Review

Classification of stationary phases and other materials by gas chromatography

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Abstract

The origin and evolution of solute descriptors for use in the solvation parameter model applied to the classification of stationary phases and other materials by gas chromatography are described. The model system constants provide a breakdown of solute–stationary phase interactions in terms of the contribution to retention of cavity formation and dispersion interactions, lone-pair electron interactions, interactions of a dipole-type, and hydrogen-bonding interactions. The solvation properties of additional stationary phases with useful complementary selectivity to existing phases for method development in gas chromatography are identified. The influence of temperature on system selectivity and stationary phase classification is discussed. The contribution of interfacial adsorption to the estimation of retention in method development in gas chromatography is outlined. In addition, for materials characterization, it is shown that the solvation parameter model provides a conceptual mechanism for the evaluation of the sorption properties of a wide range of materials compatible with the operation characteristics of gas chromatography.   © 1999 Elsevier Science B.V. All rights reserved.

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Contents

1. Introduction

Separations are achieved in gas chromatography (GC) by distribution of a solute between an immobile solid or liquid stationary phase and a gas phase that percolates over the stationary phase. The distribution constant is determined by the column temperature and the extent of intermolecular interactions between the solute and stationary phase. The mobile phase is responsible for transport through the column but otherwise does not participate in the retention mechanism provided that sample sizes are small, column pressures are low, and low-molecular-mass gases are used as the mobile phase [1–3]; conditions generally used in analytical GC. It follows, therefore, that gas–solute vapor mixtures behave ideally, and selectivity differences observed for different stationary phases result from solute–stationary phase interactions alone. This will not be true for extreme operating conditions or intentional selection of conditions were gas–vapor interactions are known to be important [4,5], but is a reasonable simplifying assumption for the typical case.

Useful separations require kinetically optimized conditions achieved through column design, independent of selectivity optimization, since this is a thermodynamic consideration. The general optimization of kinetic parameters is achieved through the use of open tubular columns of capillary dimensions containing a uniform thin coating of stationary phase, and by using gases of high diffusivity [1,6,7]. The optimization of selectivity is achieved by either temperature variation or by using different stationary phases. The former is easily achieved by external means, but is rather limited in scope, since large changes in temperature result in either excessive or insufficient retention to provide practically useful separations, and small changes in temperature, in insufficient variation in the relative strengths of intermolecular interactions to provide wide changes in selectivity. Temperature remains an important and useful optimization parameter in GC, but effective selectivity optimization requires that a wide range of stationary phases distinguished by their capacity for varied intermolecular interactions be employed [8]. For this purpose it is important to have a reliable, systematic approach to stationary phase classification so that selectivity differences between stationary phases can be quantified; phases with redundant properties can be identified and replaced by a smaller group of preferred phases; and for computer-aided method development in GC. From this perspective we review early developments in stationary phase classification approaches leading to the solvation parameter model and applications of the latter to stationary phase chemistry with an emphasis on the requirements of modern stationary phases for use in open tubular column GC.

1.1. Solvent strength (polarity) and selectivity

In attempting to organize a discussion on approaches to stationary phase characterization in GC it is necessary to consider two primary properties of a stationary phase, namely, its solvent strength (polarity) and selectivity. Historically, the difficulty in adequately defining these terms is in part responsible for the mushrooming of experimental procedures for their determination. Polarity is sometimes considered to be the capacity of a stationary phase for dipole-type interactions [9,10] but is more generally defined as the capacity of a stationary phase for all inter-

molecular interactions consisting of dispersion, dipole-type and complexation including hydrogen-bonding [10–12]. The latter definition is quite sensible but its experimental measurement is not straightforward. No solute possesses the general quality of ''polarity'' but simply possesses a capacity for intermolecular interactions that is a property of its intrinsic structure and composition. Thus any ''polarity'' ranking of stationary phases based on the retention of an individual substance are specific to that substance and substances with similar properties, but cannot be considered universal. A solute with a large dipole-moment does not experience the same interactions with a hydrogen-bond base stationary phase as would a solute which is a strong hydrogen-bond acid, and so forth. In each case the ''polarity'' scale is massed in favor of the specific interaction dominated by the property of the selected ''polar'' solute. Thus, for example, the ΔC scale defined as the difference in apparent carbon number of linear alkanes and alcohols with the same retention time, provides a reasonable scale for the ranking the ability of stationary phases to interact with compounds with similar properties to alcohols but could not be expected to reflect the ''polarity'' of non hydrogen-bonding and hydrogen-bonding stationary phases to interact with nitroalkanes [13–15]. In addition, those scales based on retention index values are strongly dependent on the solubility of the retention index standards in the stationary phase as well as the specific interaction of the ''polar'' solute with the stationary phase [16–18]. This is the reason why McReynolds' P_M value [sum of the first five McReynolds' selectivity indices (benzene, *n*-butanol, nitropropane, 2-pentanone and pyridine)], Snyder's P' value (sum of the logarithms of the corresponding corrected distribution constants for ethanol, dioxane and nitromethane) and other single compound polarity indices show a strong correlation with the retention of the *n*-alkanes employed as retention index standards [15–19]. Alternative approaches to defining a ''polarity'' scale are based on the reluctance of a ''polar'' stationary phase to interact with a hydrocarbon solute expressed as the partial molar or excess Gibbs free energy of solution for a methylene group [10,12,20] or the solvent strength parameter (the partial molar Gibbs free energy of solution for a methylene group per unit solvent volume) [21].

These approaches are also quite illogical, since an *n*-alkane or methylene group is capable of dispersion and induction interactions only, and is incapable of representing interactions due to orientation and hydrogen-bonding. This is true even if we assume that ''polar'' solvent–solvent interactions are largely responsible for the low solubility of *n*-alkanes in ''polar'' stationary phases, and this is taken as an indirect measure of ''polarity''. No consideration is possible for the range of ''polar'' solute–solvent interactions responsible for the solubility of ''polar'' solutes. For the above reasons it is necessary to abandon the use of classification of stationary phase properties by a single parameter, indicated as ''polarity'', in spite of the obvious emotive attributes of such a simple scale.

1.2. Selectivity ranking of stationary phases based on retention index differences

The selectivity of a stationary phase is defined as its relative capacity to enter into specific intermolecular interactions such as dispersion, induction, orientation, hydrogen-bond formation, and charge-transfer complexation. Unlike ''polarity'' it should be possible to provide meaningful experimentally-derived scales for selectivity. Early attempts to define selectivity scales were based on the system of characteristic phase constants introduced by Rohrschneider [22,23] and subsequently modified by McReynolds [24], Snyder's solvent selectivity triangle [17,25], selectivity indices [26], Hawkes polarity indices [27], solubility parameters [28–30], and the partial molar Gibbs free energy of solution for functional groups or specified solutes [12,21,31–35]. These approaches are reviewed in detail elsewhere [1,8,11,32,36–38] and only a few general comments are given here.

Historically the most important contribution to stationary phase classification was the Rohrschneider–McReynolds system of phase constants. Even today these values can be found in most vendor's catalogues of stationary phases and extensive compilations of tabulated values for over 300 phases are available [8] with others scattered throughout the literature. Perhaps the most significant impact of the Rohrschneider–McReynolds system of phase constants was the demonstration of the

great similarity that existed among the common stationary phases in general use in the late 1970s. This brought to an end a period of stationary-phase proliferation, by providing the first logical basis for the selection of a manageable group of ''preferred stationary phases'' with separation characteristics that could represent the larger number of characterized phases [38–40]. The founding principle of Rohrschneider's method was that intermolecular forces were assumed to be additive, and that their individual contributions to retention can be evaluated from the differences in retention index values for a series of selected solutes on the stationary phase to be characterized and on squalane, used as a non-polar reference phase [22,23]. Rohrschneider assumed that the retention index of a substance on a non-polar phase, such as squalane, was determined solely by dispersion forces, and that any difference in the retention index values for a polar phase (ΔI) was due to polar interactions. These retention index differences representing polar interactions were represented as a series of terms composed of a solute specific contribution (a, ..., e) and a stationary phase characteristic term (X', ..., S') allowing the retention index difference to be written as

$$\Delta I = aX' + bY' + cZ' + dU' + eS' \qquad (1)$$

Five solutes, Table 1, were selected to characterize the principal intermolecular interactions responsible for retention. Determination of the stationary phase characteristic constants was performed by measuring

ΔI for each solute in turn and assigning a value of 100 for the solute specific constant associated with that solute. Thus, by determining the retention index for the five selected solutes on the stationary phase to be characterized, and on squalane, at a fixed reference temperature of 100°C, it was possible to assign numerical values for the five stationary phase characteristic constants. McReynolds modified Rohrschneider's approach by increasing the number of solutes used in Eq. (1) from five to 10, replacing three of the Rohrschneider's solutes (ethanol, nitromethane and 2-butanone) by less volatile homologues (*n*-butanol, nitropropane and 2-pentanone) to provide easier access to retention index values on some phases where Rohrschneider's solutes possessed low retention, proposed 120°C instead of 100°C as the standard reference temperature, and used ΔI instead of $\Delta I/100$ for the calculation of the characteristic phase constants (thus values of McReynolds' characteristic phase constants are 100-times larger than Rohrschneider's constants). It is McReynolds' characteristic phase constants that are usually found in the contemporary scientific and commercial literature.

It is now realized for a number of fundamental and practical reasons, reviewed elsewhere [3,11,16–18,37,41], that Rohrschneider's approach is unsound for stationary phase characterization. The *n*-alkane retention index standards, particularly on polar phases, are often retained by a combination of partition and interfacial adsorption, while the solutes used for evaluating specific interactions are (usually)

Table 1
Characteristic solute interactions associated with the first five McReynolds' probes (Rohrschneider's probes in parentheses)

Symbol	Solute	Interaction measured
X'	Benzene	Primarily dispersion with weak hydrogen-bond base properties. Polarizable in induction interactions.
Y'	Butanol (ethanol)	Orientation with both hydrogen-bond acid and base capabilities.
Z'	2-Pentanone (2-butanone)	Orientation with some weak hydrogen-bond base capabilities. No hydrogen-bond acidity.
U'	Nitropropane (Nitromethane)	Orientation with some weak hydrogen-bond basicity. No hydrogen-bond acidity.
S'	Pyridine	Strong hydrogen-bond base with moderate orientation capability. No hydrogen-bond acidity.

retained solely by partitioning [41]. This results in retention index values and retention index differences that depend on column characteristics and injected sample size. Under these circumstances retention indices are likely to be irreproducible and can no longer be simply related to solvation properties of the test solutes. More importantly, the retention index differences are composite terms, the magnitude of which depends on both the choice of standards for the retention index scale as well as properties of the specified solutes [16–18]. In fact, when *n*-alkanes are used as retention index standards, the usual choice, the magnitude of the characteristic phase constants is largely determined by the difference in retention of the *n*-alkanes on the compared phases, and to a much lesser extent retention differences of the specified solutes, such that on most phases a good correlation exists between the characteristic phase constants and the partial molar Gibbs free energy of solution for a methylene group. Inferring the contribution of individual intermolecular interactions to the retention of the selected solutes is less than straightforward, although commonly indicated, since each solute is retained by several simultaneous interactions (see Table 1). For example, *n*-butanol is dipolar with a significant capacity for both hydrogen-bond acid and hydrogen-bond base interactions, and will be retained by dipole-type interactions on non-hydrogen bonding phases, and by dipole-type and hydrogen-bond interactions on hydrogen-bonding phases. Thus, simply from the retention index difference value for butanol on a series of phases we can learn little about the characteristic properties of the stationary phase that contributed to the observed retention. This was subsequently recognized by Rohrschneider [23,42], who demonstrated that the characteristic phase constants represent mixed retention and intermolecular interactions. It is important to divorce the prediction of retention from the needs for stationary phase characterization. An empirical model can predict retention under favorable circumstances without providing details of the intermolecular interactions involved if the choice of solutes used to establish the model participate in the full range of intermolecular interactions possible for the stationary phase. Thus, one may have a useful model for retention that is simultaneously a poor model for characterizing

stationary phase selectivity, as defined here. The above comments apply equally well to any of the other methods of selectivity characterization employing retention index differences to calculate selectivity indices of one form or another. It is noteworthy that until recently these were the most common approaches employed for stationary phase selectivity ranking.

1.3. Selectivity ranking of stationary phases based on solution free energies

To overcome the above difficulties of selectivity ranking of stationary phases based on retention index differences attention turned to the use of retention scales employing either the partial molal Gibbs free energy of solution for a select group of solutes or the difference in partial molal Gibbs free energy of solution for a select group of solutes on the phase to be characterized and a hydrocarbon reference solvent, such as squalane [21,32,34,35,37]. This approach had to be abandoned for two principal reasons. Firstly, it was shown that the free energy selectivity parameters were solute-size dependent and unsuitable for characterizing the strength of solute–solvent interactions in highly cohesive phases [21,34]. Secondly, identification of appropriate solutes which expressed a strong singular intermolecular interaction against a weak background of all other interactions could not be found [34,35]. When phases were ranked by their capacity to interact with individual solutes the ranking was inadequate (and at times illogical) since the intermolecular forces involved were the summation of all forces experienced by the solute and rarely, if ever, represented a single, implied interaction. To overcome these difficulties Kollie and Poole [35] reasoned that the size dependence of the solutes could be removed by separating the free energy into a cavity term and an interaction term, the latter being independent of solute size and representative of polar solute–solvent interactions. Further deconvolution of the interaction term into factors related to fundamental intermolecular interactions could be achieved by principal component factor analysis [43,44].

From the above considerations a general model was derived, Eq. (2) [35]:

$$\Delta G_S^{SOLN}(X) = \Delta G_S^{SOLN}(HC)^V + \Delta G_{SQ}^P(X)$$
$$+ \Delta G_S^{INT}(X) \qquad (2)$$

where $\Delta G_S^{SOLN}(X)$ is the partial molar Gibbs free energy of solution for the transfer of solute X from the gas phase to the stationary phase S, $\Delta G_S^{SOLN}(HC)^V$ the partial molar Gibbs free energy of solution for the transfer of a (hypothetical) n-alkane with an identical Van der Waals volume to solute X from the gas phase to the stationary phase, $\Delta G_{SQ}^P(X)$ the partial molar Gibbs free energy of interaction for the polar part of solute X with a hydrocarbon solvent (squalane) [equivalent to $\Delta G_{SQ}^{SOLN}(X) - \Delta G_{SQ}^{SOLN}(HC)^V$], and $\Delta G_S^{INT}(X)$ the polar interaction term. The polar interaction term is the only term in Eq. (2) that cannot be determined by experiment, and is evaluated from Eq. (2) (or other more convenient forms of Eq. (2) for calculation purposes [43,44]). $\Delta G_S^{INT}(X)$ is defined as the component of the free energy of solution that is equivalent to the solute–solvent interactions of solute X that exceeds those interactions typified by a hypothetical n-alkane of the same volume in stationary phase S reduced by the identical interactions of solute X in a hydrocarbon solvent (squalane). The $\Delta G_S^{INT}(X)$ term was shown to be independent of solute size and stationary phase cohesion, as required of a general parameter to characterize polar solute–solvent interactions. The sum of the first two terms on the right-hand side of Eq. (2), $\Sigma[\Delta G_S^{SOLN}(HC)^V + \Delta G_{SQ}^P(X)]$, is referred to as the cavity/dispersion term and represents the free energy contribution associated with breaking solvent–solvent interactions to form an appropriate sized cavity for the solute and the contribution of solute–solvent dispersion interactions established when the solute is located in the cavity. Subsequently, Poole and co-workers [45–48] demonstrated that the cavity/dispersion term defined as above and the equivalent cavity/dispersion term in the solvation parameter model were nearly identical for a large number of solutes and at several different temperatures. Deconvolution of the polar interaction term by principal component factor analysis and the contribution of dipole-type interactions and hydrogen-bond interactions to retention obtained from the solvation parameter model were also well correlated [44]. Thus, it seemed unnecessary to continue with two independent models for stationary phase characteri-

zation that produced virtually equivalent results. Subsequent studies have been restricted to the solvation parameter model, which has the additional appeal of more direct evaluation of the contribution of individual intermolecular interactions to retention and broad applicability to many other distribution processes involving condensed phases, such as liquid–liquid distribution, liquid chromatography, and micellar electrokinetic chromatography [49–51].

2. Solvation parameter model

The role of hydrogen bonding in partitioning processes has long been recognized, although not always explicitly stated [52–54]. Taft and co-workers [55,56] were the first to construct a quantitative scale of hydrogen bonding for more than just a few compounds, specifically the hydrogen-bond basicity of solutes towards 4-fluorophenol in tetrachloromethane. Unfortunately, this scale had no zero origin and hence could not be used in linear free energy relationships (LFERs) or quantitative structure-activity relationships (QSARs). Some years later, Kamlet and Taft outlined their ''solvatochromic comparison method'' for the determination of the dipolarity/polarizability (π^*) [57], the hydrogen-bond acidity (α) [58], and the hydrogen-bond basicity (β) [59] of solvents. Because these three scales all had a zero origin, they could be used in numerous correlations of solvent effects [57–62].

Kamlet et al. [63,64] then extended the application of their solvatochromic parameters to solute effects, on the assumption that π^*, α and β for solvents could be taken as descriptors for solutes. Of course, it was recognized that this was an approximation even for compounds that are unassociated as solvents, and that for associated compounds such as water and alcohols, the solvent descriptors must be replaced by more appropriate descriptors for solutes. This work of Kamlet et al. [64] was a major step forward, but the use of solvatochromic parameters as solute descriptors suffers from two particular disadvantages. First of all, most solute effects that have been analyzed are Gibbs free energy related. In gas–liquid chromatography they are partitions between the gas phase and the stationary phase, K, which as ($RT\log K$) are Gibbs free energies. Then in

order to construct a correlation equation that has any physical interpretation, it is necessary that the various descriptors should also be related to Gibbs free energy. The solvatochromic parameters are defined in terms of spectroscopic energy, they are not Gibbs free energies, and they are to be avoided as descriptors for the correlation of dependent variables that are related to Gibbs free energy. We suggest the phrase ''descriptor-quality'' to denote whether or not parameters used as independent variables do actually describe the same type of process as the dependent variable. Thus if the latter is a gas chromatographic retention parameter such as log K, log V_g or log t_{rel} that are Gibbs free energy related, any descriptor that is itself a Gibbs free energy quantity will be of the correct descriptor-quality. Linear correlation equations constructed on these lines are then linear free energy relationships.

Secondly, there is no protocol for the determination of the Kamlet–Taft parameters for additional (especially solid) compounds. Hickey and Passino-Reader [65] have set out rules for the estimation of these parameters, but these rules do not include a number of important heterocyclic fragments or take into account many of the neighboring group interactions that influence solute parameters.

2.1. Origin of the solute descriptors

In order to correlate dependent variables that are Gibbs free energy related, it is necessary to devise solute descriptors that are related to Gibbs free energy and which can be determined through standard protocols. As it happens, almost in parallel with the above studies [64,65], Abraham et al. were setting out scales of solute hydrogen-bond acidity, α_2^H [66,67], and solute hydrogen-bond basicity, β_2^H [68,69], using 1:1 complexation constants in tetrachloromethane, Eq. (3):

$$AH + :B \rightleftharpoons AH---:B \tag{3}$$

Unlike the work of Taft and co-workers [55,56], these studies led to scales that had a zero origin, confirming the analysis of Abboud and Bellon [70]. Since α_2^H and β_2^H are derived from log K values for Eq. (3), they are strictly Gibbs free energy quantities

and so could be used in LFERs for the correlation of log K as the dependent variable.

The α_2^H and β_2^H scales represented the first general quantitative parameters of hydrogen-bond strength. Although construction of these scales removed the disadvantages outlined for the solvatochromic parameters above, a new difficulty was introduced as regards the use of such scales in the correlation of solute effects on partitioning systems: α_2^H and β_2^H define the influence of solute structure on 1:1 equilibrium constants, whereas the influence of solute structure on partitioning processes will be a consequence of hydrogen bonding of the solute to any surrounding solvent molecules, not just to one. What are needed are scales of ''summation'' or ''overall'' hydrogen bonding that refer to the propensity of a solute to interact with a large excess of solvent molecules. These hydrogen-bond descriptors are denoted as $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ to distinguish them from the 1:1 descriptors. The construction of such overall or summation solute descriptors is best done in conjunction with the construction of other solute descriptors that will be needed for a full analysis of partitioning phenomena.

In the solvation parameter model of Abraham [49], the partition of a solute between the gas phase and a solvent is described by a cavity theory of solution [71–73] in which the solvation process is broken down into three steps:

(A) A cavity of suitable size to accommodate the solute is created in the solvent. This process is endoergic because work is required to disrupt solvent–solvent interactions.

(B) The solvent molecules around the cavity are reorganized from their original (solvent) positions to the positions they will adopt when the solute is in equilibrium with the solvent. Of course, these positions are not fixed but are averages of solvent positions. The Gibbs energy change for such reorganization is assumed to be negligible [64], by analogy with the melting of a solid. However, enthalpy and entropy changes in reorganizations may be large, again by analogy with the melting of a solid.

(C) The solute is introduced into the reorganized cavity, and various solute–solvent interactions are set up, all of which are exoergic.

Descriptors are needed for the various interactions

in A and C. Considerable simplification is achieved if the solvation process is restricted to the solubility of a series of solutes in the same solvent system, because the properties of the solvent remain constant and only the solute properties vary.

Any solute descriptor for step A will be related to solute size, because the larger the solute the larger will be the cavity. However, the larger is a solute, the greater will be its tendency to take part in solute–solvent interactions of the general London dispersion type, in step C. There seems no way to disentangle these two effects, and Abraham et al. [74] combined the two in a new solute descriptor, log L^{16}, where L^{16} is the Ostwald solubility coefficient (or gas–liquid partition coefficient K) of hexadecane at 25°C:

$$L^{16} = \frac{[\text{concentration of solute in hexadecane}]}{[\text{concentration of solute in gas phase}]} \quad (4)$$

An advantage of this descriptor is that it can be easily experimentally determined by gas–liquid chromatography, at least for reasonably volatile solutes.

The molar refraction (MR) is sometimes used as a solute descriptor but is too closely related to solute size to be used in the same correlation equation as log L^{16}. A molar refraction was defined through Eq. (5) [75], where η is the refractive index of a liquid solute at 20°C for the sodium D-line, and V_X is McGowan's characteristic volume [76]. The latter can be calculated quite simply from the structure of any solute [49,76].

$$MR = V_X(\eta^2 - 1)/(\eta^2 + 2) \quad (5)$$

In Eq. (5), the units of V_X and of MR are cm^3 mol^{-1}/10. Then in order to avoid correlation between MR and log L^{16}, an excess molar refraction, R_2, was defined as MR for the given solute, less MR for an alkane of the same characteristic volume [75]. This method of determining R_2 is simple to apply to solutes that are liquid at 20°C. However, R_2, like the molar refraction, is almost an additive quantity, and values for solid solutes can be estimated through addition of known R_2 values for fragments.

Although R_2 is not generally an important descriptor, it is valuable in the correlation of gas–liquid chromatographic retention data on nonpolar phases. For example, Abraham and Whiting [77] showed

that the retention index of solutes on squalane at 96°C [78] could be correlated by a simple equation in R_2 and log L^{16}:

$$I = 76.04 + 41.89R_2 + 197.47\log L^{16}$$

$$n = 67, r^2 = 0.9994, \text{S.D.} = 3.77, F = 39976 \quad (6)$$

Here, n is the number of solutes, r is the correlation coefficient, S.D. is the standard deviation in the dependent variable, and F is the F-statistic. Since R_2 can be determined or estimated for any solute, further values of log L^{16} can be obtained for any solute for which I-values are recorded [78]. Numerous equations of the type of Eq. (6) have been set up for rather non-polar phases, and this has enabled some 2000 values of log L^{16} to be determined [77,79–81].

It would be very useful to have descriptors that were related to the propensity of a solute to engage in dipole–dipole and induced dipole–dipole interactions. A possible descriptor for the former would be the solute dipole moment, but Abraham et al. [75] showed that this was not satisfactory. In the event, it proved impossible to separate out descriptors for the two types of interaction, and Abraham et al. [79] constructed a solute descriptor for dipolarity/polarizability, π_2^H, through gas–liquid chromatographic measurements on polar stationary phases. If retention data for a series of compounds are obtained on a stationary phase that is polar and hence basic, but non-acidic, they may be correlated through an extension to Eq. (6),

$$\log SP = c + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + l\log L^{16} \quad (7)$$

Here log SP refers to gas chromatographic data for a series of solutes on a given stationary phase, for example log V_g or log t_{rel} or I. The new descriptor prefers to interactions between a dipolar or a polarizable solute and the polar stationary phase. However, for solutes that are hydrogen-bond acids, the overall or summation descriptor, $\Sigma\alpha_2^H$, is needed in Eq. (7) to characterize the hydrogen-bond interaction between the solute and stationary phase. As a first approximation for monoacidic solutes, $\Sigma\alpha_2^H$ was taken as α_2^H. For solutes that have no hydrogen-bond acidity, Eq. (7) reduces to Eq. (8) and it is rather

simple to construct a scale of π_2^H values, knowing R_2 and $\log L^{16}$.

$$\log SP = c + rR_2 + s\pi_2^H + l\log L^{16} \qquad (8)$$

Sometimes it is convenient to solve a set of equations, rather than a single equation of type Eq. (7) or Eq. (8). Abraham et al. [79] analyzed the extensive retention data of Laffort et al. [82] and obtained the correlation equations summarized in Table 2 for 199 out of the 240 solutes listed; note that the data is in the form of $[\log L - \log L(\text{decane})]$ at 120°C. Values of R_2 are known for the remaining 41 solutes, and so the descriptors π_2^H, $\Sigma\alpha_2^H$ and $\log L^{16}$ for these solutes can be found from the set of five equations in Table 2. Since for any given solute we have three unknowns (the three above descriptors) and five equations, the system is over-specified. Values of the three unknown descriptors are chosen so that the standard deviation between the observed and calculated values of $[\log L - \log L(\text{decane})]$ is a minimum. More detailed examples of this type of analysis are given later. The composition, identification, and a number code used in figures for the stationary phases used by Laffort et al. [82], and other common stationary phases discussed throughout the text, is provided in Table 3.

The final descriptor needed to deal with the various interactions in c, is the overall or summation hydrogen-bond basicity scale, $\Sigma\beta_2^H$. When retention data on a stationary phase that was polar, basic and acidic are correlated with solute descriptors, the full solvation equation has to be used,

$$\log SP = c + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2^H + l\log L^{16} \qquad (9)$$

Although some use was made of the application of Eq. (9) to gas chromatographic data, Abraham et al. [83,84] found it more convenient to analyze the extensive literature data on water–solvent partition coefficients, P, defined as,

$$P = \frac{[\text{concentration of solute in solvent}]}{[\text{concentration of solute in water}]} \qquad (10)$$

Water–solvent partition coefficients are better correlated, as $\log P$ values, using the alternative Eq. (11), where the $\log L^{16}$ descriptor is replaced by V_X, McGowan's characteristic volume.

$$\log P = c + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2^H + vV_X \qquad (11)$$

A first set of equations was constructed [51,83] for a series of $\log P$ values in various water–solvent systems. The $\log P$ values referred to simple monofunctional compounds, and the β_2^H descriptor was used as a first approximation to $\Sigma\beta_2^H$ in equations of type Eq. (11). The values of β_2^H were then adjusted where necessary so as to conform to Eq. (11), and these adjusted values were taken as a second approximation of $\Sigma\beta_2^H$. A second set of equations was then constructed using the second approximation $\Sigma\beta_2^H$ values, and the process was repeated in a round-robin procedure, until the $\Sigma\beta_2^H$ values had converged to a constant set, and until the LFER coefficients had also converged. During the round-robin process, the $\Sigma\alpha_2^H$ descriptor was occasionally adjusted as well. Sixteen water–solvent systems were used in the round-robin process, including water–gas as a special case. Once the round-robin process had been completed, the final set of LFERs, Eqs. (9) and (11) could be used for the determination of descriptors for

Table 2
Application of Eq. (7) to the retention data of Laffort et al. [82]

Stationary phase	System constants					Statistics		
	c	r	s	a	l	n	S.D.	r^2
Carbowax	−2.01	0.25	1.26	2.07	0.429	199	0.07	0.994
DEGS	−1.77	0.35	1.58	1.84	0.383	199	0.07	0.994
PPE	−2.51	0.14	0.89	0.67	0.547	199	0.06	0.994
TCEP	−1.69	0.26	1.93	1.88	0.365	199	0.06	0.996
ZE7	−1.99	−0.41	1.46	0.77	0.432	199	0.07	0.990

Table 3
Identification and abbreviations for stationary phases

Number	Abbreviation	Name
1	SQ	Squalane
2	SE-30	Poly(dimethylsiloxane)
3	OV-105	Poly(cyanopropylmethyldimethylsiloxane)
4	OV-3	Poly(dimethylmethylphenylsiloxane) 10 mol% phenyl groups
5	OV-7	Poly(dimethylmethylphenylsiloxane) 20 mol% phenyl groups
6	OV-11	Poly(dimethylmethylphenylsiloxane) 35 mol% phenyl groups
7	OV-17	Poly(methylphenylsiloxane)
8	OV-22	Poly(methylphenyldiphenylsiloxane) 65 mol% phenyl groups
9	OV-25	Poly(methylphenyldiphenylsiloxane) 75 mol% phenyl groups
10	OV-330	Poly(dimethylsiloxane)/carbowax copolymer
11	OV-225	Poly(cyanopropylmethylphenylmethylsiloxane)
12	OV-275	Poly(dicyanoallylsiloxane)
13	QF-1	Poly(trifluoropropylmethylsiloxane)
14	PSF6	Poly(methylsiloxane) containing 2-(4-butanephenyl)-1,1,1,3,3,3-hexafluoropropan-2-ol substituent groups 70% dimethylsiloxane, 26% methylsiloxane with the alcohol containing substituent attached, and 4% methyloctylsiloxane
15	DOP	Di-n-octylphthalate
16	DDP	Di-n-decylphthalate
17	DOTP	Di-n-octyltetrachlorophthalate
18	PPE-5	1,3-Bis(3-phenoxyphenoxy)benzene
19	CW20M	Poly(ethylene glycol)
20	U50HB	Poly(ethylene glycol) (Ucon 50 HB 660)
21	THPED	N,N,N',N'-Tetrakis(2-hydroxypropyl)ethylenediamine
22	EGAD	Poly(ethylene glycol adipate)
23	DEGS	Poly(diethylene glycol succinate)
24	TCEP	1,2,3-Tris(2-cyanoethoxypropane)
25	TCEPE	Tetra(cyanoethoxy)pentaerythritol
26	SN	Sebaconitrile [NC–CO(CH$_2$)$_6$–COCN]
27	H10	Bis(3-allyl-4-hydroxyphenyl)sulfone
28	DEHPA	Di(2-ethylhexyl)phosphoric acid
	ZE7	Fluoroalkyl ester of pyromellitic acid

any solute, no matter how many functionalities it possessed.

Although the above method seems complicated, it was necessary to ensure that the same set of solute descriptors (R_2, π_2^{H}, $\Sigma\alpha_2^{\mathrm{H}}$, $\Sigma\beta_2^{\mathrm{H}}$) could be used in Eq. (9) for the correlation of gas chromatographic data and in Eq. (11) for the correlation of log P values. A difficulty that fortunately is irrelevant in the correlation of gas chromatographic data is that certain specific solutes in specific water–solvent systems require an alternative basicity descriptor [83].

We give in Table 4 a summary of Abraham's solute descriptors for use in the solvation equations and list various statistical details. Compilations of solute descriptors have been published [51,84] and a selection of solutes is given in Table 5. There are two interesting points as follows. Firstly, across families, there is little connection between $\Sigma\alpha_2^{\mathrm{H}}$ and proton acidity and between $\Sigma\beta_2^{\mathrm{H}}$ and proton basicity;

Table 4
Solute descriptors for use in the solvation equations (number, maximum and minimum value indicate the number of solutes for which the descriptor is currently available together with the maximum and minimum values of the given solute descriptor. V_X can easily be calculated for any structure)

Symbol	Description	Number	Maximum value	Minimum value
R_2	The excess molar refraction	3432	4.62	-1.37
π_2^H	The dipolarity/polarizability	2920	5.60	-0.54
$\Sigma\alpha_2^H$	The overall or summation hydrogen-bond acidity	3748	2.10	0.00
$\Sigma\beta_2^H$	The overall or summation hydrogen-bond basicity	2594	4.52	0.00
Log L^{16}	The gas–hexadecane partition coefficient at 25°C	1962	29.97	-1.74
V_X	The McGowan characteristic volume	3600	8.56	0.07

thus propanoic acid and phenol are equally strong hydrogen-bond acids, but K_A for propanoic acid is 105-times as large as K_A for phenol in water. Butylamine is a strong proton base in water, whereas 1,4-dioxane is very weak, yet the two have almost the same strength as hydrogen-bond bases.

Secondly, values of $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ for bifunction-al compounds are not simply the sum of values for the monofunctionalities. The effective hydrogen-bond acidity of ethan-1,2-diol (0.78) is not twice that of ethanol (2×0.37), and $\Sigma\beta_2^H$ for 1,4-dioxane (0.64) is not twice that for diethyl ether (2×0.45) or for tetrahydrofuran (2×0.48). Hence, at present, it is difficult to deduce hydrogen-bond descriptors for

Table 5
Solute descriptors for use in the solvation parameter model

Solute	R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	V_X	Log L^{16}
Helium	0.000	0.00	0.00	0.00	0.0680	-1.741
Ethane	0.000	0.00	0.00	0.00	0.3904	0.492
Pentane	0.000	0.00	0.00	0.00	0.8131	2.162
Diethyl ether	0.041	0.25	0.00	0.45	0.7309	2.015
Tetrahydrofuran	0.289	0.52	0.00	0.48	0.6223	2.636
1,4-Dioxane	0.329	0.75	0.00	0.64	0.6810	2.892
Pentan-2-one	0.143	0.68	0.00	0.51	0.8288	2.755
Ethyl acetate	0.106	0.62	0.00	0.45	0.7466	2.314
n-Butylamine	0.224	0.35	0.16	0.61	0.7720	2.618
Propanoic acid	0.233	0.65	0.60	0.45	0.6057	2.290
Ethanol	0.246	0.42	0.37	0.48	0.4491	1.485
Ethan-1,2-diol	0.404	0.90	0.58	0.78	0.5078	2.661
Hexafluoroisopropanol	-0.240	0.55	0.77	0.10	0.6962	1.392
Toluene	0.601	0.52	0.00	0.14	0.8573	3.325
Naphthalene	1.340	0.92	0.00	0.20	1.0854	5.161
Acetophenone	0.818	1.01	0.00	0.48	1.0139	4.501
Methyl benzoate	0.733	0.85	0.00	0.46	1.0726	4.704
Dimethyl phthalate	0.780	1.40	0.00	0.84	1.4288	6.051
Phenol	0.805	0.89	0.60	0.30	0.7751	3.766
Hydroquinone	1.063	1.27	1.06	0.57	0.8338	4.827
Furan	0.369	0.53	0.00	0.13	0.5363	1.830
Pyridine	0.631	0.84	0.00	0.52	0.6753	3.022
Quinoline	1.268	0.97	0.00	0.54	1.0443	5.457

multifunctional solutes, and these descriptors have to be determined by experiment.

2.2. Protocol for the determination of solute descriptors

Although the development of the methods used to derive solute solvation parameters was quite involved, the actual determination of the parameters is now straightforward. The R_2 descriptor can be obtained easily from either an experimental or a calculated liquid refractive index at 20°C, and the McGowan volume can be calculated for any structure. A simple computer program is available [85] that will calculate R_2 and V_X using as input only the liquid refractive index, the solute molecular formula, and the number of rings in the molecular structure. For solids, the hypothetical liquid refractive index can be calculated using a commercial software package [86].

The log L^{16} descriptor can be obtained directly through gas chromatographic retention data on hexadecane at 25°C, and also through the calibration of any non-polar stationary phase using the solvation equation with only the R_2 and log L^{16} terms, see for example Eq. (6).

Determination of the remaining three descriptors is best carried out through the use of water–solvent partition coefficients. The coefficients in Eq. (11) are known for numerous such processes, and a selection is given in Table 6 [51,81,87,88]. If partition coefficients for a particular solute are available for at least three water–solvent systems, that have significantly different coefficients then π_2^H, $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ can be determined as the solutions to three

simultaneous equations. If the number of equations is larger than the number of descriptors to be determined, the descriptor values that give the best-fit solution (i.e., the smallest standard deviation in observed and calculated log P values) are taken. In many cases, the necessary log P values will be available from the very extensive collection of Leo [89], so that no further experimentation will be needed.

For ethyl trifluoroacetate, log P values were available [89] in three water–solvent systems only. Fortunately, these systems are different enough to allow the calculation of the best-fit values of π_2^H and $\Sigma\beta_2^H$ ($\Sigma\alpha_2^H$ is zero), as shown in Table 7. In the case of 2,6-dimethoxyphenol, the best-fit values of π_2^H,

Table 7
The calculation of solute descriptors for ethyl trifluoroacetate and 2,6-dimethoxyphenol

Distribution system	Log P(calc)	Log P(obs)
Ethyl trifluoroacetate[a]		
Water–octanol	1.16	1.18
Water–chloroform	2.00	2.00
Water–alkane	0.94	0.92
2,6-Dimethoxyphenol[b]		
Water–octanol	1.10	1.15
Water–diethyl ether	0.79	0.74
Water–olive oil	0.56	0.57
Water–hexadecane	−0.35	−0.36
Water–cyclohexane	−0.15	−0.15

[a] R_2 and V_X were determined as −0.20 and 0.7997, respectively, and the best-fit values of the remaining parameters that yield the log P(obs) values were $\pi_2^H = 0.23$ and $\Sigma\beta_2^H = 0.47$ ($\Sigma\alpha_2^H = 0$).
[b] R_2 and V_X were determined as 0.84 and 1.1743, respectively, and the best-fit values of the remaining parameters that yield the log P(obs) values were $\pi_2^H = 1.41$, $\Sigma\alpha_2^H = 0.13$ and $\Sigma\beta_2^H = 0.71$.

Table 6
System constants in Eq. (11) for water–solvent partitions

Distribution system	System constants					
	c	*r*	*s*	*a*	*b*	*v*
Water–octanol	0.09	0.56	−1.05	0.03	−3.46	3.81
Water–chloroform	0.33	0.16	−0.39	−3.19	−3.44	4.19
Water–dichloromethane	0.31	0.00	0.02	−3.24	−4.14	4.26
Water–cyclohexane	0.13	0.82	−1.73	−3.78	−4.90	4.65
Water–alkane	0.29	0.65	−1.66	−3.52	−4.82	4.28
Water–hexadecane	0.09	0.67	−1.62	−3.59	−4.87	4.43
Water–diethyl ether	0.26	0.60	−1.10	−0.10	−5.00	4.38
Water–olive oil	−0.01	0.58	−0.80	−1.47	−4.92	4.17

$\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ were obtained from five water–solvent partition equations as shown in Table 7.

This method of obtaining π, $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ is not restricted to the use of water–solvent log P values. Any equation of the general form of Eq. (9) or Eq. (11) can be used, including equations for gas chromatographic retention data and for liquid chromatographic retention factors. Abraham et al. [90] have detailed the use of a variety of processes in the determination of descriptors for terpenes.

2.3. Carr's solute descriptors

The method used by Carr et al. [91] starts in a similar way to that of Abraham, and uses a very similar equation to that of Eq. (9), viz. Eq. (12). This equation includes two already-determined solute descriptors, the log L^{16} descriptor of Abraham et al. [74,75,92] and an empirical descriptor, δ, introduced by Kamlet et al. [64,93] and taken as zero except for aromatic compounds (1.0), and for polychlorinated aliphatic compounds (0.5). The remaining three scales of descriptors are to be determined. As first approximations, the solute dipolarity/polarizability, π_2^c, was taken either from Abraham et al. [75] or from Kamlet et al. [93], and the solute overall hydrogen-bond acidity, α_2^c, was taken as the 1:1 acidity parameter of Abraham, α. The 1:1 solute hydrogen-bond basicity parameter was also included in Eq. (12), although this was of minor importance in the determined correlations.

$$\log SP = c + d\delta_2 + s\pi_2^c + a\alpha_2^c + b\beta_2^H + l\log L^{16} \tag{12}$$

Carr et al. [91] applied Eq. (12) to retention data of solutes on a large number of stationary phases, and through a round-robin procedure set up the two new scales, π_2^c and α_2^c, for 200 solutes. There was actually very little difference between these scales and the π_2^H and $\Sigma\alpha_2^H$ scales of Abraham, bearing in mind that the π_2^c and π_2^H scales had different zero points (cyclohexane for π_2^c and alkanes for π_2^H). However, it should be noted that all the solutes studied by Carr et al. [91] were monofunctional.

In the gas chromatographic equations constructed by Carr et al. [91], the $b\beta_2^H$ term was always quite small, and so the equations were not suitable for

setting up any new hydrogen-bond basicity scale. Carr et al. [94] then proceeded to devise a scale of solute overall hydrogen-bond basicity that they denoted as β_2^c. They synthesized two stationary phases, 4-dodecyl-α-α-bis(trifluoromethyl)benzyl alcohol and the corresponding methyl ether, denoted here as ROH and ROMe. Retention factors were obtained for a set of 84 solutes on each phase, and the ratio log k(ROH)/k(ROMe) was shown to have no dependence on any parameter except the Kamlet δ_2 and the Abraham's β_2^H descriptors,

$$\log k(\text{ROH})/k(\text{ROMe}) = -0.089 + 2.15\beta_2^H - 0.23\delta_2$$
$$n = 84, r = 0.967, \text{S.D.} = 0.22, F = 583 \tag{13}$$

Eq. (13) was then used to calculate further values of the solute hydrogen-bond basicity, through Eq. (14),

$$\beta_2^c = [\log k\{(\text{ROH})/k(\text{ROMe})\} + 0.089 + 0.23\delta_2]/2.15 \tag{14}$$

In this way, values of β_2^c for a further 59 solutes were obtained. Perhaps unexpectedly, these 59 values did not correlate very well with either β_2^H or to $\Sigma\beta_2^H$, so β_2^c is a new measure of the hydrogen-bond basicity of solutes. A comparison of β_2^c with β_2^H and $\Sigma\beta_2^H$ is in Table 8; for many weak bases there is reasonable agreement, but for amines and strong hydrogen-bond bases such as amides and sulfoxides the two scales diverge considerably. Carr et al. [94] suggested that β_2^c represented 1:1 hydrogen bonding of solutes with the fluorinated alcohol phase, except for the strong hydrogen-bond bases such as amides and dimethyl sulfoxide. If this were the case, then over a range of hydrogen-bond basicities the β_2^c parameter would not be expected to correlate with either the 1:1 β_2^H descriptor or the overall $\Sigma\beta_2^H$ descriptor.

2.4. Laffort's solute descriptors

Laffort et al. [82] obtained retention data for 240 solutes on the five stationary phases listed in Table 2. They showed how linear combinations of the five sets of retention indexes could be used to determine five solute descriptors that were referred to as "solubility factors" (a = the apolar factor, propor-

Table 8
Comparison of β_2^c with β_2^H and $\Sigma\beta_2^H$

Solute	β_2^c	β_2^H	$\Sigma\beta_2^H$
Ethylcyclohexane	0.00	0.00	0.00
Oct-1-ene	0.02	0.07	0.07
1-Chloropentane	0.08	0.11	0.10
Styrene	0.11	0.18	0.16
Mesitylene	0.13	0.20	0.19
Naphthalene	0.10	0.21	0.20
4-Fluorophenol	0.22	0.21	0.23
4-Methylphenol	0.25	0.24	0.31
4-Chloroaniline	0.35	0.34	0.31
Phenyl ethyl ether	0.19	0.26	0.32
Acetonitrile	0.37		0.32
p-Toluonitrile	0.42	0.42	0.34
Proprionitrile	0.41		0.36
3-Chloropyridine	0.76	0.49	0.40
4-Ethylaniline	0.47	0.42	0.45
Hexanal	0.38	0.39	0.45
Ethyl propanoate	0.45	0.45	0.45
3-Methylbutanol	0.52	0.45	0.48
Propriophenone	0.43	0.51	0.51
4-Methylpyridine	1.07	0.66	0.54
2-Methylpyridine	0.98	0.63	0.58
Butylamine	1.00	0.71	0.61
Hexylamine	0.88	0.69	0.61
Diethylamine	0.93	0.70	0.69
Dibutylamine	0.87	0.71	0.69
N,N-Dimethylformamide	0.97		0.74
N,N-Dimethylacetamide	1.06		0.78
Dimethyl sulfoxide	1.54		0.88

tional to molecular volume; w = the orientation factor; for small molecules proportional to the dipole moment squared; e = the electron factor, related to molecular refraction; p = the proton donor, or acidity factor; and b = the basicity factor). Although Laffort and Patte [95] subsequently interpreted a number of olfactory phenomena through the e parameter, and also analyzed a few physicochemical processes, no extension of the method seems to have been carried

out. Hence the solubility factors are restricted to the original 240 solutes.

2.5. Comparison of Abraham's and Carr's methods

These two methods yield similar results as regards descriptors of solute dipolarity/polarizability and solute hydrogen-bond acidity. If the Abraham log L^{16} descriptor is included in the Carr equation, as done by Li and Carr [96],

$$\log SP = c + d\delta_2 + s\pi_2^c + a\alpha_2^c + b\beta_2^c + l\log L^{16}$$

(15)

then analyses of gas chromatographic retention data on non-acidic stationary phases will be almost the same by either method. However, values of the basicity descriptor are not the same for the two methods, and so analyses of data on acidic stationary phases will not agree if the solute set contains solutes with different $\Sigma\beta_2^H$ and β_2^c values. Poole et al. [97] have synthesized an acidic stationary phase, PSF6, rather similar to the one used by Carr et al. [94]; both phases contain the $R\text{-}C_6H_4C(CF_3)_2OH$ entity. It might be expected that the Carr method would be the most appropriate for examination of a phase structurally very close to the phase used to define β_2^c. In the event, Poole et al. [97] found little difference in statistical fits to log K_L values obtained for the same set of solutes in each case, see Table 9. If a selection of solutes with a larger spread of hydrogen-bond basicity, $\Sigma\beta_2^H$ and β_2^c, is used, then differences in statistical goodness-of-fits appear. Abraham et al. [88] used Eq. (9) to correlate 150 values of log L for the solubility of gases and vapors in chloroform at 25°C, yielding Eq. (16),

Table 9
Statistical fits of log L values on phase PSF6

Temperature (°C)	Abraham's model				Carr's model			
	n	r^2	S.D.	F	n	r^2	S.D.	F
81.2	33	0.992	0.057	815	33	0.996	0.042	1704
101.2	33	0.994	0.045	1068	33	0.994	0.045	920
121.2	33	0.990	0.052	611	33	0.992	0.043	969
141.2	32	0.990	0.041	454	32	0.992	0.039	801
171.2	30	0.980	0.046	270	30	0.980	0.058	304

$$\log L = 0.17 - 0.60R_2 + 1.26\pi_2^H + 0.28\Sigma\alpha_2^H$$
$$+ 1.37\Sigma\beta_2^H + 0.98\log L^{16}$$
$$n = 150, r^2 = 0.985, \text{S.D.} = 0.23, F = 1919 \quad (16)$$

Descriptors in the Li and Carr [96] equation were available for only 61 out of the 150 solutes in Eq. (16), and so we have applied Eq. (9) to the same set of 61 solutes,

$$\log L = 0.14 - 0.68R_2 + 1.30\pi_2^H + 0.43\Sigma\alpha_2^H$$
$$+ 1.39\Sigma\beta_2^H + 0.98\log L^{16}$$
$$n = 61, r^2 = 0.970, \text{S.D.} = 0.18, F = 358 \quad (17)$$

There is good agreement between Eqs. (16) and (17), so that the 61 solutes are a representative subset of all 150. Application of Eq. (15) gave a significantly poorer correlation,

$$\log L = 0.53 - 0.43\delta_2 + 1.40\pi_2^c + 0.13\alpha_2^c$$
$$+ 0.09\beta_2^c + 0.95\log L^{16}$$
$$n = 61, r^2 = 0.950, \text{S.D.} = 0.24, F = 207 \quad (18)$$

If the hydrogen-bond basicity term becomes larger, then the Carr equation performs much worse than the Abraham equation. The latter has been applied [84] to the solubility of gases and vapors in water at 25°C,

$$\log L = -1.27 + 0.82R_2 + 2.74\pi_2^H + 3.90\Sigma\alpha_2^H$$
$$+ 4.81\Sigma\beta_2^H - 0.21\log L^{16}$$
$$n = 392, r^2 = 0.992, \text{S.D.} = 0.19, F = 10229 \quad (19)$$

Again, Carr descriptors were available for only 61 solutes, the Abraham equation leading to,

$$\log L = -1.05 + 0.65R_2 + 2.69\pi_2^H + 3.86\Sigma\alpha_2^H$$
$$+ 4.66\Sigma\beta_2^H - 0.22\log L^{16}$$
$$n = 61, r^2 = 0.989, \text{S.D.} = 0.19, F = 1038 \quad (20)$$

But now the Carr equation when applied to the same set of data shows relatively poor statistics, with a standard deviation twice that in Eq. (20),

$$\log L = -0.11 - 0.19\delta_2 + 3.50\pi_2^c + 3.15\alpha_2^c$$
$$+ 3.26\beta_2^c - 0.16\log L^{16}$$
$$n = 61, r^2 = 0.953, \text{S.D.} = 0.39, F = 224 \quad (21)$$

Carr et al. [98] applied Eq. (13) to retention data on a number of acidic phases, and obtained a good correlation for the fluorinated alcohol phase R-OH, see also Eqs. (13) and (14). However, since phase R-OH was used to set up the β_2^c scale, this is as expected. Several new phases were examined through Eq. (15): 1,1,1-trifluoro-2-eicosanol, penta-tadecylphenol, stearic acid and *N*-tetradecyltri-fluoroacetamide. Unfortunately, the key strongly basic solutes dimethyl sulfoxide, dimethylformamide and dimethylacetamide either could not be studied or were outliers.

The conclusion is that the Abraham and Carr equations perform about the same when applied to processes in which solute hydrogen-bond basicity is not very important. As soon as this becomes important, then for solute sets that contain strong hydrogen-bond bases, the Abraham equation is to be preferred.

As regards the determination of descriptors, those for the Abraham equation can be obtained from a wide variety of sources. The extensive water–solvent data base of Leo [89] is here very useful, especially as the relevant correlation equations have been published, [51,87]. The Carr descriptors π_2^c and α_2^c can be obtained from gas chromatographic data on generally available stationary phases [91], but the β_2^c descriptor can only be determined by experiments on the two stationary phases synthesized by Carr et al. [94]. This seems to preclude the full Eq. (13) from any general use. In the event, little use has been made of the Carr equation, but there have been a considerable number of published papers that de-scribe applications of the Abraham solvation parame-ter equation. Poole and co-workers [44–47] have compared the Abraham model with their own cavity model of solvation, and have concluded that the two models are quite compatible. Poole and co-workers investigated temperature effects on retention [43,59,97,99] and the solvent properties of liquid organic salts, Table 10 [44–46,100]. Other workers have used the equation to characterize various gas chromatographic stationary phases [101,102] includ-

Table 10
System constants for liquid organic salts determined from the gas–liquid distribution constant (120–122°C)

Counterion	Number	c	r	s	a	b	l
Tetra-n-butylammonium salts							
Chloride	29	−1.305	0.198	2.036	5.677	0	0.548
Bromide	30	−0.894	0.231	1.849	4.425	0	0.467
Nitrate	31	−0.829	0.145	1.864	3.535	0	0.453
Nitrite	32	−0.821	0.179	1.854	4.476	0	0.443
Picrate	33	−0.542	0.100	1.557	1.424	0	0.445
Sulfamate	34	−1.040	0.157	1.944	3.956	0	0.451
Tetra-*n*-butylborate	35	−0.499	0	1.440	3.230	0	0.476
1,1,2,3,3-Pentacyanopropionide	36	−0.406	0	1.541	1.517	0	0.438
Methanesulfonate	37	−0.612	0.334	1.454	3.762	0	0.435
Trifluoromethanesulfonate	38	−0.552	0	1.579	2.135	0	0.416
Ethanesulfonate	39	−0.804	0.139	1.805	4.021	0	0.442
Benzenesulfonate	40	−0.924	0.121	1.756	3.507	0	0.464
Perfluorobenzenesulfonate	41	−0.723	−0.088	1.647	2.238	0	0.459
4-Toluenesulfonate	42	−0.686	0.156	1.582	3.295	0	0.459
2-(Cyclohexylamino)ethanesulfonate	43	−0.827	0.073	1.572	3.667	0	0.505
3-(Cyclohexylamino)propanesulfonate	44	−0.934	0	1.577	3.710	0	0.541
4-Morpholineethanesulfonate	45	−0.631	0.095	1.595	3.408	0	0.437
4-Morpholinepropanesulfonate	46	−0.937	0	1.748	3.538	0	0.550
2-Hydroxy-4-morpholine-propanesulfonate	47	−0.906	0	1.764	3.204	0	0.494
3-{[Tris(hydroxymethyl)methyl]amino}-1-propanesulfonate	48	−1.040	0.396	2.204	3.690	0	0.265
3-{[Tris(hydroxymethyl)methyl]amino}-2-hydroxy-1-propanesulfonate	49	−0.860	0.266	1.959	3.058	0	0.317
2-[Bis(2-hydroxyethyl)amino]-ethanesulfonate	50	−0.805	0.253	1.760	3.368	0	0.382
2-[(2-acetamido)amino]-ethanesulfonate	51	−0.666	0.283	1.809	3.417	0	0.329
Tetraalkylammonium 4-toluenesulsonates							
Tetraethylammonium	52	−0.762	0.330	2.045	3.429	0	0.304
Tetrapropylammonium	53	−0.902	0.165	1.987	3.569	0	0.404
Tetrapentylammonium	54	−0.795	0.013	1.636	3.430	0	0.529
Tetrabutylphosphonium salts							
Chloride	55	−1.009	0.244	1.854	5.418	0	0.468
Bromide	56	−0.848	0.249	1.810	4.255	0	0.449
Iodide	57	−0.708	0.210	1.798	3.150	0	0.429
Nitrate	58	−0.758	0.183	1.829	3.538	0	0.421
2-(Cyclohexylamino)ethanesulfonate	59	−0.816	0.107	1.582	3.633	0	0.493
4-Morpholinepropanesulfonate	60	−0.774	0.126	1.682	3.659	0	0.494
3-{[Tris(hydroxymethyl)methyl]amino}-2-hydroxy-1-propanesulfonate	61	−0.849	0.205	1.957	3.091	0	0.330
Miscellaneous							
n-Octyltriphenylphosphonium bromide	62	−1.029	0.413	1.926	3.964	0	0.389
Ethylpyridinium 4-toluenesulfonate	63	−0.987	0.366	2.119	3.630	0	0.281
1-Ethyl-3-hydroxypyridinium 4-toluenesulfonate	64	−1.030	0.449	1.958	2.890	0.368	0.305
1-Ethyl-3-hydroxypyridinium bromide	65	−1.083	0.497	2.108	3.214	0.320	0.242
Tri-*n*-butylammonium 4-toluenesulfonate	66	−0.717	0.110	1.546	2.917	0	0.466

Table 11
System constants for tris[3-(trifluoromethylhydroxy-methylene)camphorato derivatives of lanthanides dissolved in the poly(dimethylsiloxane) OV-1 to give a concentration of 0.1 mol/kg at 120°C

Lanthanide chelate	System constant				
	r	s	a	b	l
Pr(tfc)$_3$	−0.20	0.93	1.43	0.69	0.46
Eu(tfc)$_3$	−0.15	0.92	1.69	0.59	0.44
Dy(tfc)$_3$	0	0.85	1.89	0.60	0.43
Er(tfc)$_3$	−0.07	0.92	2.17	0.43	0.41
Yb(tfc)$_3$	0	0.90	2.36	0.29	0.40

The dependent variable was log k.

ing lanthanide chelates dissolved in a poly(dimethylsiloxane) solvent [103], Table 11, and various substituted cyclodextrins [104], Table 12, and nonionic stationary phases, Table 13. Further applications of the model to GC are presented in the sections that follow. In addition, Abraham and co-workers [105–112] have made considerable use of the solvation parameter equation in the correlation and interpretation of biological effects of gases and vapors on both mice and human subjects and to characterize the response of solvent-coated microsensors to organic vapors.

The use of the alternative solvation parameter equation, Eq. (11), in the correlation and interpretation of all kinds of liquid chromatographic, solid-phase extraction, and micellar electrokinetic chromatographic processes ([113–120] and references therein) and of numerous biological processes [49–51,121] is now well established.

3. General interpretation of system constants

3.1. System constants in the solvation parameter model

The cavity theory of solvation that was used to set up the solvation parameter model has been discussed in Section 2.1, and the origin of the descriptors in the general Eq. (9) has been described in Section 2.2. Since the descriptors are supposed to represent the solute effect on various solute-phase interactions, the coefficients in Eq. (9) will correspond to the complimentary effect of the stationary phase on these

Table 12
System constants for chiral stationary phases at 100°C

Abbreviation	Type	System constants				
		r	s	a	b	l
PH-A	Permethylated *S*-hydroxypropyl-α-cyclodextrin	0.25	0.67	1.41	0.29	0.571
PH-B	Permethylated *S*-hydroxypropyl-β-cyclodextrin	0.38	0.57	1.27	0	0.406
PH-G	Permethylated *S*-hydroxypropyl-γ-cyclodextrin	0.25	0.67	1.31	0.48	0.489
DA-A	2,6-*O*-Dipentylated 3-*O*-acetylated α-cyclodextrin	0.20	0.43	1.17	0	0.605
DA-B	2,6-*O*-Dipentylated 3-*O*-acetylated β-cyclodextrin	0.38	0.63	1.56	0	0.732
DA-G	2,6-*O*-Dipentylated 3-*O*-acetylated γ-cyclodextrin	0.23	0.51	1.18	0	0.548
TA-A	2,6-*O*-Dipentylated 3-*O*-trifluoroacetylated α-cyclodextrin	−0.21	0.91	0.45	0	0.538
TA-B	2,6-*O*-Dipentylated 3-*O*-trifluoroacetylated β-cyclodextrin	0.43	0.50	1.21	0	0.573
TA-G	2,6-*O*-Dipentylated 3-*O*-trifluoroacetylated γ-cyclodextrin	0.50	0.38	1.48	0	0.558
Hydrodex	Permethylated β-cyclodextrin dissolved in a poly(siloxane)	0.08	0.69	1.06	0	0.575
Cyclodex	Permethylated β-cyclodextrin dissolved in DB1701	0.03	0.73	1.05	0	0.592
Lip-A	2,3,6-Tri-*O*-pentyl-α-cyclodextrin	0.15	0.68	1.13	0	0.653
Lip-C	2,3,6-Tri-*O*-pentyl-β-cyclodextrin	0.08	0.44	0.74	0	0.535
Lip-B	2,6-Di-*O*-pentyl-3-*O*-acetyl-α-cyclodextrin	0.10	0.56	0.99	0	0.465
Lip-D	2,6-Di-*O*-pentyl-3-*O*-acetyl-β-cyclodextrin	−0.71	1.77	0.83	0	0.584
Lip-E	2,3-Di-*O*-pentyl-3-*O*-butyryl-γ-cyclodextrin	−0.55	1.43	0.75	0	0.596
CTC-SV	L-Valine *tert*.-butylamide coated	0.11	0.55	1.10	0	0.500
PBC-SV	L-Valine *tert*.-butylamide bonded	0.13	0.62	1.17	0	0.589
B-1:4	Allylpermethylated β-cyclodextrin dissolved in PS537 (1:4, w/w)	0.37	0.59	1.42	0	0.703

The dependent variable was log V_g determined indirectly from the retention index values.

interactions. The regression coefficients are thus very important, because they will encode stationary phase properties. The coefficients can then be regarded as system constants or as constants that characterize the stationary phase. The reference or baseline for such characterization will be the gas phase, because all gas chromatographic data refers to transfer from the gas phase to the stationary phase. Not only do the system constants represent a new method for the characterization of stationary phases, but they contain chemical information about the stationary phase.

The system constants can be interpreted as follows [49]. The _r_-coefficient shows the tendency of the phase to interact with solutes through π- and n-electron pairs. Usually the _r_-coefficient is positive, but for phases that contain fluorine atoms, the _r_-coefficient can be negative. The _s_-coefficient gives the tendency of the phase to interact with dipolar/polarizable solutes, the _a_-coefficient denotes the hydrogen-bond basicity of the phase (because acidic solutes will interact with a basic phase), and the _b_-coefficient is a measure of the hydrogen-bond acidity of the phase (because basic solutes will interact with an acidic phase). The _l_-coefficient is a combination of exoergic dispersion forces that make a positive contribution to the _l_-coefficient, and an endoergic cavity term that makes a negative contribution. In the event, the dispersion interaction nearly always dominates, so that the _l_-coefficient is positive. The only phase for which a negative value is observed [84] is for solution of gases and vapors into water, Eq. (19). Since the _l_-coefficient varies between -0.21 for water at 25°C and $+1.00$ for hexadecane at 25°C, it seems to be a useful measure of the hydrophobicity of the stationary phase. It is important to note that for gas-phase processes, the _s_, _a_ and _b_ system constants must always be positive (or zero), because interactions between the phase and a solute will increase the solubility of a gaseous solute. The _r_ system constant is an exception, because it is tied to hydrocarbons as a zero; hence fluorine-containing phases may give rise to a negative _r_-constant. As shown above, the _l_ system constant must always be positive for gas chromatographic stationary phases. The coefficients in the solvation parameter equation are therefore not just fitting constants, but must obey general chemical principles. It should be noted that the regression equation remains the same,

except for the _c_-constant, no matter whether the dependent variable is log K_L (log _L_), or log V_g or even log t_{rel}, where t_{rel} is the relative retention time. However, the retention index, _I_, cannot be used to characterize stationary phases through Eq. (19), although it is very useful in the determination of descriptors, see Eq. (6). An early example [122] of the application of Eq. (9) was to log _L_ values [20] at 121.4°C on the rather non-polar stationary phase OV-3,

$$\log L = -0.18 + 0.03R_2 + 0.33\pi_2^H + 0.15\Sigma\alpha_2^H$$
$$+ 0.50\log L^{16}$$
$$n = 39, \ r^2 = 0.998, \ \text{S.D.} = 0.02, \ F = 5306 \qquad (22)$$

The presence of Si–O–Si bonds confers a small amount of dipolarity/polarizability and a small amount of hydrogen-bond basicity onto the stationary phase. Hence the small and positive (as required) _s_ and _a_ system constants. The phase has no acidity and so there is no term in $b\Sigma\beta_2^H$. The _l_ system constant (at 121.4°C) is reasonably large; for squalane at the same temperature the _l_ system constant was found to be 0.58, and for liquid organic salts it was as low as 0.24 units [100].

Since the system constants change markedly with temperature, as discussed in Section 3.3, comparisons of phases are best made at a common temperature. The coefficients in Eq. (22) can be compared with those shown in Table 2, at 120°C, for the Laffort phases, and with those for a number of other interesting phases Table 13 [44,45,47,97,99,101,122]. Most common stationary phases cover a reasonably wide range of dipolarity/polarizability (_s_ constant) and hydrogen-bond basicity (_b_ constant). Squalane, SE-30 and OV-3 are all rather non-polar with small or negligible hydrogen-bond basicity. Carbowax and TCEP, for example, are both dipolar/polarizable and of considerable hydrogen-bond basicity. It is possible to devise phases that are even more basic, for example, the liquid organic salts indicated in Table 10. None of the common stationary phases possess any substantial hydrogen-bond acidity, but application of the solvation parameter model to a number of custom synthesized phases has revealed considerable acidity. The phenolic stationary phase of Abraham et al. [47], H-10, is a

Table 13
System constants for non-ionic stationary phases (120–122°C)

Stationary phase	System constants					
	c	r	s	a	b	l
SQ	−0.222	0.129	0.011	0	0	0.583
SE-30	−0.194	0.024	0.190	0.125	0	0.498
OV-105	−0.203	0	0.364	0.407	0	0.496
OV-3	−0.181	0.033	0.328	0.152	0	0.503
OV-7	−0.231	0.056	0.433	0.165	0	0.510
OV-11	−0.303	0.097	0.544	0.174	0	0.516
OV-17	−0.372	0.071	0.653	0.263	0	0.518
OV-22	−0.328	0.201	0.664	0.190	0	0.482
OV-25	−0.273	0.277	0.644	0.182	0	0.472
OV-330	−0.430	0.104	1.056	1.419	0	0.481
OV-225	−0.541	0	1.226	1.065	0	0.466
OV-275	−0.909	0.206	2.080	1.986	0	0.294
QF-1	−0.269	−0.449	1.157	0.187	0	0.419
PSF6	−0.510	−0.360	0.820	0	1.110	0.540
DOP	−0.275	0	0.797	1.004	0	0.571
DDP	−0.328	0	0.748	0.765	0	0.560
DOTP	−0.475	0.203	0.590	0.740	0	0.607
PPE-5	−0.395	0.230	0.829	0.337	0	0.527
CW20M	−0.560	0.317	1.256	1.883	0	0.447
U50HB	−0.184	0.372	0.632	1.277	0	0.499
THPED	−0.445	0	1.128	2.069	0	0.477
EGAD	−0.688	0.132	1.394	1.720	0	0.410
DEGS	−0.669	0.197	1.668	2.246	0	0.411
TCEP	−0.489	0.278	1.913	1.678	0	0.290
TCEPE	−0.570	0.090	1.510	1.770	0	0.453
SN	−0.440	0.050	1.300	1.450	0	0.543
H10	−0.568	−0.051	1.323	1.266	1.457	0.418
DEHPA	−0.251	0.021	0.565	1.528	0	0.556

See Table 3 for identification and compositions.

reasonably strong hydrogen-bond acid, but also has considerable hydrogen-bond basicity. This is in line with the presence of the strongly basic sulfone functionality as shown in Fig. 1. The alcohol phases of Carr et al. [94] and Poole et al. (PSF6) [97] both contain the $-C(CF_3)_2OH$ moiety that leads to hydro-
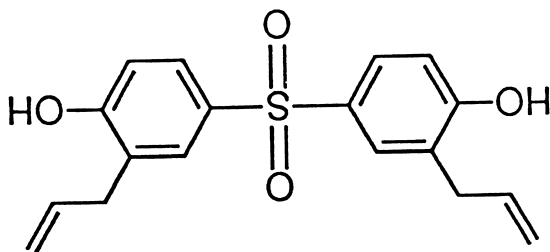

Fig. 1. The structure of phase H-10.

gen-bond acidity but negligible basicity. It is therefore possible to use the Abraham equation, Eq. (9), to deduce important chemical properties of stationary phases from the regression coefficients (or system constants).

3.2. Relationship between system constants and separation characteristics

The separation of two solutes by GC depends on a number of column parameters, such as the number of theoretical plates, but also on the chemical properties of the stationary phase. The latter can usefully be discussed in terms of Eq. (9), which contains information on the solute-phase interactions that will influence separation of two or more solutes. In a simple case of a non-polar stationary phase, the only system constant of any importance is the *l*-constant. Hence separations of non-polar and polar solutes will depend almost entirely on the values of the $\log L^{16}$ descriptor. If a series of homologues is studied, then along the series, the R_2, π_2^H, $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ descriptors will be almost the same, and the only descriptor to vary will be $\log L^{16}$. Then no matter what the properties of the stationary phase are, the only factor that will influence a separation will be the *l* constant; the larger the value of this system constant, the better will be the separation of homologues.

In the general case of a polar stationary phase and polar solutes, a term-by-term analysis of the particular correlation equation is necessary. This can be illustrated for retention, as $\log L$ values, on the phase H-10 at 121°C, the correlation equation being [47],

$$\log L = -0.568 - 0.051R_2 + 1.323\pi_2^H$$
$$+ 1.266\Sigma\alpha_2^H + 1.457\Sigma\beta_2^H + 0.418\log L^{16}$$

$$n = 58, r^2 = 0.988, \text{S.D.} = 0.069, F = 856 \qquad (23)$$

The various terms in Eq. (23) can be calculated for any solute, and the factors leading to retention obtained quantitatively. If this is done for two solutes, the factors leading to differences in retention can be assessed similarly. Details for pairs of solutes are in Table 14. The first pair illustrates our comment on homologous series; the only solute property that has any effect on the relative retention of

Table 14
Factors that lead to differences in log L values for solutes on phase H-10 at 121°C (the constant term is -0.568 in all cases)

Solute	Contribution to log L					Log L	
	rR_2	$s\pi_2^H$	$a\Sigma\alpha_2^H$	$b\Sigma\beta_2^H$	$l\log L^{16}$	Calculated	Observed
Butan-1-ol	-0.01	0.56	0.47	0.70	1.09	2.24	2.30
Octan-1-ol	-0.01	0.56	0.47	0.70	1.93	3.08	3.17
N-Methylaniline	-0.05	1.19	0.22	0.66	1.87	3.32	3.30
N,N-Dimethylaniline	-0.05	1.11	0.00	0.60	1.97	3.06	3.05
Iodobenzene	-0.06	1.08	0.00	0.17	1.88	2.50	2.57
Acetophenone	-0.04	1.34	0.00	0.70	1.88	3.31	3.38

butanol and octanol is log L^{16}. The pair of solutes N-methylaniline and N,N-dimethylaniline are closely related, but the former has a small but significant hydrogen-bond acidity that is the major factor in its longer retention. Iodobenzene and acetophenone differ considerably in dipolarity/polarizability and hydrogen-bond basicity; not surprisingly, acetophenone is retained much more than iodobenzene.

This type of analysis can be applied to any stationary phase for which the system constants are known. Not only can retention data be rationalized, but predictions can be made for any solutes for which the Abraham solvation descriptors are known, see Table 4.

3.3. Influence of temperature on system constants

Polar intermolecular interactions in general decrease with an increase in temperature. Hydrogen-bond interactions have been widely studied as a function of temperature, and in Table 15 we give values of the 1:1 hydrogen-bond complexation constants, Eq. (3), between thioacetamide and N,N-dimethylformamide in tetrachloromethane [122]. There are numerous other examples that all show a decrease in complexation with increase in temperature.

Following the work of Kamlet et al. [64], we can regard any term in Eq. (9) as being made up of a solute factor, a stationary phase factor, and a coeffi-

Table 15
The influence of temperature on 1:1 complexation constants between thioacetamide and N,N-dimethylformamide [122]

Temperature (°C)	5	15	25	35	45	55
Complexation constant (1 mol^{-1})	85	70	58	48	41	36

cient. Thus the $a\Sigma\alpha_2^H$ term can be rewritten as $a\Sigma\alpha_2^H = Ab_1\Sigma\alpha_2^H$ where b_1 is the phase hydrogen-bond basicity. In principle, all three components of the $Ab_1\Sigma\alpha_2^H$ term could alter with temperature. However, we have already regarded the solute descriptors as invariant with temperature. This is actually a practical necessity, because otherwise it would be essential to determine a new set of descriptors at any given temperature (unless by chance descriptors at one temperature were linearly related to those at another temperature for all solutes). Granted that the solute descriptors are taken as invariant with temperature, the term $Ab_1\Sigma\alpha_2^H$ will alter if either or both A and b_1 alter. Again, at present there is no way of knowing if solvent descriptors alter, and so all that can be done is to evaluate the Ab_1 factor, i.e., the a-coefficient in the solvation equation.

We expect that the s, a and b system constants should all decrease with an increase in temperature, reflecting the smaller solute–solvent interactions. The l constant encompasses two different interactions, solute–solvent and solvent–solvent. If the former decreases with temperature then the l constant will decrease, but if solvent–solvent interactions decrease with temperature, the l constant will increase (because the solvent–solvent interactions have to be broken). For all the gas chromatographic stationary phases that have been examined, the l constant decreases with increase in temperature. The rR_2 term is constructed on a different basis to all the other terms in Eq. (9), because the reference is a hydrocarbon rather than the gas phase, and it is difficult to predict the variation with temperature for the r constant. Poole and co-workers [48,97] and others [47] have shown that the r constant increases with increase in temperature, and that all the other

Table 16
The effect of temperature on system constants for some stationary phases

Stationary phase	Temperature (°C)	System constants					
		c	r	s	a	b	l
OV-175	141.2	−0.44	0.07	0.63	0.23	0.00	0.485
	121.2	−0.37	0.07	0.65	0.26	0.00	0.518
	101.2	−0.35	0.03	0.72	0.31	0.00	0.563
	61.2	−0.29	−0.04	0.93	0.51	0.00	0.746
QPTS	141.2	−0.47	0.04	1.49	3.07	0.00	0.391
	121.2	−0.53	0.04	1.60	3.33	0.00	0.430
	101.2	−0.62	0.10	1.69	3.64	0.00	0.489
	81.2	−0.76	0.11	1.92	4.20	0.00	0.569
PSF6	171.2	−0.92	−0.23	0.68	0.00	0.69	0.46
	141.2	−0.76	−0.28	0.63	0.00	0.96	0.49
	121.2	−0.51	−0.36	0.82	0.00	1.11	0.54
	101.2	−0.48	−0.38	0.76	0.00	1.52	0.60
	81.2	−0.40	−0.50	0.89	0.00	1.79	0.66

coefficients in Eq. (9) decrease with increase in temperature, as expected.

In Table 16 is a selection of the results of Poole and co-workers [48,97] with a rather non-polar phase (OV-17), a polar and basic phase (QPTS, tetra-butylammonium 4-toluenesulfonate), and the polar and acidic phase PSF6. The system constants shown in Table 16, and those for other stationary phases [47] usually alter quite regularly with temperature. In the main, but not always, plots of system constants against $1/T$ are linear.

4. Chemometric classification of stationary phases

Chemometric classification procedures allow us to evaluate the extent of the separation space that can be employed for separations in GC based on the range of properties of stationary phases that have been characterized by the solvation parameter model, and to observe whether the selectivity space is generally or partially occupied by existing phases. In this way it is possible to deduce the properties required of new stationary phases that would add to, rather than duplicate, the separation characteristics of stationary phases already available. From the previous discussion it is obvious that new phases with significant hydrogen-bond acid properties would

have a most profound influence on selectivity optimization in GC, if only because many solutes are hydrogen-bond bases, and therefore their relative retention will be influenced by the extent to which they can participate in solute hydrogen-bond base solvent hydrogen-bond acid interactions, and also because the majority of characterized stationary phases evaluated to date possess no capacity for such interactions. Chemometric classification procedures have been used to characterize the solvent properties of 33 conventional and liquid organic salt solvents [123], 38 liquid organic salts [100], and 13 poly-(siloxanes) including one phase with hydrogen-bond acid properties [97,124]. Instead of simply summarizing these results we have chosen to combine the individual studies, adding new information where available, and to reanalyze the data sets. Our conclusions are not in conflict with earlier studies.

Principal component factor analysis was applied to the collection of 28 non-ionic stationary phases identified in Table 3 using the system constants given in Table 13. These results are summarized in Table 17. About 97% of the variance can be explained with three principal components. The first principal component (PC-1) is dominated by stationary phase dipole-type and hydrogen-bond base interactions (a and s system constants); the second principal component (PC-2) is strongly influenced by hydrogen-bond acidity as well as dipole-type and

Table 17
Summary of results from principal component factor analysis using the system constants for the stationary phases in Tables 10 and 13

Principal component	Variance (%)	Cumulative variance (%)	
28 non-ionic stationary phases			
1	76.06	76.06	
2	13.99	90.05	
3	6.87	96.92	
4	2.18	99.10	
5	0.73	99.83	
66 ionic and non-ionic stationary phases			
1	93.35	93.35	
2	3.65	97.00	
3	1.83	98.83	
4	0.79	99.62	
Loadings for principal components			
System constant	PC-1	PC-2	PC-3
28 non-ionic stationary phases			
r	0.058	−0.250	0.009
s	0.522	0.393	−0.689
a	0.834	−0.253	0.473
b	−0.011	0.829	0.512
l	−0.053	−0.049	0.127
c	−0.160	−0.169	0.149
38 ionic and 28 non-ionic stationary phases			
r	0.043	0.023	−0.260
s	0.309	0.843	−0.275
a	0.938	−0.315	0.119
b	−0.023	0.306	0.912
l	−0.019	−0.176	0.092
c	−0.150	−0.255	−0.050

The data were mean centered followed by raw rotation of initial components.

lone-pair electron interactions (*b*, *s* and *r* system constants); the third principal component (PC-3) is a blend of all interactions (except *r*). The score plot of PC-2 against PC-1, which accounts for about 90% of the variance, is shown in Fig. 2. The selectivity space is unevenly occupied reflecting the absence of phases with hydrogen-bond acid properties. In terms of dipole-type and hydrogen-bond base interactions there is a reasonable filling of the selectivity space. The extreme values of PC-1 are marked by squalane (minimum capacity for polar interactions) and OV-275 and DEGS with the maximum capacity for polar interactions (excluding hydrogen-bond acidity). The *l* constant appears as a minor component in both principal component analyses, even though it is often the major factor that influences retention. Presumab-

ly this is because of the rather small variation in the values of the *l* constant among stationary phases at 120°C.

Modern open tubular column technology relies on a more restricted range of stationary phases than those depicted in Fig. 2. In practice stationary phases with a poly(siloxane) backbone or poly(ethylene glycols) virtually monopolize the market for commercially prepared open tubular capillary columns. That is because these materials can be immobilized providing stable films resistant to disruption caused by changes in temperature or solvent stripping, while at the same time retaining reasonable diffusion properties that maintain high column efficiencies. The position of the poly(siloxane) and poly(ethylene glycol) phases is highlighted on Fig. 2. They occupy
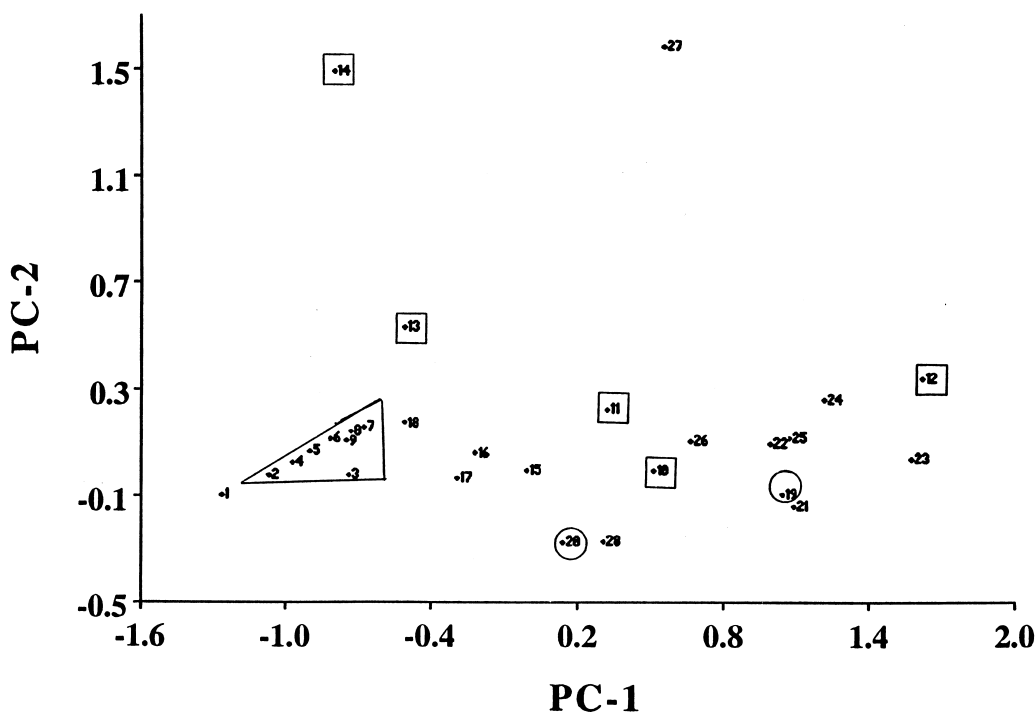
Fig. 2. Score plot for principal component 2 against component 1 for the 28 non-ionic stationary phases. Numbers refer to the phases identified in Table 3. The boxes and triangle denote the position of poly(siloxane) phases and the circles poly(ethylene glycol) phases.

only a small fraction of the selectivity space but potentially through composition variation could provide wide coverage of all the properties identified by the non-ionic solvents. The hydrogen-bond acid poly(siloxane) phase, PSF6, has not been coated or immobilized on open tubular columns but is possibly amenable to modern column fabrication techniques by analogy to related poly(siloxanes) [97]. Poly-(siloxanes) containing cyanoalkyl and trifluoropropyl groups and the poly(ethylene glycols) provide a reasonable fill of the selectivity space for non-hydrogen-bond acid polar stationary phases, although at the extreme end of the scale, poly(siloxanes) as highly substituted with cyanoalkyl groups as OV-275 cannot be immobilized by current methods of column manufacturing. The most common stationary phases in use are poly(methylphenylsiloxanes) of different compositions. These occupy a very small portion of the selectivity space and provide limited opportunities for selectivity optimization. They are located in the selectivity space close to squalane and should be considered as moderately polar stationary

phases. Composition variation and selectivity of the poly(methylphenylsiloxanes) are well correlated [124] as might be anticipated by their alignment in Fig. 2.

The dendrogram in Fig. 3 provides a convenient visual classification of the non-ionic solvents. It is easy to identify those phases with separation properties that are most similar to each other (represented by the smallest paired descendants); phases behaving singularly like squalane and QF-1 that have no close descendants; and phases with the least similarity to the general group such as the hydrogen-bond acid phases PSF6 and H10, and a large group of cohesive polar phases with large s and a system constants that includes OV-275 and TCEP.

Combining the 38 ionic stationary phases from Table 10 with the non-ionic phases produced the results indicated in Table 17. The first principal component accounts for about 93% of the variance and is dominated by hydrogen-bond base and dipole-type interactions (a and s system constants); the second principal component accounts for 3.65% of
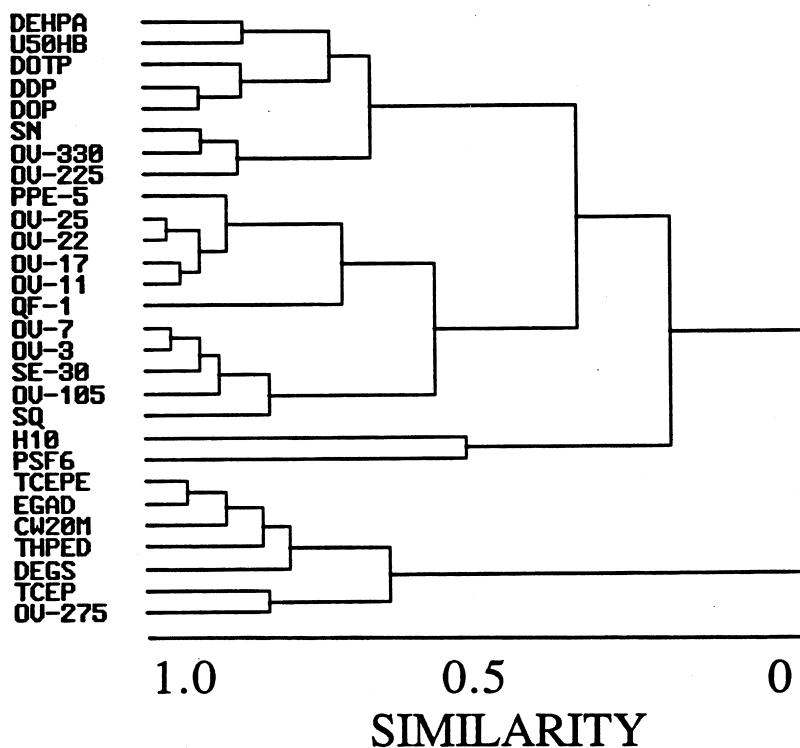
Fig. 3. Complete link dendrogram obtained by cluster analysis of the data in Table 13.

the variance and is dominated by dipole-type interactions combined with a significant contribution from hydrogen-bond acid and base interactions (s, b and a system constants); and the third principal component accounts for 1.83% of the variance and is dominated by hydrogen-bond acidity combined with a significant contribution from dipole-type and lone pair electron interactions (b, s, r system constants). The score plot for PC-1 against PC-2, which accounts for 97% of the variance, is shown in Fig. 4. The most obvious feature is an artificial near dividing plane between the ionic and non-ionic solvents. Only four liquid organic salts are located in the same selectivity space occupied by the non-ionic solvents. These salts contain anions which can delocalize their ionic charge. They are weaker hydrogen-bond bases and less dipolar than the remaining liquid organic salts, resulting in properties that are similar to the polar non-ionic stationary phases. It is the large a and s

system constants, with in some cases, unusually large l constants for such polar stationary phases, that distinguishes the liquid organic salts from the non-ionic phases. The point we want to make here is that the liquid organic salts provide an opportunity to extend the selectivity space dominated by dipole-type and hydrogen-bond base interactions significantly beyond that which can be explored using the non-ionic solvents. Liquid organic salts have been used as stationary phase coatings for open tubular columns [125–129] but not as immobilized phases. It is unclear whether ionic groups could be tethered to poly(siloxanes) to produce immobilized phases or whether in the diluted state the ionic substituent groups would behave in the same way as they do in simple melted salts. The score plot of PC-3 against PC-1, Fig. 5, is largely dictated by the hydrogen-bond acidity (PC-3) and hydrogen-bond basicity (PC-1) of the stationary phases. It reaffirms that a
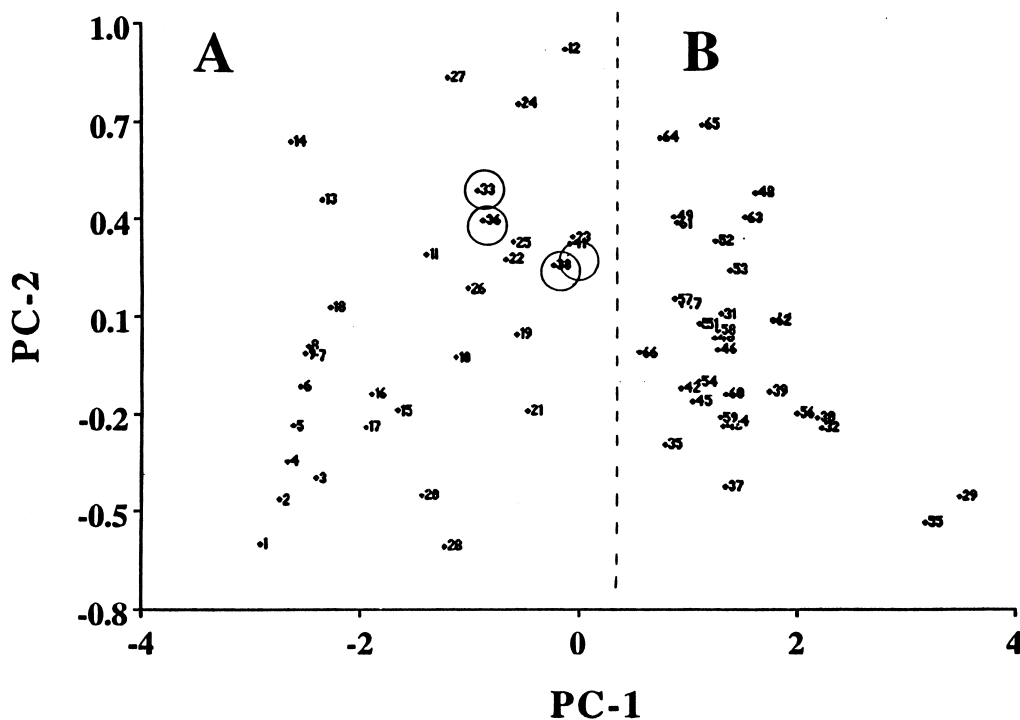
Fig. 4. Score plot for principal component 2 against component 1 for 38 liquid organic salts (B) and 28 non-ionic phases (A). Numbers refer to the phases identified in Tables 3 and 10. The circles indicate the position of the four liquid organic salts with properties similar to the non-ionic phases.

wider range of stationary phases with hydrogen-bond acid properties would be useful for selectivity optimization, as noted previously.

Many phases posses some capacity for lone pair electron interactions (*r* constant) but selectivity for this interaction is all but non-existent among the non-ionic and liquid organic salt stationary phases evaluated. It would seem difficult to make suggestions as to how this interaction might be optimized for conventional stationary phases. Perhaps phases containing metal co-ordination centers might have a significant capacity for these interactions compared to other phases, but corroboration is lacking. One study of stationary phase interactions that employed lanthanide chelates failed to demonstrate significant selectivity for lone pair electron interactions, Table 11 [103].

Some care is needed in using rankings or comparisons of stationary phases at a single reference temperature. The few studies available indicate that selectivity changes with temperature are dependent on the identity of the stationary phase [48,97,99,130]. The phase constants decline with increasing temperature, often in a linear manner, at least for the relatively narrow temperature ranges of 60 to 80°C for which data are available. For different phase constants on the same stationary phase and for the same phase constant on different stationary phases these slopes are not identical. For these reasons it cannot be assumed that the selectivity ranking of stationary phases at one temperature will be the same at all temperatures, particularly when the temperature difference between the temperature at which the phases were characterized and that at which they are to be used is significant. The solution to this problem is to evaluate stationary phases
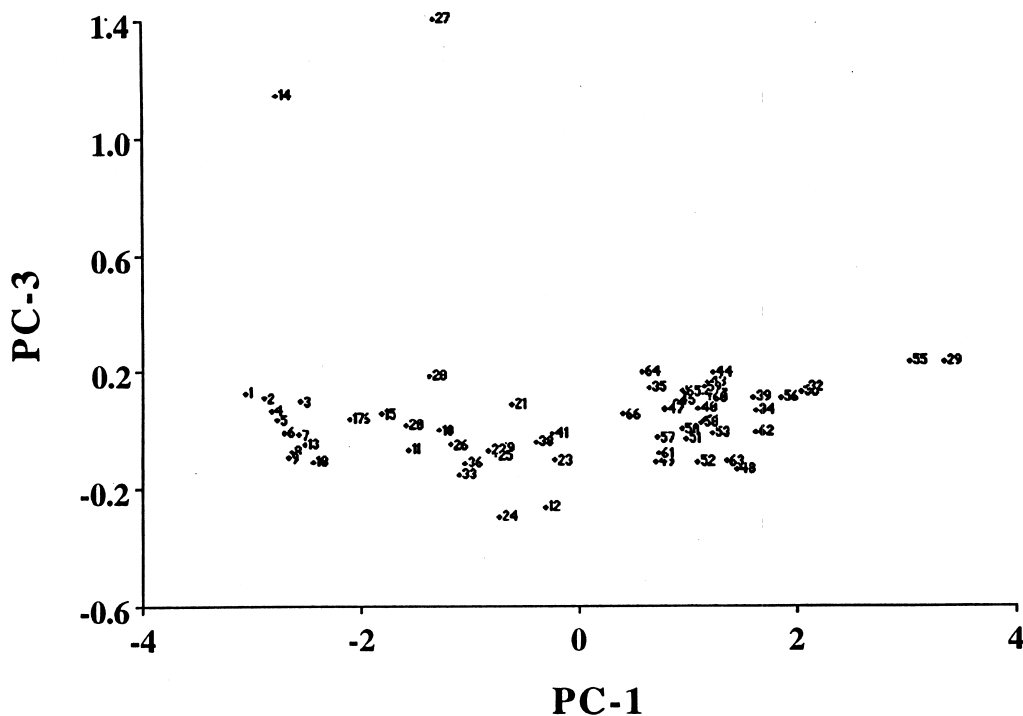
Fig. 5. Score plot for principal component 3 against component 1 for 38 liquid organic salts and 28 non-ionic phases. Numbers refer to the phases identified in Tables 3 and 10.

solvation properties over a range of temperatures and then fit the individual phase constants to a relationship as a function of temperature as part of the general classification procedure. This would allow stationary phases to be classified at any temperature or at a series of selected nominal temperatures throughout their useful working range.

5. Predicting retention

The solvation parameter model is well suited to the prediction of retention in gas–liquid chromatography. Application requires that the systems to be studied are first characterized and a suitable model generated. Then the retention for any solute with known solute descriptors, or solutes for which reasonable estimates of the descriptors are possible, can be estimated by simple arithmetic. On an individual compound basis the accuracy of the prediction will depend on the uncertainty in the solute descriptors and the model system constants. The average uncertainty in model predictions is available as the standard error in the estimate extracted from the multiple linear regression analysis of the data used to establish the model. For gas–liquid chromatography values of 0.01 to 0.05 log units are quite common when the gas–liquid partition coefficient, retention factor, or relative retention values in logarithmic form are used as the dependent variable in the solvation parameter model. In spite of ease of application, we are unaware of any practical applications of the use of the solvation parameter model in method development in GC outside the genera of stationary phase classification. An obvious contributing factor is the early stage of evolution of the model within the general framework of computer-aided method development in chromatography and the fact that most system constants are available for packed column stationary phases at a time when open tubular columns dominate the applications area of GC. A further consideration is that published phase constants tend to be available for a single temperature only (with just a few exceptions [48,97,99,130])

reflecting the emphasis on classification of stationary phases rather than method development. In practice, almost any approach to method development in GC would have to include temperature optimization, since it is unlikely that individually optimized separations of a mixture on stationary phases of different selectivity would occur at a common temperature. This is not a problem for the application of the solvation parameter model because the individual phase constants can be represented as a simple continuous function of temperature. Retention, therefore, could be predicted as a function of temperature, and an objective function employed to define the temperature yielding the desired separation by computer-aided techniques.

5.1. Influence of interfacial adsorption

Although gas–liquid partitioning is the dominant retention mechanism in gas–liquid chromatography it is not the only possible retention mechanism. Partitioning may be accompanied by interfacial adsorption at the gas–liquid interface and by adsorption at the support or capillary column wall. If the stationary phase film is reasonably thick, it will be possible to ignore any differences in retention that might arise from modification of the properties of the thin film of liquid in immediate contact with the support–wall surface and to write a general retention equation as

$$V_N = K_L V_L + K_{GL} A_{GL} + K_{GLS} A_{LS} \tag{24}$$

where V_N is the net retention volume, K_L the gas–liquid distribution constant, V_L the volume of stationary phase in the column, K_{GL} the adsorption coefficient at the gas–liquid interface, A_{GL} the gas–liquid interfacial surface area for the column, K_{GLS} the coefficient for adsorption at the liquid–solid interface, and A_{LS} the liquid–solid interfacial surface area for the column. Eq. (24) has been widely used to determine gas–liquid distribution constants in packed column GC by extrapolation of V_N/V_L against $1/V_L$ for several phase loadings to $1/V_L = 0$ (for a detailed bibliography, discussion of approximations used in deriving equation, and experimental requirements see Refs. [1,11,12,37,43,131–133]). Application of Eq. (24) to open tubular columns to de-

termine the gas–liquid distribution constant is less common, but feasible for smooth wall columns, by substituting the film thickness for the volume of stationary phase and assuming that the surface area of the column wall and liquid surface are identical [134,135]. A more general application of Eq. (24) to open tubular columns has been to demonstrate the importance of interfacial adsorption as a general retention mechanism and its impact on the reproducibility of retention and retention index values for different columns prepared with the same stationary phase [136–139]. The general results for open tubular columns and packed columns are similar. Adsorption at the support–wall interface is not generally important for well deactivated supports–walls when normal to thick films are employed. Any exceptions are found for the separation of polar solutes on low polarity stationary phases with limited support–wall activity masking ability [33,34,132,140]. Gas–liquid partitioning is the dominant retention mechanism for nearly all solutes and for solutes retained by a mixed retention mechanism liquid-interfacial adsorption is of increasing importance for thin films (larger surface area to volume ratio), low temperatures (the contribution from adsorption relative to absorption usually declines at higher temperatures), and for solutes of significantly different polarity to the stationary phase. The prime example of the latter is the retention of *n*-alkanes on polar phases, where interfacial adsorption may be as important as partitioning, and retention index values calculated from the adjusted retention time, in the usual way, of limited value for interlaboratory studies. Further observations of the consequences of a mixed retention mechanism on the reliability of retention index values are discussed elsewhere [11,37,131,132,138]. It is uncommon to use absolute values of retention for interlaboratory studies because of the difficulty of measurement. A new procedure for the calculation of specific retention volumes in open tubular column GC may alleviate some of this problem, particularly when the results are intended for thermodynamic calculations of stationary phase properties, rather than for solute identification purposes [19,141].

The problem with gas–liquid interfacial adsorption is far more significant when either absolute stationary phase or solute properties are to be determined or

interlaboratory reproducibility of retention data is considered. It is likely less important for method development. With the possible exception of *n*-alkanes it has always proven possible to fit retention data in the form of the apparent gas–liquid distribution constant or retention factor to the solvation parameter model and obtain a good statistical fit. It seems likely that adsorption at the liquid surface and absorption in the bulk stationary phase involve the same types of intermolecular interactions but with different intensities. The specific retention volume for solutes of different polarity change quite smoothly as the contribution from interfacial adsorption and partitioning are varied by changing the phase loading, temperature, or chain length for a homologous series of compounds [37,43]. Local fits of the retention factor for a varied group of solutes determined for different temperatures should allow models to be built and a relationship between temperature and phase constants established for method development. Li and co-workers [96,142] used a similar approach, and a related model to the solvation parameter model, to fit the retention factors for a varied group of solutes on different open tubular columns at several temperatures to derive thermodynamic information about the properties of the stationary phases. Their interest was not method development, but their work illustrates the feasibility of constructing models that by their internal consistency suggest that method development by the approach described should be feasible.

6. Applications of the solvation parameter model in materials and function characterization

GC is an ideal tool for characterizing bulk solvent or surface interactions of solutes with materials that can be coated as liquid films or particle layers on chromatographic supports or the walls of open tubular columns. Alternatively, materials that can be obtained in narrow particle size ranges can be used without a support. Only small amounts of materials are required and physicochemical properties can be determined over a wide temperature range when allowed by the physical properties of the materials. The use of solutes with known properties to characterize the unknown complementary properties of

materials employed as a stationary phase in GC is often referred to as inverse GC. The classification of stationary phases could be considered an example of an application of inverse GC. The gas chromatographic experiment provides a retention parameter, such as a distribution constant, specific retention volume, etc., that requires a model to express the results in a form suitable for interpretation of material properties. The solvation parameter is one such model that provides information about the contribution of defined intermolecular interactions to the sorption properties of the material. The derived phase constants may be used directly, as in the classification of stationary phases, or used indirectly by relationship analysis employing various chemometric procedures to construct functional models based on quantitative structure–behavior relationships. In this section we will briefly summarize those studies using GC and the solvation parameter model for materials property and function characterization.

6.1. Low volatility oils

An obvious application area is the characterization of solvent-dependent properties of low volatility oils. An early example was the determination of the gas–liquid distribution constant for the transfer of solutes from the gas phase to olive oil used subsequently to estimate oil–water partition coefficients and tissue–gas and blood–gas partition correlations [74]. Gas–liquid chromatography has been used to determine the solubility of compounds in soybean oil and for the estimation of the solubility of soybean oil in other solvents from the mass-fraction activity coefficient [143]. The results for the solubility of solutes in soybean oil at four temperatures are summarized in Table 18. Soybean oil is moderately

Table 18
System constants for the solubility of varied solutes in soybean oil at different temperatures (r and $b = 0$ in all cases)

Temperature (°C)	System constants			
	c	s	a	l
58.7	−0.415	0.815	1.602	0.820
79.0	−0.421	0.735	1.322	0.744
100.0	−0.414	0.649	1.089	0.671
123.4	−0.427	0.584	0.901	0.611

dipolar and polarizable, appreciably hydrogen-bond basic but not a hydrogen-bond acid, and has favorable lipophilic interactions. Its solubility properties are closest to those of long chain esters of aliphatic dicarboxylic acids.

The solvation parameter model was used to classify 47 crude oils of different geographical and geological origins by using the oils as stationary phases in GC [144–146]. The determination of crude oil processing and storage behavior from small scale production experiments are generally expensive and time consuming. This has created an interest in laboratory or computer-aided procedures for property estimates needed to predict process conditions. Crude oils are complex chemical mixtures and general attempts to predict processing properties from chemical groups have been unsuccessful because they fail to account for the variation of interactions of chemical groups that occur because of compositional differences between different oils. The mean, standard deviation and range of the phase constants for the crude oils at 50°C were as follows: $l = 0.851 \pm 0.009$ (0.840 to 0.874); $r = -0.016 \pm 0.035$ (−0.16 to 0.061, most values are 0); $s = 0.0452 \pm 0.085$ (0.290 to 0.637); $a = 0.896 \pm 0.115$ (0.603 to 1.153); and $b = 0.015 \pm 0.024$ (−0.035 to 0.326, largest value is exceptional and the next highest value is 0.067, many values are 0). The crude oils are lipophilic and moderately dipolar and polarizable with significant hydrogen-bond basicity, and some are weak hydrogen-bond acids. Three phase constants (l, s and a) after scaling and normalizing were selected for classification of the crude

oils in a triangular plot. The apexes of the triangle, corresponding to the maximum values of the phase constants, could be related to the paraffinic, asphaltenic and aromatic tendency of the crude oils. Two quantitative structure–behavior models to predict the kinematic viscosity and stability of oil–water emulsions from the phase constants of the solvation parameter models were established.

6.2. Liquid polymers

Application of the solvation parameter model to liquid polymers could be considered an extension of the earlier discussion on stationary phase classification, since many of the common phases used for GC are liquid polymers. As well as characterizing polymers in chemical terms other important properties of interest to polymer scientists such as the Flory–Huggins interaction parameter and the mass fraction activity coefficient can be predicted from the model equations. The system constants for a number of hydrocarbon polymers are summarized in Table 19 [147]. As is to be expected these polymers have a limited capacity for polar interactions. In this respect the weak hydrogen-bond basicity of the unsaturated hydrocarbon polymer, poly(1,2-butadiene), associated with the presence of alkene bonds, is the most notable feature. Poly(epichlorohydrin) and poly(methyl acrylate) are significantly more polar than the hydrocarbon polymers with a significant capacity for dipole-type and hydrogen-bond interactions, Table 20 [148]. Poly(methyl acrylate) is significantly more dipolar and a stronger hydrogen-bond base but

Table 19
System constants for hydrocarbon polymers determined at 100°C ($b = 0$ in all cases)

Polymer	System constant				
	l	r	s	a	c
Octacosane	0.663	0.156	0.021	0	−0.216
Dotriacontane	0.663	0.174	0.024	0	−0.230
Hexatriacontane	0.659	0.189	0.012	0	−0.235
Atactic polypropene	0.639	0.170	0.067	0	−0.298
Atactic polypropene	0.640	0.157	0.080	0	−0.276
Polyethylene	0.626	0.228	0.034	0	−0.279
Hydrogenated poly(2,3-dimethyl--1,4-butadiene)	0.643	0.253	0.062	0	−0.351
Poly(isobutene)	0.637	0.228	0.107	0	−0.425
Poly(1,2-butadiene)	0.623	0.133	0.355	0.201	−0.275

Table 20
System constants for poly(epichlorohydrin) and poly(methyl acrylate) polymers and a 50:50 blend at 76°C

System constant	Poly(epichlorohydrin)	Poly(methyl acrylate)	Polymer blend	Predicted volume average value
l	0.61	0.61	0.61	0.61
r	0.17	0.13	0.14	0.15
s	1.38	1.80	1.41	1.60
a	1.11	2.40	1.62	1.81
b	0.36	0.08	0.20	0.23
c	-0.77	-0.93	-0.60	-0.86

weaker hydrogen-bond acid than poly(epichlorohydrin). When the two polymers are blended together the significant deviation of the phase constants from the predicted volume average values is a strong indication of the formation of strong polymer–polymer interactions, and an indication of polymer compatibility. The phase constants for a series of poly(ethylene oxide) polymers differing by molecular mass are summarized in Table 21 [149]. The r and l phase constants increase with molecular mass while the s and a phase constants decrease, the latter reflecting the relative decrease in the concentration of terminal hydroxyl groups. There is a step change for the a constant as a function of molecular mass suggesting that poly(ethylene oxide) oligomers with a molecular mass below 3000 are characterized by an increasing hydrogen-bond basicity. Endcapping of the poly(ethylene oxide) polymer with a methyl group primarily affects the hydrogen-bond basicity of the polymer with a less significant change in the r phase constant. It was also shown that the free energy of acid–base and dipole-type interactions of

Table 21
System constants for monodisperse poly(ethylene oxide) polymers of different molecular mass at 120°C ($b = 0$ in all cases)

Number-average molecular mass	System constant				
	l	r	s	a	c
300	0.434	0.144	1.518	2.253	-0.769
400	0.437	0.162	1.482	2.120	-0.737
600	0.455	0.186	1.472	2.119	-0.805
1000	0.449	0.217	1.372	1.942	-0.726
1540	0.453	0.217	1.350	1.895	-0.722
4000	0.462	0.241	1.321	1.846	-0.728
6000	0.462	0.252	1.309	1.801	-0.714
20 000	0.462	0.260	1.301	1.782	-0.723

poly(ethylene oxide) polymers decrease with increasing temperature.

There is a difficulty in nomenclature when dealing with solute–polymer interactions, as follows. If we consider a binary system of a polymer and a second component, polymer chemists will refer to the second component as a "solvent" whereas chromatographers will treat the second component as a "solute". We shall use the same nomenclature as we have done throughout this review, and denote the polymeric stationary phase by the subscript "1" and the second component by the subscript "2". The second component, which in GC is the solute, will also be referred to as a "probe". An important use of GC in polymer chemistry, is for the determination of the Flory–Huggins polymer–probe interaction parameter, χ, and the mass fraction activity coefficient, Ω, of the probe in the polymer. The former is a particularly valuable parameter because it encodes the various polymer–probe interactions. If χ is less than about 0.5, the polymer and probe are compatible and the polymer will dissolve in the probe (as a solvent); if χ is greater than about 0.5, the polymer and probe are incompatible. Both χ and Ω can be calculated [150,151] from the specific retention volume of the probe on the polymeric stationary phase, V_g, where the latter refers to the column temperature, T.

$$\chi_\infty = \ln\left(RTV_1/V_g P_2^0 V_2\right) - 1 + V_2/M_1V_1$$
$$- (B_{22} - V_2)P_2^0/RT \qquad (25)$$

$$\Omega_\infty = \left(RT/V_g P_2^0 M_2\right)\exp\left[-P_2^0(B_{22} - V_2)/RT\right] \qquad (26)$$

In these equations V_1 and M_1 are the specific

volume and number average molecular mass of the polymer, and P_2^0, V_2 and B_{22} are the probe saturated vapor pressure, molar volume and second virial coefficient. All the polymer and probe parameters refer to the column temperature.

Romdhane and Danner [152] determined V_g values at 80, 90 and 100°C for probes on poly(butadiene) and used Eqs. (25) and (26) to calculate χ_∞ and Ω_∞. Abraham et al. [153] attempted to use the solvation equation, Eq. (9), to correlate χ_∞ and Ω_∞ and hence to be able to predict values for other probes. Rather poor equations were obtained, as shown in Eqs. (27) and (28) for data at 90°C.

$$\chi_\infty = -0.163 - 0.988R_2 + 1.152\pi_2^H + 3.316\Sigma\alpha_2^H$$
$$+ 0.538\Sigma\beta_2^H - 0.027\log L^{16}$$

$$n = 24, r^2 = 0.835, \text{S.D.} = 0.300 \tag{27}$$

$$\log \Omega_\infty = -0.525 - 0.519R_2 + 0.287\pi_2^H$$
$$+ 1.171\Sigma\alpha_2^H + 0.563\Sigma\beta_2^H + 0.008\log L^{16}$$

$$n = 24, r^2 = 0.722, \text{S.D.} = 0.191 \tag{28}$$

This result is not unexpected; Eqs. (25) and (26) contain not only V_g for the probe (as a solute) but also the saturated vapor pressure of the probe (as a solvent). Hence two sets of probe properties are involved, those for the probe as a solute and those for the probe as a solvent, and use of only one set will not be satisfactory [153].

Abraham et al. [153] reasoned as follows: direct predictions of χ_∞ and Ω_∞ are difficult, but indirect predictions could be made through predictions of V_g via the solvation equation. They divided the 24 probes into two sets, A and B, and obtained the solvation equations for V_g at 90°C,

$$\log V_g(A) = -0.025 + 0.401R_2 + 0.284\pi_2^H$$
$$+ 0.426\Sigma\alpha_2^H + 0.579\log L^{16}$$

$$n = 12, r^2 = 0.996, \text{S.D.} = 0.046 \tag{29}$$

$$\log V_g(B) = -0.155 + 0.204R_2 + 0.420\pi_2^H$$
$$+ 0.315\Sigma\alpha_2^H + 0.624\log L^{16}$$

$$n = 12, r^2 = 0.999, \text{S.D.} = 0.028 \tag{30}$$

In both cases the term $b\Sigma\beta_2^H$ was not significant,

as required for a stationary phase that has no hydrogen-bond acidity.

From Eq. (29), values of $\log V_g$ were predicted for the B series, and from the predicted $\log V_g$ values, χ_∞ and $\log \Omega_\infty$ were predicted for the B series. Similarly, Eq. (30) was used to predict $\log V_g$, χ_∞ and $\log \Omega_\infty$ for the A series. Results for 90°C are summarized in Table 22. The indirect method predicts χ_∞ with a standard deviation of 0.131 as compared to the standard deviation of 0.300 by the direct method. Since the range of observed χ_∞ values is 1.83 [152], the indirect method is very reasonable. Likewise, the indirect method predicts $\log \Omega_\infty$ with a standard deviation of 0.057 and the direct method with a standard deviation of 0.191, Eq. (28); the range of observed values is 1.10 [152] and a standard deviation of 0.057 is again quite good.

Abraham and Whiting [143] applied the same procedure to soybean oil as the stationary phase, and Morales and Acosta [154] to a set of probes on poly(propylene oxide). The latter workers found also that excellent correlations were obtained for $\log V_g$ but poorer correlations for χ_∞ and $\log \Omega_\infty$, and explained their results exactly (word for word!) as Abraham et al. [153] had done.

6.3. Carbon and organic polymer adsorbents

Although developed as a partition model, the solvation parameter model has been applied to adsorption and sorption systems in both gas and

Table 22
Prediction of $\log V_g$, χ_∞ and $\log \Omega_\infty$ for solutes on poly(butadiene) at 90°C

Term	Series	Average deviation	Standard deviation
Log V_g	A	0.038	0.064
	B	0.041	0.052
	Total	0.039	0.057
χ_∞	A	0.094	0.119
	B	0.087	0.147
	Total	0.090	0.131
Log Ω_∞	A	0.041	0.052
	B	0.038	0.063
	Total	0.039	0.057

liquid chromatography. This has provided useful information about the fundamental nature of surface interactions for popular adsorbents such as porous polymers [119,155] and carbon [156–158] in GC and porous polymers [116,121,159], carbon [160], silica gel [113], and chemically bonded phases [114,161] in liquid chromatography. The predictive ability of these models is not as good as for partition systems, but the results are chemically sensible and can be used for material characterization purposes.

The phase constants for materials studied by GC are summarized in Table 23. Multiple entries indicate either results for the same material at different temperatures or different studies of the same nominal polymer. The c term cannot be compared in different studies since the dependent variables are not the same in all cases. For the styrene–divinylbenzene sorbents the main contribution to retention is dispersion (positive l constant); lone-pair electron repulsion reduces retention (r constant is generally nega-

Table 23
System constants for sorbents studied by gas chromatography

Sorbent[a]	Temperature (°C)	Dependent variable	Phase constants					
			l	r	s	a	b	c
3M(a)	20	Log V_g	1.21	−0.70	0	0.54	0.85	−1.92
	70		1.01	−0.38	0	0.57	0.80	−2.73
	75		1.00	−0.32	0	0.64	0.68	−2.81
	80		0.98	−0.32	0	0.61	0.69	−2.88
	85		0.95	−0.26	0	0.61	0.66	−2.89
	90		0.93	−0.22	0	0.56	0.63	−2.92
3M(b)	20	Log V_g	1.27	−0.75	0	0	0.91	−1.87
	70		1.03	−0.33	0	0	0.59	−2.60
	80		1.02	−0.33	0	0	0.62	−2.77
	85		0.99	−0.29	0	0	0.60	−2.82
	90		0.98	−0.26	0	0	0.60	−2.90
PS–DVB	20	Log V_g	1.29	0.44	0	0.85	0.65	−2.46
Chromosorb 106	20		1.51	−1.17	0	0.67	0.83	−1.69
Porapak R	20		1.19	−0.67	0.37	2.02	0	−1.75
Tenax GC	10	Log V_B	0.97	0	1.07	0	0.31	−1.32
	20	Log V_g	1.39	−0.61	1.26	0	0	−2.54
	20	Log V_R	1.41	−0.37	0.73	0	0.48	−3.31
	20	Log V_R	1.40	−0.45	0.62	0	0	−2.87
	20	Log V_g	1.01	−0.52	0.47	0.54	0	−2.11
Tenax TA	20	Log V_B	1.35	−0.54	0.55	0.36	0.43	−2.18
Carbotrap	0	Log V_g	2.65	−2.27	0	0	0	−4.73
Graphite	25	Log K_g	0.46	−0.27	0.86	0.94	0	−0.86
Fullerene	25	Log K_g	0.48	−0.24	0.72	1.04	0	−1.58

[a] 3M(a): Poly(styrene–divinyl benzene) (PS–DVB) macroreticular porous polymer with a surface area of 350 m^2/g; 3M(b): poly(styrene–divinyl benzene) macroreticular porous polymer with a surface area of 880 m^2/g; Chromosorb 106: poly(styrene) macroreticular porous polymer with a surface area of 700–800 m^2/g; Porapak R: poly(vinylpyrolidone) macroreticular porous polymer with a surface area of 450–600 m^2/g; Tenax: poly(2,6-diphenylphenylene oxide) polymer with a surface area <20 m^2/g; Carbotrap: graphitized carbon black with a surface area of about 100 m^2/g; Fullerene: a mixture of 83.9% C_{60} and 16.1% C_{70}.

tive); dipole-type interactions are not significant ($s = 0$); all four sorbents are weak hydrogen-bond acids (positive b constant); and three of the four sorbents are weak hydrogen-bond bases (positive a constant). Since the formal structure of these polymers contains no hydrogen-bond acid groups, and only a limited ability to function as a hydrogen-bond base is anticipated through the aromatic rings and alkene groups, then it is likely that these polymers contain unexpected polar groups introduced during synthesis or thermal conditioning. The poly(vinylpyrolidone) sorbent is more dipolar and a significantly stronger hydrogen-bond base than the styrene–divinylbenzene polymers, as would be expected from its structure. It also has no hydrogen-bond acidity, as expected. Retention on Tenax is dominated by dispersion, but in contrast to the styrene–divinylbenzene sorbents, a significant contribution results from dipole-type interactions (large s constant). The dominance of dispersion and the sorbent's capacity for induction interactions resulting from its polarizability are anticipated from the structure of Tenax (a polymer of 2,6-diphenylene oxide), but as for the styrene–divinylbenzene sorbents, the weak hydrogen-bond acidity identified for some samples is difficult to rationalize, and is presumably an indication of impurities or structural heterogeneity in some samples of the polymer. Where a comparison is possible, increasing the surface area of the sorbent leads to an increase in retention, primarily through an increase in the contribution from dispersion interactions, and increasing temperature reduces retention through its influence on all phase constants (except for r which becomes less negative).

Polar interactions are not important for retention on Carbotrap ($s = a = b = 0$) and only dispersion interactions, which lead to retention (positive l constant), and lone-pair electron repulsion, which reduces retention (negative r constant), need be considered. By contrast, graphite is rather weakly polarizable, has significant hydrogen-bond basicity, and a lower capacity for dispersion interactions. The results for Carbotrap and graphite serve to illustrate the wide range of properties common to different forms of carbon related to their manufacture and thermal history [162]. The sorbents characterized in Table 23 are often used for sorbent trapping of volatile organic compounds from air. The variation

in their phase constants provides a rational basis for both understanding why sorbents behave differently as well as a basis for sorbent selection for a particular problem [119,155].

The solvation parameter approach can also be used to determine physicochemical characteristics of adsorbents, and to obtain information difficult to collect by any other method. Grate et al. [157,158] measured adsorption isotherms of solutes on fullerene and graphite at 25°C by the method of elution by characteristic point; from the isotherms they calculated gas–solid distribution constant at zero surface coverage, K_C, defined as,

$$K_C = (C_S / C_g); \quad C_g \to 0 \qquad (31)$$

where C_S and C_g are the concentrations of solute in the solid and in the gas phase. Application of the solvation parameter equation to the determined log K_C values resulted in very similar correlation equations for graphite and fullerene, see Table 23, so that the adsorption properties of these two forms of carbon are virtually the same. The full correlation equation for fullerene log K_C values was,

$$\log K_C = -1.58 - 0.24 R_2 + 0.72 \pi_2^H + 1.04 \Sigma \alpha_2^H$$
$$+ 0.48 \log L^{16}$$
$$n = 22, \, r^2 = 0.904, \, \text{S.D.} = 0.12, \, F = 40 \qquad (32)$$

Hence fullerene can be deduced to be weakly polarisable, a significant but not very strong hydrogen-bond base, of no hydrogen-bond acidity at all, and not very lipophilic. These properties are not in accord with fullerene as a highly aromatic molecule, but are quite consistent with fullerene as a giant closed-cage polyalkene [157]. Extrapolation of the system constants [153] for log V_g on poly(butadiene) to 25°C gives an s constant of 0.49 and an a constant of 0.67, not too far away from the system constants for fullerene in Eq. (32).

7. Conclusions

We have outlined the properties of a new solvation model for GC and its subsequent interpretation in terms of cavity formation and solute–solvent interactions applied to the classification of stationary

phases, the prediction of retention for method development, and for materials and function characterization. From the large number of stationary phases that have been characterized, further stationary phases with properties that complement existing phases, such as polar phases with a significant hydrogen-bond acidity, are identified as potentially useful new stationary phases for selectivity optimization in GC. In the future, expanded use of the solvation parameter model for the prediction of retention and temperature optimization in computer-aided method development can be expected. In addition, GC is shown to be a suitable technique for the determination of further solute descriptors using fully characterized stationary phases, as well as for the characterization of the sorption properties of materials, using fully characterized solutes. The fact that the solvation parameter model has a firm fundamental basis and has been applied to a large number of chromatographic systems containing both gas and condensed phases, without recorded failure, is a strong indication that the model will gain in importance as the primary tool for interpretation of retention related properties in chromatography.

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