any accurate conclusions being reached by applying refined mathematical and statistical techniques to their analysis. There is a very urgent need for the creation of a new data base for high-quality synthetic phases in common use to replace these older data compilations. In this case, particular attention should be paid to the influence of interfacial adsorption as a retention mechanism and allowance made for its effect when determining gas–liquid partition data.

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XI. References

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