

Influence of temperature on the mechanism by which compounds are retained in gas–liquid chromatography

Salwa K. Poole, Theophilus O. Kollie, Colin F. Poole*

Department of Chemistry, Wayne State University, Detroit, MI 48202, USA

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Abstract

The influence of temperature on the retention mechanism and solvation interactions of 46 varied solutes in 10 representative stationary phases of different polarity within the temperature range of 60 to 140°C is discussed. Gas–liquid partition is shown to be the dominant retention mechanism for most solutes with interfacial adsorption of increasing importance at low phase loadings, low temperatures and for solutes of different polarity to that of the stationary phase. Guidelines are presented for predicting those conditions for which interfacial adsorption is likely to be a significant retention mechanism.

A cavity model is used to characterize the solvation process in terms of the free energy contributions to solvation from the cavity–dispersion interactions and the sum of the remaining polar interactions. As a function of temperature it is shown that the contribution from polar interactions are only weakly temperature dependent over the temperature range studied while the cavity–dispersion interactions term shows a much more significant variation becoming less favorable for solute transfer at higher temperatures. In all cases, the contribution of the cavity–dispersion interactions term is favorable for solute transfer from the gas phase to the liquid phase.

Principal component analysis is used to identify the factors contributing to the solvation process and their individual temperature dependence. In the case of the cavity–dispersion interactions term one factor accounts for more than 99.7% of the total variance. Three factors are identified as contributing to the polar interactions term. The first principal component accounts for more than 95% of the total variance at all temperatures and by correlation with other independent scales of dipolarity/polarizability is identified as representing the contribution from orientation and induction interactions. The two remaining principal components are shown to represent hydrogen-bond formation and charge-transfer complexation involving systems with π -electrons. The temperature dependence of the principal components provides insights into the general role of polar intermolecular interactions on the solvation process and their temperature variation.

1. Introduction

Temperature is a fundamental parameter that affects both resolution and the separation time in gas–liquid chromatography [1–3]. Its optimization in both isothermal and temperature-pro-

grammed separations has been discussed extensively in the contemporary literature and will not be elaborated on here. The topic of this paper is the influence of temperature on the retention mechanism in gas–liquid chromatography and on the contribution of specific intermolecular interactions participating in the retention process. These are topics that need to be addressed

* Corresponding author.

before the applicability of the cavity model of the solvation process in gas–liquid chromatography can be assessed as a general approach to the prediction of retention and the selection of the optimum stationary phase and temperature for a given separation [4,5].

Retention in gas–liquid chromatography can be a complex process involving partitioning with the liquid stationary phase and interfacial adsorption at the support surface and/or the liquid surface [6–9]. This can be expressed as

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

where V_N^* is the net retention volume per gram of column packing, V_L the volume of liquid stationary phase per gram of column packing, K_L the gas–liquid partition coefficient, A_{GL} the gas–liquid interfacial area per gram of packing, K_{GL} the adsorption coefficient at the gas–liquid interface, A_{LS} the liquid–solid interfacial area per gram of packing and K_{GLS} the coefficient for adsorption at the liquid–solid interface. Eq. 1 was originally proposed by Martin [10] and within the constraints discussed below has been validated as an accurate representation of the retention process in gas–liquid chromatography by Purnell and co-workers [11,12], Riedo and Kováts [13], Liao and Martire [14], Nikolov [15], Karger and Liao [16], Castells and co-workers [17,18], Berezkin [9] and Poole and co-workers [4,6,7,19–22]; the general applications of Eq. 1 are reviewed in refs. 1, 4, 6–9 and 23. In deriving Eq. 1 it is assumed that the individual retention mechanisms are independent and additive, the solute concentration is in a region where the infinite dilution and zero surface coverage approximations apply, and the contributions to retention from the structured liquid-phase layer in close contact with the support surface can be neglected (generally the case at high phase loadings). The experimental data reported in this paper were obtained under conditions where the above constraints can safely be assumed to apply [24]; otherwise it would be necessary to use an alternative model to describe the retention process in terms of the same general contributions identified in Eq. 1 [3,11]. Division of both sides of Eq. 1 by V_L allows the

gas–liquid partition coefficient to be evaluated independently of the other contributions to retention by extrapolating the experimental data to obtain the intercept on the V_N^*/V_L axis corresponding to an infinite stationary liquid phase volume. In virtually all cases investigated for which the general conditions used to derive Eq. 1 are applicable it has proven possible to obtain accurate values for the gas–liquid partition coefficient by a linear extrapolation, at least for intermediate temperatures around 100°C. This indicates that when adsorption contributes to the retention mechanism the dominant contribution for non-polar liquids is adsorption at the support–liquid interface and for polar liquids adsorption at the gas–liquid interface. In theory it should be possible to determine the coefficients for adsorption in Eq. 1 from a knowledge of the surface area terms A_{LS} and A_{GL} ; in practice this is difficult to do because of a lack of a straightforward and reliable experimental method for determining surface areas as a function of the stationary liquid phase loading [10,13,16,25]. Insights into the importance of adsorption as a retention mechanism, however, may be obtained by comparing the observed experimental retention with the value calculated assuming that the only contribution to retention was from gas–liquid partitioning [21,26]. A lack of knowledge of the adsorption contribution to retention in gas–liquid chromatography is the primary problem in predicting retention since the solvation models that are available are applicable to gas–liquid partition chromatography and there is no easy way to extend them to situations in which a mixed retention mechanism occurs without knowing the particulars of the relationship between the surface area of the liquid and of the support as a function of the bulk liquid stationary phase volume. This is currently impractical and therefore the contributions of adsorption to retention establishes one limit to the usefulness of solvation models for the prediction of retention.

In this paper we will provide a general assessment of the importance of interfacial adsorption as a retention mechanism in gas–liquid chromatography to identify those conditions and com-

pound types for which interfacial adsorption is unimportant. This discussion will include temperature, since it impacts on the relative importance of adsorption and partitioning mechanisms for defined solutes. Previous studies have indicated that for those compounds which are retained by a mixed retention mechanism the relative contribution from gas–liquid partitioning increases with temperature when data are compared at 120 and 80°C [4]. To our knowledge there are no true studies describing how the relative contribution of partitioning and adsorption change over a wide temperature range employing a large group of solutes of varied character on a significant number of stationary liquid phases selected to encompass a wide capacity range for selective solvent intermolecular interactions.

There are numerous models that have been proposed to characterize retention in gas–liquid chromatography as a function of solvent and solute properties, reviewed in refs. 1, 6, 19, 20 and 27]. The most recent and generally useful approaches are the solvation parameter model developed by Abraham and co-workers [28–31] and Carr and co-workers [32–34] and the free energy solvation model developed by Poole and co-workers [4,35–37]. These models are derived from the cavity model of solvation, in which the process of solute transfer from the gas phase to solution in the stationary phase is considered to occur in three stages: (1) the creation of a cavity in the solvent of a suitable size to accommodate the solute, (2) reorganization of the solvent molecules around the cavity and (3) introduction of the solute into the cavity where it is able to interact with the surrounding solvent molecules. The Gibbs free energy change for the transfer process is simply the sum of the free energy changes for each step. There is no exact method to calculate the individual contributions to the total free energy change for the solvation process, as just defined, and it is necessary to resort to empirical approaches to estimate the changes involved using experimentally accessible parameters. The approach of Abraham and co-workers (and essentially also that of Carr and co-workers with some differences in the explanatory vari-

ables) results in the following general equation relating the gas–liquid partition coefficient, K_L , to the characteristic parameters for the solvation process

$$\log K_L = c + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H + l \log L^{16} \quad (2)$$

where c is a constant, R_2 the solute excess molar refraction, π_2^H the effective solute dipolarity/polarizability, α_2^H the effective hydrogen-bond acidity, β_2^H the effective hydrogen-bond basicity, and L^{16} the gas–liquid partition coefficient on *n*-hexadecane at 25°C. The explanatory variables (R_2 , π_2^H , α_2^H , β_2^H and $\log L^{16}$) are solvation parameters derived from equilibrium measurements. Values of the solvation parameters for in excess of 1000 compounds are currently available and in many cases unknown values can be estimated using simple combining rules [38]. The solvent parameters r , s , a , b and l are unambiguously defined: the r constant refers to the ability of the phase to interact with solute π - and n -electron pairs; the s constant to the ability of the phase to take part in dipole–dipole and dipole–induced dipole interactions; the a constant is a measure of the hydrogen-bond basicity of the phase; the b constant is a measure of the hydrogen-bond acidity of the phase; and the l constant incorporates contributions from solvent cavity formation and dispersion interactions, and more specifically indicates how well the phase will separate members in a homologous series. The phase constants can be determined for any solvent by multiple linear regression analysis of measured values of K_L for solutes with known values of their explanatory variables. Once the phase constants are defined, the retention of any solute for which explanatory variables are known or can be estimated with sufficient accuracy can then be estimated from Eq. 2. The validity of this approach has been demonstrated in a number of papers by Abraham and co-workers referenced above. Nearly all this work refers to a single temperature or temperatures which are close together. The explanatory variables used in the regression analysis are determined at room temperature. Any change in solute–solvent in-

teractions as a function of temperature is clearly a function of the properties of both the solute and the solvent. There is no means to separate these different contributions in multiple linear regression models and it has proved necessary to adopt the convention that any change in the characteristic phase constants with temperature are due to changes in solvent properties alone. This is not too significant for the comparison of different solvents at a fixed temperature but it precludes the phase constants being used as absolute solvent properties. It is also unclear if they can be used to quantitatively represent changes in solvent properties as a function of temperature, although a recent study has demonstrated that the individual phase constants show smooth changes as a function of temperature and can generally be fitted to a second order polynomial function (except for the constant c) [39].

The model proposed by Poole and co-workers should be more tractable to studying the influence of temperature on solvation properties. In its most useful form for this investigation it can be written as

$$\Delta G_s^{\text{SOLN}}(\text{X}) = \Delta G_s^{\text{SOLN}}(\text{HC})^{\text{V}} + \Delta G_{\text{SQ}}^{\text{P}}(\text{X}) + \Delta G_s^{\text{INT}}(\text{X}) \quad (3)$$

where $\Delta G_s^{\text{SOLN}}(\text{X})$ is the partial molal Gibbs free energy of solution for the transfer of solute X from the gas phase to the stationary phase S, $\Delta G_s^{\text{SOLN}}(\text{HC})^{\text{V}}$ is the partial Gibbs free energy of solution for an n -alkane with an identical Van der Waals volume to solute X in the stationary phase S, $\Delta G_{\text{SQ}}^{\text{P}}(\text{X})$ is the partial Gibbs free energy of interaction for the polar contribution of solute X in a non-polar reference solvent squalane, SQ, and $\Delta G_s^{\text{INT}}(\text{X})$ is the partial Gibbs free energy of interaction for the polar contribution of solute X to solvation in solvent S. Experimentally, the Van der Waals volume of solute X is calculated along with the coefficients describing the linear fit for $\log K_L$ against the Van der Waals volume of the homologous series of n -alkanes on the non-polar reference phase squalane and the stationary phase S, together with the gas-liquid partition coefficient for solute X on squalane and stationary phase S. All

the terms in Eq. 3 can then be evaluated. The contribution from cavity formation and solute-solvent dispersion interactions is represented by the sum of the first two terms on the right-hand side of Eq. 3. These two contributions cannot be evaluated separately. The $\Delta G_s^{\text{INT}}(\text{X})$ parameter represents the sum of the polar interactions, such as orientation and hydrogen-bond formation, which must be further deconvoluted by principle component analysis for a representative collection of solutes to identify the capacity of the solvent S for specific polar intermolecular interactions.

Although the models proposed by Abraham and co-workers and Poole and co-workers were developed independently and use different approaches to evaluate the contribution of cavity formation and solute-solvent interactions to the solvation process, both models in fact yield similar results for the cavity-dispersion contribution and the contribution of polar interactions to the solution of a large number of varied solutes in a wide variety of liquid stationary phases [4,26,39,40]. There is, perhaps, a small numerical difference in the magnitude of the cavity-dispersion contribution to solvation predicted by both models but this does not affect the agreement in general trends in solvation properties that have been characterized by both models. The availability of two complementary approaches for exploring the solvation processes in gas-liquid chromatography provides additional flexibility with the final choice of the model employed resting on the type of available experimental data. For studies involving the affect of temperature on the solvational process Poole's model is preferred since it involves no unambiguous assumptions as to the nature of the temperature dependence of solute-solvent interactions.

2. Experimental

The names, abbreviations, compositions and temperature ranges studied for the stationary phases used in this study are summarized in Table 1. Squalane, QF-1, CW-20M, DEGS, TCEP and Chromosorb W AW (177–250 μm)

Table 1
Stationary phases and the temperature range studied

Abbreviation	Chemical description	Temperature range (°C)
SQ	Squalane	60–120
OV-105	Poly(cyanopropylmethyldimethylsiloxane)	60–120
OV-17	Poly(methylphenylsiloxane)	80–140
QF-1	Poly(trifluoropropylmethylsiloxane)	60–120
OV-225	Poly(cyanopropylmethylphenylmethylsiloxane)	80–140
CW-20M	Poly(ethylene glycol)	80–140
THPED	N,N,N',N'-Tetrakis(2-hydroxypropyl)ethylenediamine	60–120
TCEP	1,2,3-Tris(2-cyanoethoxypropane)	80–140
DEGS	Poly(diethylene glycol succinate)	80–140
QPTS	Tetra- <i>n</i> -butylammonium 4-toluenesulfonate	80–140

were obtained from Anspec (Ann Arbor, MI, USA); OV-105, OV-17, OV-225 from Ohio Specialty Chemicals (Marietta, OH, USA); and THPED and QPTS from Aldrich (Milwaukee, WI, USA). All solvents were of OmniSolv grade from EM Science (Gibbstown, NJ, USA). The

test solutes in Table 2 were obtained from several sources and were of the highest purity generally available. The homologous series of *n*-alkanes with carbon numbers from 7 to 16 were obtained from Aldrich.

Columns containing form about 8 to 20% (w/

Table 2
Solute and their Van der Waals volumes selected to evaluate polar interactions in the temperature range 60–140°C

Solute	Van der Waals volume (V_A)	Solute	Van der Waals volume (V_A)
Benzene	50.46	1-Nitropentane	69.61
Toluene	70.34	1-Nitrohexane	80.27
Ethylbenzene	71.00	Nitrocyclohexane	72.81
Butylbenzene	92.72	Chlorobenzene	59.50
Oct-2-yne	81.84	Bromobenzene	64.68
Dodec-1-yne	122.79	Iodobenzene	68.29
Butan-2-one	48.21	Benzaldehyde	60.64
Pentan-2-one	58.36	Acetophenone	70.34
Hexan-2-one	68.59	Methylphenyl ether	64.86
Heptan-2-one	78.47	Benzonitrile	61.30
Octan-2-one	88.95	Nitrobenzene	61.61
Nonan-2-one	98.94	Aniline	57.03
Decan-2-one	109.12	N-Methylaniline	67.15
Undecan-2-one	119.27	N,N-Dimethylaniline	78.29
Dodecan-2-one	129.42	Pyridine	47.75
Methyl hexanoate	93.40	2,4,6-Trimethylpyridine	77.44
Methyl heptanoate	103.40	Dioxane	52.99
Methyl octanoate	114.00	1,1,2,2-Tetrachloroethane	65.28
Butan-1-ol	53.42	Nonanal	99.85
Pentan-1-ol	63.54	N,N-Dimethylacetamide	55.46
Hexan-1-ol	73.79	<i>o</i> -Dichlorobenzene	68.41
Heptan-1-ol	83.47		
Octan-1-ol	94.79		
2-Methyl-1-pentanol	73.59		
1-Nitropropane	49.32		

w) of liquid phase were prepared using the rotary evaporator technique [1]. After coating the damp packings were dried in a fluidized-bed dryer and packed into glass columns 2 m × 2 mm I.D. with the aid of vacuum suction and gentle vibration. Gas chromatographic measurements were made using a Varian 3700 gas chromatograph (Walnut Creek, CA, USA) fitted with a flame ionization detector.

The experimental protocol used to determine gas–liquid partition coefficients is described in detail elsewhere [24,41]. A minimum of four phase loadings was used in the extrapolation method to define the gas–liquid partition coefficients and in the study of the influence of phase loading on the contribution of interfacial adsorption to the general retention mechanism as a function of temperature. Phase loadings were determined by exhaustive Soxhlet extraction. A modified Lipkin bicapillary pycnometer was used to determine solvent densities as a function of temperature [24,42]. A mercury manometer was used to measure the column inlet pressure and a US National Institute of Standards and Technology (NIST)-certified thermometer ($\pm 0.2^\circ\text{C}$) to measure ambient and column temperatures. The uncertainty in K_L values is typically 3–5% R.S.D. for K_L values between 10 and 100 and 2–3% R.S.D. for values > 100 .

The experimental specific retention volume, $V_g^0(\text{ex})$, which includes contributions from all retention mechanisms, was determined using Eq. 4

$$V_g^0(\text{ex}) = \frac{273.2V_N}{w_L T_c} \quad (4)$$

where V_N is the net retention volume, w_L the weight of liquid phase in the column and T_c the column temperature. The specific retention volume for gas–liquid partitioning only, $V_g^0(\text{part})$, was determined using Eq. 5

$$V_g^0(\text{part}) = \frac{273.2K_L}{T_c \rho_c} \quad (5)$$

where ρ_c is the liquid phase density at the column temperature. The contribution of interfacial adsorption to the retention mechanism was evaluated by difference defining the contribution

of interfacial adsorption to the specific retention volume, $V_g^0(\text{ads})$, as

$$V_g^0(\text{ads}) = V_g^0(\text{exp}) - V_g^0(\text{part}) \quad (6)$$

which for convenience can be expressed as a percentage as $100V_g^0(\text{ads})/V_g^0(\text{exp})$.

The free energy terms in the model of Poole and co-workers can be calculated in a number of ways. The following equations are useful when using a spread sheet program to perform the computations. The partial molal Gibbs free energy of solution for solute (X) on any phase S is given by

$$\Delta G_m^0(\text{X}) = -2.303 RT_c \log \frac{1000K_L(\text{X})}{RT_c \rho_c} \quad (7)$$

where R is the molar gas constant. $\Delta G_m^0(\text{X})$ is equivalent to $\Delta G_s^{\text{SOLN}}(\text{X})$ in Eq. 3 when the molal standard state is adopted for the calculation. The cavity–dispersion term for the molal standard state is given by

$$\begin{aligned} \Delta G_s^{\text{SOLN}}(\text{HC})^V + \Delta G_{sO}^P(\text{X}) \\ = -2.303RT_c \log(1000[K_L^{\text{NV}}(\text{X})]_s \\ \cdot [K_L(\text{X})]_{sO}) / RT_c \rho_c [K_L^{\text{NV}}(\text{X})]_{sO} \quad (8) \end{aligned}$$

where $K_L^{\text{NV}}(\text{X})$ is the gas–liquid partition coefficient for an n -alkane with an identical Van der Waals volume to solute (X) and is derived from the linear correlation between $\log K_L^{\text{NV}}$ and the Van der Waals volume for the n -alkanes on any phase at a specified temperature

$$\log K_L^{\text{NV}}(\text{X}) = m_s V_A + b_s \quad (9)$$

where m_s and b_s are the coefficients obtained by linear regression on the stationary phase S. The method used to calculate the Van der Waals volumes is discussed below; appropriate values for the test solutes are summarized in Table 2. The polar interaction term in Eq. 3 is given by

$$\begin{aligned} \Delta G_s^{\text{INT}}(\text{X}) = -2.303RT_c \log([K_L(\text{X})]_s \\ \cdot [K_L^{\text{NV}}(\text{X})]_{sO}) / ([K_L(\text{X})]_{sO} \cdot [K_L^{\text{NV}}(\text{X})]_s) \quad (10) \end{aligned}$$

There were some instances where it was impossible to generate accurate data for the gas–

liquid partition coefficients and alternative methods were used for their estimation to enable the data set to be evaluated as homogeneously as possible for chemometric analysis. Squalane was too volatile at 141.2°C to determine reliable values for the gas–liquid partition coefficients of any solutes. These values were needed to make use of the data that could be obtained on the polar phases at 141.2°C. In this instance estimated values were obtained by fitting the experimental data obtained over the temperature range 60–120°C to a second order polynomial for $\log K_L(X)$ against $1000/T_c$. This equation was then used to estimate the value of $K_L(X)$ at 141.2°C. These data are summarized in Table 3. The correlation for the fit is very good, $r^2 = 1.000$, but it cannot be assumed that these estimated values are as reliable as the experimental values obtained at a lower temperature since it is impossible to define exactly the physical relationship describing the data set. The

plot of $\log K_L(X)$ against $1000/T_c$ shows genuine curvature over the temperature range used to collect the experimental data and a linear extrapolation is therefore inappropriate. A small number of gas–liquid partition coefficients were difficult to determine because of excessive retention on the stationary phases and these were estimated using the model of Abraham and co-workers, Eq. 2, and the appropriate characteristic phase constants and explanatory variables are summarized in ref. 39. These data are summarized in Table 4. It is estimated that the typical error in these values is about 0.01 to 0.04 log units.

The Van der Waals volumes for the test solutes in Table 2 were calculated with the molecular modeling program MacroModel 2.0 (Department of Chemistry, University of New York, New York, NY, USA) executed on a VAX 11/750 computer (Digital Equipment, Merrimack, NH, USA). The polynomial fit for $\log K_L$ against

Table 3
Estimated $\log K_L(X)$ values for squalane at 141.2°C

Solute	Log $K_L(X)$	Solute	Log $K_L(X)$
<i>n</i> -Heptane	1.548	Hexan-1-ol	1.811
<i>n</i> -Octane	1.829	Heptan-1-ol	2.092
<i>n</i> -Nonane	2.111	Octan-1-ol	2.391
<i>n</i> -Decane	2.382	2-Methyl-2-pentanol	1.488
<i>n</i> -Undecane	2.672	1-Nitropropane	1.406
<i>n</i> -Dodecane	2.954	1-Nitropentane	1.967
<i>n</i> -Tridecane	3.236	1-Nitrohexane	2.273
<i>n</i> -Tetradecane	3.519	Nitrocyclohexane	2.537
<i>n</i> -Pentadecane	3.800	Chlorobenzene	1.918
<i>n</i> -Hexadecane	4.080	Bromobenzene	2.156
Benzene	1.446	Iodobenzene	2.455
Toluene	1.717	Benzaldehyde	2.130
Ethylbenzene	1.971	Acetophenone	2.406
<i>n</i> -Butylbenzene	2.541	Methylphenyl ether	2.097
Oct-2-yne	1.959	Benzonitrile	2.112
Dodec-1-yne	2.863	Nitrobenzene	2.444
Butan-2-one	1.089	Aniline	2.121
Pentan-2-one	1.332	<i>N</i> -Methylaniline	2.456
Hexan-2-one	1.618	<i>N,N</i> -Dimethylaniline	2.605
Heptan-2-one	1.898	Pyridine	1.555
Octan-2-one	2.170	2,4,6-Trimethylpyridine	2.215
Methyl hexanoate	1.950	Dioxane	1.368
Methyl heptanoate	2.222	1,1,2,2-Tetrachloroethane	2.129
Methyl octanoate	2.489	Nonanal	2.485
Butan-1-ol	1.106	<i>N,N</i> -Dimethylacetamide	1.912
Pentan-1-ol	1.532	<i>o</i> -Dichlorobenzene	2.420

Table 4
Gas-liquid partition coefficients estimated using Eq. 2

Stationary phase	Temperature (°C)	Solute	Log $K_L(X)$
SQ	61.2	Nitrobenzene	3.756
		N,N-Dimethylaniline	3.886
		Nonanal	3.9864
		Octan-1-ol	3.7755
		Acetophenone	3.7133
		Nitrocyclohexane	3.9715
		Methyl octanoate	3.9670
QF-1	61.2	1-Nitrohexane	4.0311
		Nitrocyclohexane	3.3731
		N,N-Dimethylacetamide	4.0745
THPED	61.2	Hexan-1-ol	4.1527
		Heptan-1-ol	4.5180
		Octan-1-ol	4.8929
		1-Nitrohexane	3.9767
		N,N-Dimethylacetamide	4.1285
		N-Methylaniline	4.0482
OV-105	61.2	Nitrocyclohexane	3.9834
QPTS	81.2	Nitrobenzene	4.1310
		Aniline	4.5453
		N-Methylaniline	4.2147
TCEP	81.2	N,N-Dimethylacetamide	3.9397
QPTS	101.2	Aniline	3.9806

$1000/T_c$ was performed on a Macintosh IIsi computer (Apple Computer, Cupertino, CA, USA) using Cricket Graph V1.3 (Cricket Software, Malvern, PA USA). Multiple linear regression analysis was performed on an Epson Apex 200 computer (Epson America, Torrance, CA, USA) using the program SPSS/PC + V3.1 (SPSS, Chicago, IL, USA). For multivariate analysis Pirouette V1.1 (Infometrix, Seattle, WA, USA) was used on the Epson Apex 200 computer. The experimental data was used without scaling for principal component analysis.

3. Results and discussion

Numerous studies have considered the gross effect of temperature on the retention properties of individual compounds and it is widely accepted that temperature is an important variable

in the optimization of any separation. Where information is lacking is in the influence temperature has on the fundamental retention mechanism itself, whether individual compounds are retained by absorption and/or interfacial adsorption and the relative importance of temperature in regulating this process. Intuitively it is expected that absorption would be favored by higher temperatures and that adsorption behavior would be favored by lower temperatures, and thus temperature has to be considered as a critical variable in establishing the contributing factors to the gross retention mechanism. This becomes of additional importance because we now have good models that can predict absorption behavior of compounds and thus have the potential to simulate chromatographic separations on many stationary phases as a logical direction to approach an organized scheme for computer-aided methods development in gas-

liquid chromatography. These models, of course, will be limited in their general applications for systems that involve significant contributions to the retention mechanism from interfacial adsorption since this mechanism is not considered in their formulation. Thus we need a general picture of the importance of interfacial adsorption as a retention mechanism in gas–liquid chromatography with temperature as a variable since any useful simulation approach to separations by gas–liquid chromatography would incorporate temperature optimization, and for different phases it is likely that different optimum temperatures would be required.

Intuitively it is also anticipated that the relative strength of specific intermolecular interactions will vary with temperature in a manner that will depend on individual properties of the solvent and that a solvent will possess different capacities for these interactions at different temperatures so that a single measure of solvent selectivity at one temperature cannot be used to predict the contribution of intermolecular forces to retention at other temperatures. Where different solvents are involved, the capacities for individual intermolecular interactions are unlikely to change in a proportionate manner with temperature. Thus some indication of changes in the solvation properties of a stationary phase as a continuous function of temperature is needed.

To shed some light on both of the above issues we have designed a study to define the general effect of temperature on the retention mechanism and the solvation process for a group of ten liquid stationary phases representing a wide range of solvent properties and a varied group of solutes representing an equally diverse range of solute size and polarity. To make the study realistic we have attempted to cover the widest possible temperature range over which individual solutes could be studied while still exhibiting acceptable chromatographic behavior. Experimentally it was determined that a 60°C temperature range was the maximum that could be explored if the extrapolation method was used to determine gas–liquid partition coefficients since a fairly wide range of phase loadings must be available to minimize the error in fitting

the data to Eq. 1. The collection of experimental data was commenced using approximately 70 varied solutes from which about 46 gave acceptable retention properties on all stationary phases at all temperatures. These compounds are identified in Table 2. Two factors dictated the choice of temperature region employed. Solute–solvent intermolecular interactions should contribute more significantly to the retention process at lower temperatures and be more readily distinguished. Secondly, the model used to interpret the solution properties of the solutes uses squalane as a non-polar reference solvent and is constrained by the range of temperatures over which this solvent can be used. This is not a fundamental problem with the model and the change to another less volatile hydrocarbon solvent such as Apolane-87 would eliminate many of the deficiencies of squalane in future studies [4,43]. For the present we have continued to use squalane because of its connection to earlier studies so as to provide consistency in model evaluations and have accepted an upper temperature limit for its use of 120°C.

In this particular study it was necessary to make some compromises to create a complete data set with no missing entries for chemometric analysis. The most significant was that to calculate some solvent properties it was necessary to estimate partition coefficients for squalane at 141.2°C (Table 3). This was done by extrapolating experimental data from lower temperatures to the required temperature as explained in the experimental section. This data set should not be considered as reliable as the experimental data and we have only used it to illustrate general trends. Also, we used the solvation parameter model to calculate the gas–liquid partition coefficients for some solutes that had very long retention times on some phases at the lowest temperature extreme used for data acquisition. These values are less questionable and an estimate of the uncertainty in the data can be made as indicated in the experimental section. The number of solutes requiring this treatment are few in number and are collected in Table 4.

The effect of temperature on the retention mechanism can be deduced from the difference

in the specific retention volume calculated experimentally and the specific retention volume obtained from the gas–liquid partition coefficient. For any solute retained totally by gas–liquid partitioning the two values should agree within experimental error; where the two values differ the difference represents the contribution from interfacial adsorption. As well as temperature the relative contribution of absorption and interfacial adsorption will depend on the surface area to volume ratio of the stationary liquid phase, which can be demonstrated qualitatively by observing differences in the contributions to the retention mechanism as a function of the phase loading. All measurements made in this report are for a single batch of support and thus the surface area is fixed but unknown. For supports with different surface areas the contribution of interfacial adsorption to the retention mechanism is expected to vary directly with the surface areas of the support and coated liquid and the accessible liquid surface area to depend on the phase loading, since the support structure is comprised of a heterogeneous array of pores with different volumes. These pores are filled with liquid to different extents and at no time is the liquid surface area likely to be identical to the support surface area. Also the liquid surface area is expected to decline in a non-linear manner with the phase loading being largest at low phase loadings and then falling to an asymptotic value as high phase loadings are reached. Even if the fine details of the above assumptions are not known exactly there is ample evidence to support them, although accurate determinations of liquid surface areas in gas–liquid chromatography are few because of the technical problems in making such measurements [6,9,10,44].

The general trend observed for mixed retention mechanisms at a constant temperature is illustrated in Fig. 1 for the variation of the specific retention volume as a function of phase loading for dodecane at 121.2 and 81.2°C. The contribution of gas–liquid partitioning to the specific retention volume is constant while the experimental, and by difference the contribution from interfacial adsorption, falls significantly with increasing phase loadings in the range 8 to

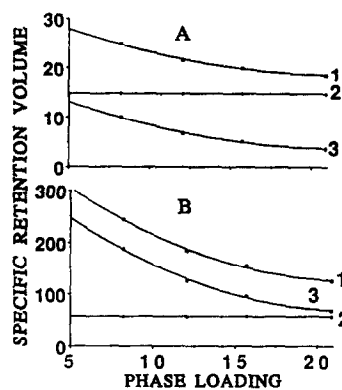


Fig. 1. Variation of the specific retention volume of dodecane as a function of phase loading for poly(diethylene glycol succinate) on Chromosorb W AW at 121.2°C (A) and 81.2°C (B). The experimental specific retention volume is designated as 1, the contribution to the experimental specific retention volume from gas–liquid partitioning as 2, and the contribution from interfacial adsorption to the experimental specific retention volume as 3.

22% (w/w). High phase loadings diminish the contribution from interfacial adsorption because the surface area of the liquid phase is diminished with respect to the increase in the volume of the bulk liquid. The contribution of interfacial adsorption will never fall to zero, however, when it is an intrinsic element of the retention mechanism, since the surface area will never fall to effectively zero with the mechanical constraints set by the available phase loadings for typical columns. Different phases may wet the support surface differently, and therefore, it cannot be assumed that at a constant phase loading the liquid surface area is constant. At a high phase loading the variation in surface area may not be great but it does mean that any further comparison of the interfacial adsorption properties of different phases, even at similar phase loadings, have to be viewed as qualitative. Also striking from Fig. 1 is the influence of temperature on the retention mechanism. For dodecane at 81.2°C on DEGS interfacial adsorption is the dominant retention mechanism, with a strong dependence on the phase loading, while at 121.2°C gas–liquid partitioning is the dominant retention mechanism accompanied by a significant contribution from interfacial adsorption.

Temperature and phase loading simultaneously affect the relative contribution of the individual retention mechanisms when solutes are retained by a mixed retention mechanism. Since we can predict the absorption component of the retention mechanism more reliably than the adsorption component it is important to note that higher temperatures and higher phase loadings favor the gas-liquid partition mechanism over the contribution from interfacial adsorption.

The effect of temperature on the retention mechanism for two phases with a fixed phase loading is shown in Fig. 2. In both cases interfacial adsorption is significant at the lowest temperatures but as the temperature increases its contribution to the retention mechanism decreases until eventually it becomes essentially zero. This is a general phenomena observed for all compounds in the data set which are retained by a mixed retention mechanism at some temperature. There always seems to be a higher temperature at which they are retained virtually exclusively by gas-liquid partitioning.

For members of a homologous series, such as

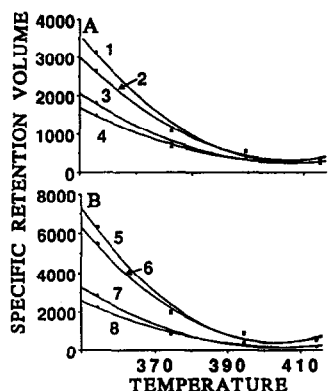


Fig. 2. Relation between temperature and the specific retention volume for four compounds at a fixed phase loading. In (A) results are shown for benzonitrile experimental (1), the contribution of gas-liquid partitioning to the retention of benzonitrile (2), benzaldehyde experimental (3) and the contribution of gas-liquid partitioning to the retention of benzaldehyde (4) on TCEP (11.94%, w/w). In (B) the results are shown for benzodioxane experimental (5), the contribution of gas-liquid partitioning to the retention of benzodioxane (6), octan-1-ol experimental (7) and the contribution of gas-liquid partitioning to the retention of octan-1-ol (8) on CW-20M (13.21%, w/w). Temperature in K.

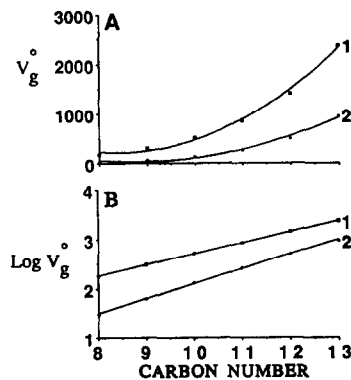


Fig. 3. Relation between chain length and the retention mechanism for members of a homologous series: the retention of fatty acid methyl esters at 81.2°C on TCEP 8.01% (w/w). In (A) the data are plotted in numerical format and (B) as the logarithm of the specific retention volume. The contribution of gas-liquid partitioning to retention is designated as 1 and interfacial adsorption as 2.

the fatty acid methyl esters illustrated in Fig. 3, the numerical contribution of the adsorption component to retention when a mixed retention mechanism occurs, increases with increasing carbon number. When plotted in logarithmic form two lines with different slopes are obtained for the adsorption and partition contribution to the retention mechanism indicating that at a constant temperature and phase loading increasing the chain length causes a proportional incremental increase in the adsorption contribution to the retention mechanism. This also explains why plots of the logarithm of the experimental specific retention volume as a function of the carbon number for a homologous series remain linear even when retention occurs by a mixed retention mechanism.

The above three illustrations serve to demonstrate the effect of temperature on the retention mechanism when an individual solute is retained by a mixed retention mechanism. It is not as easy to create a general sense of the importance of interfacial adsorption as a retention mechanism since the conditions of retention are a highly individualized matter. In Table 5 we have summarized the relative contribution of interfacial adsorption to the retention of 12 varied compounds on 10 phases under different experimen-

Table 5
Contribution of interfacial adsorption (%) to the retention of some typical solutes on 10 stationary phases at two temperatures

Compound	Stationary phase									
	SQ	OV-105	OV-17	OV-225	QF-1	CW-20M	THPED	QPTS	TCEP	DEGS
	Phase loading (%)									
	15.5	16.0	16.1	15.4	16.0	20.7	16.5	15.9	16.0	15.7
<i>Temperature 81.2°C</i>										
Tridecane	7.0	2.9	2.3	1.9	2.3	23.0	2.6	3.2	47.9	66.3
Oct-2-yne	7.8	3.5	2.1	7.0	2.9	11.9	5.0	6.0	8.3	32.3
Methyl octanoate	8.1	3.7	2.0	4.6	2.6	10.9	3.1	4.9	10.2	26.5
Heptan-2-one	8.6	3.3	1.4	6.7	2.8	7.2	5.8	5.3	3.9	9.5
Heptan-1-ol	15.5	4.5	2.3	6.0	5.5	8.9	0.7	2.1	5.2	14.7
Ethylbenzene	8.1	3.9	2.2	11.1	3.6	6.6	4.7	3.9	12.0	15.2
Acetophenone	8.1	5.6	2.1	13.7	4.0	6.1	2.3	5.1	14.9	33.1
Benzonitrile	7.8	5.6	2.1	12.2	3.9	7.2	14.7	5.4	16.0	37.1
Nitrobenzene	7.5	5.9	2.0	12.8	4.1	–	6.3	–	18.4	43.4
N-Methylaniline	11.4	6.0	2.1	27.3	5.4	–	4.4	–	19.2	38.8
N,N-Dimethylaniline	8.0	5.6	2.1	14.1	4.1	5.0	13.5	5.5	17.2	34.6
Dioxane	9.2	4.4	3.5	9.1	1.7	4.9	14.4	5.9	0.2	6.6
<i>Temperature 121.2°C</i>										
Tridecane	1.5	5.4	0.6	6.3	1.7	4.5	3.7	4.5	21.7	26.9
Oct-2-yne	2.1	4.2	0.6	0.6	6.0	5.9	4.3	3.5	7.1	11.2
Methyl octanoate	0.9	6.0	0.4	6.0	1.9	3.7	3.3	2.4	1.9	7.3
Heptan-2-one	1.0	5.4	0.8	3.9	2.3	1.8	4.3	2.9	3.3	7.0
Heptan-1-ol	2.6	4.1	0.6	10.8	2.3	1.9	0.5	3.0	2.0	6.6
Ethylbenzene	2.8	5.1	0.8	4.2	3.2	4.7	2.4	1.6	12.5	11.4
Acetophenone	2.3	5.2	0.8	2.3	1.9	4.0	2.3	2.6	1.2	7.5
Benzonitrile	2.6	5.7	0.6	3.0	1.7	2.9	15.5	2.7	1.2	5.3
Nitrobenzene	2.8	5.4	0.2	1.4	1.8	3.5	6.4	2.7	2.0	2.8
N-Methylaniline	3.1	5.5	0.6	2.1	1.9	2.7	4.4	1.6	0.6	8.4
N,N-Dimethylaniline	2.5	5.4	0.5	5.5	1.9	2.1	8.2	2.8	2.8	12.5
Dioxane	1.2	4.1	0.9	3.2	4.7	2.3	10.0	3.7	0.6	11.8

tal conditions. The relative contribution of interfacial adsorption being calculated as indicated by Eq. 6. The typical uncertainty in $V_g^0(\text{part})$ is about 3% R.S.D. [24]. $V_g^0(\text{exp})$ is obtained from a single phase loading and probably has a greater uncertainty than $V_g^0(\text{part})$. The cumulative uncertainty in the relative contribution of interfacial adsorption is about 4 to 5%. Thus, entries in Table 5 for the interfacial adsorption that are less than 5% are unlikely to be significant. In this context it can be seen that gas-liquid partition is the dominant retention mechanism for all solutes on all phases except for the hydrocarbon *n*-tridecane on TCEP and DEGS. At 81.2°C inter-

facial adsorption makes a significant contribution to the retention of several solutes on SQ, OV-225 (aromatic compounds), CW-20M (aliphatic compounds), THPED (benzonitrile and dioxane), and most solutes on TCEP and DEGS. At 121.2°C interfacial adsorption for the same compounds on the same columns is less significant, in general, but still contributes to the retention of benzonitrile and dioxane on THPED, tridecane, oct-2-yne and ethylbenzene on TCEP, and most solutes on DEGS. These results show that a partition model could be used selectively to predict the retention properties of certain solutes on a group of phases with acceptable accuracy.

The most likely failure would be the prediction of the retention properties of compounds of low polarity on polar phases, particularly at low temperatures.

To complement the data in Table 5 we have prepared a rough summary in Table 6 of our results obtained from a number of experiments reported here the elsewhere [4,41] as an aid to predicting those experimental conditions where interfacial adsorption is most likely to be a significant retention mechanism.

We now wish to discuss the influence of temperature on the solvation mechanism for the gas–liquid partition component of the retention mechanism using Eq. 3 as our model. Eq. 3 allows deconvolution of the solvation mechanism into two terms characterized as the cavity–dispersion contribution to solvation, representing the formation of a cavity in the solvent of sufficient size to hold the solute and the formation of dispersion interactions between the solute and solvent when the solute is placed into the cavity, and the sum of the polar interactions that result from solute–solvent interactions in excess of those characterized as dispersion when the solute is placed in the cavity. The general trends in the above processes can be illustrated by

typical plots of the free energy terms contributing to the solvation process as a function of temperature. These are similar for all solutes and solvents studied in this work so we will choose two examples for the extremes of the polarity range as representative cases: the solvation of a weakly polar (*n*-butylbenzene) and a polar solute (1-nitrohexane) by a moderately polar (OV-17) and a polar stationary phase (TCEP). It is the general case that increasing temperature results in a less favorable solution free energy for all solutes and, therefore, a decrease in retention. For *n*-butylbenzene and 1-nitrohexane on OV-17 the cavity–dispersion term is the dominant contribution to the total solution free energy (Fig. 4). The polar interactions term makes a smaller contribution to the total solution free energy which, as would be predicted, is numerically larger for 1-nitrohexane than for *n*-butylbenzene. For *n*-butylbenzene and 1-nitrohexane on TCEP the cavity–dispersion contribution and the contribution from polar interactions to the total solution free energy are now of comparable magnitude due to an increase in the contribution of the polar interactions term and a decrease in the contribution from the cavity–dispersion term compared to the previous data for OV-17 (Fig.

Table 6

Summary of factors that affect the relative contribution of interfacial adsorption to the retention mechanism

- 1 At intermediate column temperatures, around 100°C, gas–liquid partitioning is the dominant retention mechanism for most compounds on all stationary phases.
- 2 When the retention mechanism is characterized as a mixed retention process interfacial adsorption increases in importance at lower temperatures.
- 3 Interfacial adsorption makes a greater contribution to the retention mechanism at lower phase loadings due to a combination of a larger accessible liquid surface area and a smaller bulk liquid volume.
- 4 When interfacial adsorption makes a significant contribution to the retention mechanism its contribution at constant temperature will never reach zero at any phase loading since mechanical constraints dictate the largest phase loading which can be used. For packed columns a significant residual liquid surface area remains at the highest practical phase loadings possible.
- 5 For non-polar phases interfacial adsorption can generally be related to support properties, and at intermediate column temperatures it can usually be eliminated on adequately deactivated supports. For polar compounds at low temperatures a small contribution from adsorption at the gas–liquid interface may be observed.
- 6 Non-polar solutes such as hydrocarbons exhibit the greatest potential for interfacial adsorption on polar stationary phases. Simple aromatic compounds are far less influenced by the polarity of the stationary phase than are saturated hydrocarbons with a similar carbon number.
- 7 Interfacial adsorption is usually most significant for all compounds on highly cohesive stationary phases which includes TCEP, DEGS, THPED, OV-275, poly(ethylene glycol adipate), and the liquid organic salts tetra-*n*-butylammonium N,N-(bis-2-hydroxyethyl)-2-aminoethanesulfonate, 3-tris(hydroxymethyl)methylamino-2-hydroxy-1-propanesulfonate and 2-(2-acetamido)aminoethanesulfonate.

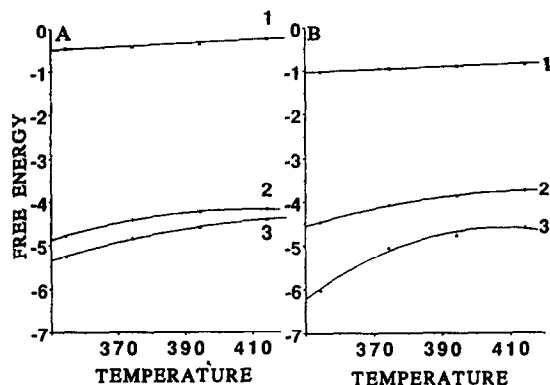


Fig. 4. Plot of the contributions from the polar interactions term (1) and the cavity–dispersion term (2) to the total solution free energy (3) for *n*-butylbenzene (A) and 1-nitrohexane (B) on OV-17 as a function of temperature (in K).

5). Within the constraints of the model the formation of dispersion interactions associated with the transfer of the solute from the gas phase (where ideal behavior is assumed) to solution must exceed the free energy required to form a cavity in the solvent of the same size as the solute since the cavity–dispersion term is always favorable for transfer. The cavity contribution is reflected in the magnitude of the cavity–dispersion term which is always less favorable for polar cohesive solvents, such as TCEP, DEGS and QPTS than for weak solvents, such as OV-105 and OV-17.

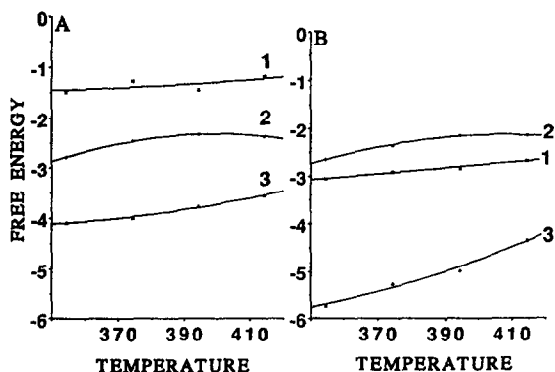


Fig. 5. Plot of the contributions from the polar interactions term (1) and the cavity–dispersion term (2) to the total solution free energy (3) for *n*-butylbenzene (A) and 1-nitrohexane (B) on TCEP as a function of temperature (in K).

In general, the cavity–dispersion term shows the largest numerical change as a function of temperature, makes a less favourable contribution to solvation at higher temperature, and tends to show a smaller numerical variation between the experimental data points at higher temperatures (at least for the temperature range over which the data was collected). By comparison the contribution from the polar interactions term is less affected by temperature over the same temperature range exhibiting, usually, a small shallow decline (contribution to the solvation process becoming less favorable) at higher temperatures, although in a few cases the opposite behavior was observed.

For members of a homologous series the total solution free energy and the contribution to the total solution free energy from the cavity–dispersion term increase incrementally with carbon number while the free energy contribution attributable to the polar interactions term is nearly constant by comparison and not strongly influenced by temperature over the temperature range studied. This is illustrated for the alkan-2-ones (Fig. 6) and the *n*-alcohols (Fig. 7), at 81.2 and 121.2°C on the stationary phase of intermediate polarity CW-20M. The increasingly favorable contribution to the total solution free energy with increasing carbon number for the two series of homologues is due almost entirely to an increasingly favorable contribution from

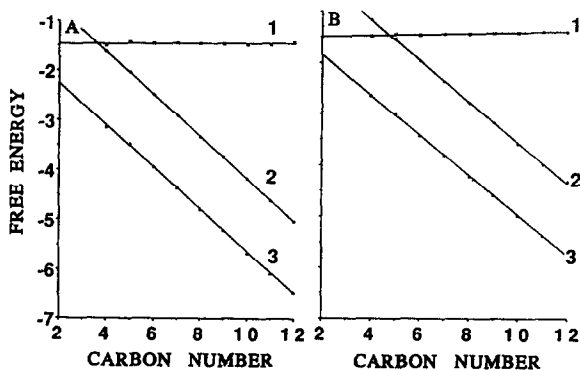


Fig. 6. Plot of the contributions from the polar interactions term (1) and the cavity–dispersion term (2) to the total solution free energy (3) for a homologous series of alkan-2-ones on CW-20M at 81.2°C (A) and 121.2°C (B).

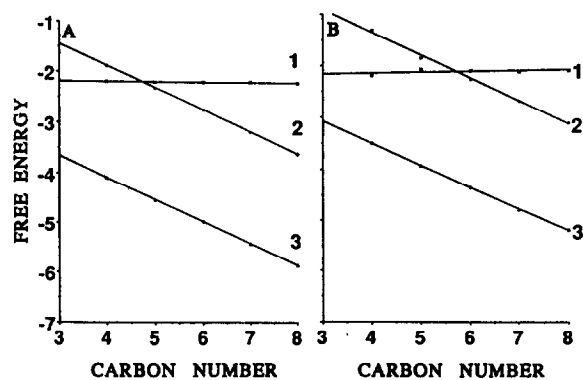


Fig. 7. Plot of the contributions from the polar interactions term (1) and the cavity-dispersion term (2) to the total solution free energy (3) for a homologous series of *n*-alcohols on CW-20M at 81.2°C (A) and 121.2°C (B).

the cavity-dispersion term. In turn this indicates that even for the most polar stationary phases studied here the contribution from dispersion interactions accompanying each incremental increase in the molecular volume of the homologs exceeds the free energy required to expand the cavity in the solvent by the same amount. The polar interactions contribution to the free energy of solution depends only on the identity of the

polar functional group in the molecule and is sensibly independent of molecular size as demonstrated by the experimental data.

To provide further insight into the factors contributing to the solvation process principal component analysis was performed on the contributions to the solvation process previously characterized as the cavity-dispersion term and the polar interactions term. The cavity-dispersion term is characterized by a single component with greater than 99.7% of the total variance at all temperatures accounted for by this factor (Table 7). The contribution to the solvation process of the free energy required to open a cavity in the solvent and the subsequent contribution to the solvation process from solute-solvent dispersion interactions must be correlated. Logic dictates that the parameter connecting the two terms must be a size-related parameter such as the solute volume or a volume-dependent term such as the solvent-accessible surface area. A plot of the first principal component (PC-1) for all phases as a function of temperature is shown in Fig. 8. The general trend is for PC-1 to be numerically smaller at higher temperatures and to vary less at the highest temperatures used

Table 7
Summary of principal component analysis of the cavity-dispersion contribution to the solvation process

Temperature (°C)	Principal component number	Variance (%)	Number of phases
61.2	1	99.986	3
	2	0.014	
81.2	1	99.896	9
	2	0.089	
	3	0.015	
101.2	1	99.833	9
	2	0.153	
	3	0.014	
121.2	1	99.833	9
	2	0.147	
	3	0.020	
141.3	1	99.758	6
	2	0.213	
	3	0.029	

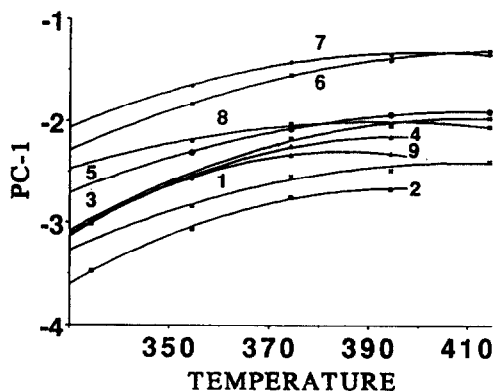


Fig. 8. Plot of the first principal component (PC-1) from the multivariate analysis of the contribution of the cavity–dispersion term to solvation from nine stationary phases as a function of temperature. Identification: 1 = OV-17; 2 = OV-105; 3 = OV-225; 4 = QF-1; 5 = CW-20M; 6 = DEGS; 7 = TCEP; 8 = QPTS; 9 = THPED. Temperature in K.

to collect the data compared to the lower temperatures. At all temperatures PC-1 is numerically larger for the weakly polar phases such as

OV-105 and OV-17 (with a more favorable contribution to the solvation process) than for the strongly polar phases such as TCEP and DEGS.

Principal component analysis of the contribution previously characterized as the polar interactions term reveals that three factors are important in describing the contributions of this term to the solvation process. The first component (PC-1) is dominant accounting for 95 to 99% of the total variance; the second component (PC-2) for about 1 to 5% of the total variance; and the third component (PC-3) for about 0.1 to 0.7% of the total variance over the temperature range used to acquire the experimental data (Table 8). Based on the following considerations we believe that PC-1 can be assigned to the capacity of a phase to enter into dipolar interactions characterized as orientation and induction. Whereas all phases have some capacity for these interactions, albeit small in some cases, other polar interactions such as hydrogen bonding are more specific and, therefore unlikely to be uni-

Table 8
Summary of principal component analysis of the polar interaction contribution to the solvation process

Temperature (°C)	Principal component number	Variance (%)	Number of phase
61.2	1	95.004	3
	2	4.788	
	3	0.212	
	4		
81.2	1	98.059	9
	2	1.133	
	3	0.703	
	4	0.063	
101.2	1	98.154	9
	2	1.113	
	3	0.625	
	4	0.068	
121.2	1	98.112	9
	2	1.085	
	3	0.700	
	4	0.043	
141.2	1	98.946	6
	2	0.806	
	3	0.170	
	4	0.052	

versal, as are the properties identified in PC-1. A summary of the loadings for each compound in the data set (the complementary solute property to the stationary phase property obtained by multivariate analysis) is given in Table 9. Qualitatively, those compounds expected to have significant dipole interactions have the most significant weighting and those compounds with little capacity for dipole interactions are found at the base of the table. A plot of the loadings against the dipole moment for the solutes (excluding those solutes which are self-associating, e.g. *n*-alcohols) shows good qualitative agreement in terms of trends even if extensive scatter exists around the best straight line (Fig. 9). This is not unexpected since the dipole moment values used for the plot are rough averages of several values from different solvents. Also, the bulk dipole moments may not accurately express the influence of the local dipole moment in

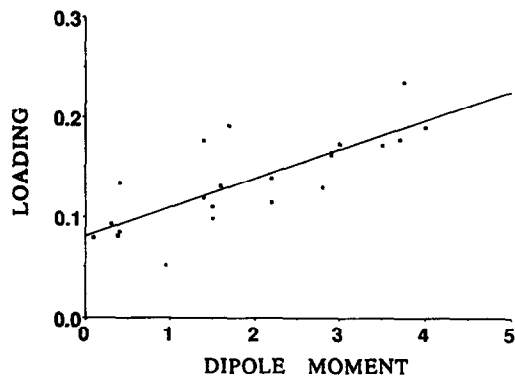


Fig. 9. Plot of the loadings for PC-1 at 101.2°C obtained by multivariate analysis of the contribution of the polar interactions term to solvation as a function of the solute dipole moment.

determining solute–solvent interactions. Further, it could be argued that the dipole moment is not a free energy-related term and is not clearly

Table 9

Summary of loadings for principal component 1 based on the polar interaction contribution of the solvation process at 101.2°C

Compound	Loading	Compound	Loading
N,N-Dimethylacetamide	0.236	Methyl octanoate	0.132
Aniline	0.227	Hexan-2-one	0.132
N-Methylaniline	0.191	N,N-Dimethylaniline	0.131
Benzonitrile	0.190	Methyl heptanoate	0.131
Octan-1-ol	0.188	Butan-2-one	0.130
Hexan-1-ol	0.184	Pentan-2-one	0.130
Heptan-1-ol	0.184	Methyl hexanoate	0.130
Pentan-1-ol	0.182	Nonanal	0.124
Butan-1-ol	0.181	2,4,6-Trimethylpyridine	0.121
Nitrobenzene	0.178	Iodobenzene	0.120
Nitrohexane	0.176	Methylphenyl ether	0.120
1,1,2,2-Tetrachloroethane	0.176	<i>o</i> -Dichlorobenzene	0.115
Nitropropane	0.173	Bromobenzene	0.110
Nitropentane	0.172	Chlorobenzene	0.098
Acetophenone	0.165	Toluene	0.093
Benzaldehyde	0.162	<i>n</i> -Butylbenzene	0.085
Nitrocyclohexane	0.158	Ethylbenzene	0.081
2-Methylpentan-2-ol	0.151	Benzene	0.079
Pyridine	0.139	Dodec-1-yne	0.076
Dodecane-2-one	0.139	Oct-2-yne	0.051
Nonan-2-one	0.135		
Undecan-2-one	0.134		
Dioxane	0.134		
Octan-2-one	0.133		
Dodecan-2-one	0.133		
Heptan-2-one	0.133		

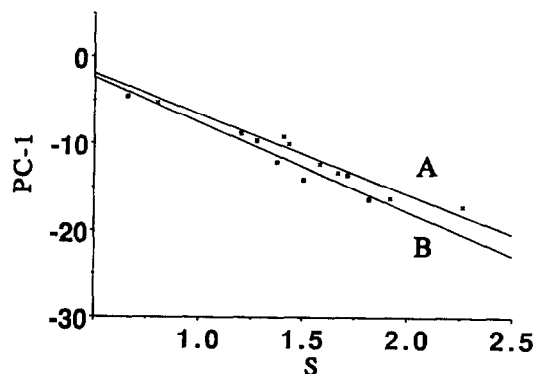


Fig. 10. Plot of PC-1 at 81.2°C (A) and 121.2°C (B) against the s parameter of Abraham and co-workers characteristic of solvent dipolarity/polarizability.

compatible with the properties of PC-1. A more significant correlation is found between PC-1 and the s coefficient of Abraham and co-workers defined in Eq. 2 (Fig. 10). The s coefficient is a

measure of a solvent's capacity for dipole–dipole and dipole–induced dipole interactions and is established by an independent scale of solute properties. With the exception of the fluorocarbon phase QF-1, there is good agreement between the two properties at all temperatures with correlation coefficients (r^2) > 0.98.

The loading factors for the second principal component (PC-2) are summarized in Table 10. The large negative values in the table are associated with solutes capable of interacting as hydrogen-bond acids and the large positive values as solutes that can interact as hydrogen-bond bases. A large number of compounds in the center of the table have very small loading values indicating that PC-2 is a selective parameter that is not possessed to a significant extent by all compounds. It seems reasonable to identify PC-2 with the capacity of a stationary phase to form a hydrogen bond by acting as a hydrogen-bond

Table 10

Summary of loading for principal component 2 based on the polar interaction contribution to the solvation process at 101.2°C

Compound	Loading	Compound	Loading
Aniline	-0.249	Benzonitrile	0.022
Butan-1-ol	-0.222	Nitrocyclohexane	0.055
Pentan-1-ol	-0.217	Dioxane	0.070
N-Methylaniline	-0.214	Nitropropane	0.125
Hexan-1-ol	-0.211	Nitropentane	0.141
Heptan-1-ol	-0.208	Butan-2-one	0.142
Octan-1-ol	-0.199	Nonanal	0.143
Iodobenzene	-0.199	Pentan-2-one	0.157
1,1,2,2-Tetrachloroethane	-0.178	Nitrohexane	0.157
Bromobenzene	-0.127	Hexan-2-one	0.169
<i>o</i> -Dichlorobenzene	-0.127	Heptan-2-one	0.169
2-Methyl-2-pentanol	-0.118	Methyl hexanoate	0.178
Chlorobenzene	-0.101	Octan-2-one	0.183
Ethylbenzene	-0.077	Decan-2-one	0.184
Benzene	-0.049	Methyl heptanoate	0.184
Methylphenyl ether	-0.047	Nonan-2-one	0.187
Toluene	-0.046	Undecan-2-one	0.191
N,N-Dimethylaniline	-0.044	Methyl octanoate	0.196
Nitrobenzene	-0.031	N,N-Dimethylacetamide	0.200
Dodec-1-yne	-0.029	Dodecan-2-one	0.217
Benzaldehyde	-0.028		
<i>n</i> -Butylbenzene	-0.023		
Acetophenone	-0.014		
2,4,6-Trimethylpyridine	-0.010		
Oct-2-yne	-0.009		
Pyridine	-0.005		

acid or hydrogen-bond base. In making this determination the position of the halobenzene compounds as moderate hydrogen-bond acids would seem to be slightly displaced based on general expectations.

The loading factors for the third principal component (PC-3) are summarized in Table 11. The large negative values are associated with the aliphatic alcohols and the large positive values with the aromatic components. PC-3 is perhaps characteristic of the capacity of a phase to form charge-transfer complexes involving π -electrons, a property that distinguishes the aromatic compounds from the aliphatic compounds in the data set. The large negative weighting of the alcohols suggests that mixed in with this mechanism is residual capacity of the alcohols to form hydrogen-bond complexes since the other aliphatic compounds have much smaller loading values than those for the alcohols. Thus to get an

accurate picture of the hydrogen-bond base properties of the stationary phases it is necessary to consider properties of PC-2 and PC-3 together. A factor which may contribute to the ambiguous identification of the hydrogen-bonding capacity of the stationary phases is that none of the phases studied here are strong hydrogen-bond acids, and indeed, there are no common stationary phases in current use that have been identified as strong hydrogen-bond acids [4,26,29,34,39,40]. These features are born out by inspecting the loadings plot for PC-2 against PC-3 (Fig. 11). The solutes in the data set are separate into three major groups. Group 1 contains all the aliphatic alcohols (non-aromatic, hydrogen-bond acids). Group 2 contains the alkan-2-ones, fatty acid methyl esters, nitroalkanes, N,N-dimethylacetamide and nonanal (non-aromatic, hydrogen-bond bases). Group 3 is more diffuse than the other two groups and

Table 11
Summary of loading for principal component 3 based on the polar interaction contribution to the solvation process at 101.2°C

Compound	Loading	Compound	Loading
Octan-1-ol	-0.277	Nitrocyclohexane	0.031
Hexan-1-ol	-0.270	N-Methylaniline	0.059
Butan-1-ol	-0.269	Benzonitrile	0.062
Pentan-1-ol	-0.257	Dioxane	0.097
Heptan-1-ol	-0.254	Nitrobenzene	0.107
2-Methyl-2-pentanol	-0.192	Pyridine	0.121
N,N-Dimethylacetamide	-0.077	Oct-2-yne	0.137
Nitrohexane	-0.065	Toluene	0.160
Undecan-2-one	-0.058	Acetophenone	0.165
Dodecan-2-one	-0.058	Benzaldehyde	0.165
Nonan-2-one	-0.053	Ethylbenzene	0.168
Nitropentane	-0.050	Chlorobenzene	0.170
Decan-2-one	-0.048	2,4,6-Trimethylpyridine	0.170
Octan-2-one	-0.042	Benzene	0.174
Heptan-2-one	-0.034	Methylphenyl ether	0.184
Hexan-2-one	-0.032	n-Butylbenzene	0.196
Nitropropane	-0.030	Bromobenzene	0.211
Pentan-2-one	-0.021	o-Dichlorobenzene	0.216
Nonanal	-0.017	N,N-Dimethylaniline	0.257
1,1,2,2-Tetrachloroethane	-0.016	Iodobenzene	0.303
Dodec-1-yne	-0.015		
Methyl octanoate	-0.014		
Aniline	-0.010		
Butan-2-one	-0.005		
Methyl heptanoate	-0.004		
Methyl hexanoate	0.001		

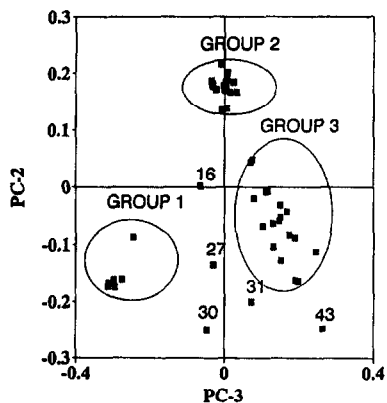


Fig. 11. Plot of the loadings for PC-2 against PC-3 extracted from the polar interactions term at 81.2°C. The compounds not assigned to a group are: 16 = dodec-1-yne; 27 = 1,1,2,2-tetrachloroethane; 30 = aniline; 31 = N-methylaniline; 43 = iodobenzene.

contains the aromatic compounds and oct-2-yne (compounds with a capacity for charge transfer interactions due to the presence of π -electrons). The weak hydrogen-bond acids dodec-1-yne, 1,1,2,2-tetrachloroethane, aniline and N-methylaniline are not assigned to any of the main groups reflecting their unusual mix of properties.

The trends in the principal components extracted from the contribution of the polar interactions term to the solvation process as a function of temperature provide some insight into how temperature influences the individual polar interactions identified in the above discussion. For the three phases, OV-105, OV-17 and QF-1, which on a relative basis have weak polar interactions, all three principal components are important to adequately define their properties (Fig. 12). OV-105, with the weakest capacity for polar interactions of the three phases, shows a sharp transition in properties in the low-temperature region. The magnitude of PC-1 is reduced sharply at first but then the decrease becomes shallower at higher temperatures. It possesses a weak capacity for hydrogen-bonding and other complexation interactions which at the higher temperatures are not strongly temperature dependent. OV-17 has a modest capacity for orientation interactions (PC-1) which shows significant temperature dependence, being less in-

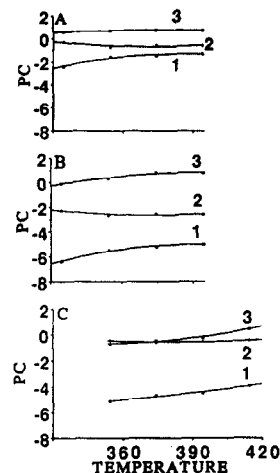


Fig. 12. Plot of the first three principal components extracted from the polar interactions term against temperature for the weakly polar phases OV-105 (A), QF-1 (B) and OV-17 (C). Temperature in K.

fluential at higher temperatures. Its capacity for hydrogen-bonding and complexation interactions (PC-2 and PC-3) are modest by comparison and decline with increasing temperature. QF-1 shows a unique blend of properties, a modest capacity for orientation interactions which declines with increasing temperature, significant capacity for hydrogen-bonding interactions (PC-2) which increases slightly with temperature, and a small contribution from PC-3 with weak temperature dependence.

The influence of temperature on the principal components extracted from the polar interactions term for the three moderately polar phases, OV-225, CW-20M and THPED is illustrated in Fig. 13. The properties of OV-225 and CW-20M are dominated by PC-1 which is only weakly temperature dependent. The capacity of both phases for hydrogen-bonding is weak (PC-2) and not strongly temperature dependent. Both phases have a weak capacity for complexation interactions (PC-3) but this is significantly more important for CW-20M than for OV-225. THPED shows different behavior; its properties are dominated by orientation interactions (PC-1) which shows a weak temperature dependence. Its capacity for hydrogen-bonding (PC-2) is significant at 61.2°C only. It retains a significant

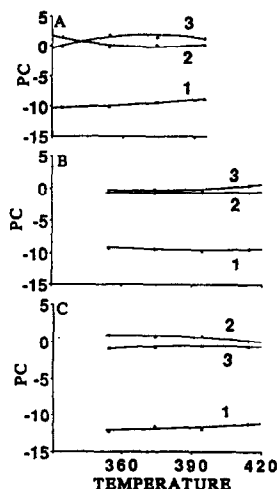


Fig. 13. Plot of the first three principal components extracted from the polar interactions term against temperature for the moderately polar phases THPED (A), OV-225 (B) and CW-20M (C). Temperature in K.

capacity for complexation interactions (PC-3) (which might be dominated by its hydrogen-bond basicity) at higher temperatures.

The influence of temperature on the principal components extracted from the polar interactions term for the three very polar phases, DEGS, TCEP and QPTS is illustrated in Fig. 14.

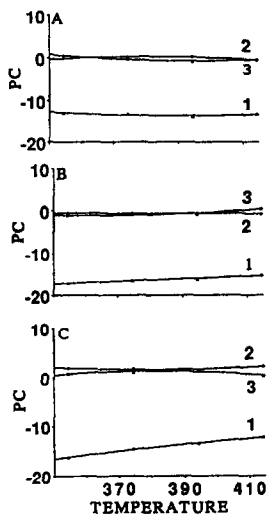


Fig. 14. Plot of the first three principal components extracted from the polar interactions term against temperature for the very polar phases DEGS (A), TCEP (B) and QPTS (C). Temperature in K.

In the case of DEGS its properties are dominated by its capacity for orientation interactions (PC-1) with only small contributions from PC-2 and PC-3. PC-1 for DEGS shows a slight temperature dependence with a slight increase in its magnitude at higher temperatures. The polar interactions of TCEP are again dominated by PC-1, which unlike DEGS shows a significant temperature dependence, declining in magnitude as the temperature is increased. PC-2 and PC-3 are small by comparison to PC-1 but are more significant than for DEGS. TCEP has a weak capacity for hydrogen-bonding and complexation interactions that is weakly temperature dependent. QPTS has a unique blend of properties compared to the other phases. Its general polar interactions are dominated by orientation interactions (PC-1) which are strongly temperature dependent, exhibiting the largest numerical change in value as a function of temperature. Hydrogen-bonding interactions (PC-2) are also significant for this phase and are only weakly temperature dependent.

The above studies provide some insights into the mechanisms by which compounds are retained in gas chromatography and their temperature variation. Gas-liquid partitioning is the major retention mechanism for most compounds. Mixed retention mechanisms are of importance when the stationary phase is unable to mask support activity and when there is a significant difference in the polarity between the solute and the stationary phase. Interfacial adsorption at the gas-liquid interface depends on both the stationary phase loading and the column temperature. The general influence of temperature is for higher temperatures to diminish the contribution to retention from interfacial adsorption. A cavity model of solvation behavior was used successfully to probe the influence of temperature on the intermolecular interactions responsible for solution. The contribution of the cavity-dispersion term to the free energy of solution showed significant temperature dependence and was always more favorable for solvation at lower temperatures. Even for the most polar phases this term remained favorable for solute transfer from the gas phase emphasizing

the importance of dispersion interactions in the solution behavior of even the most polar stationary phases. The polar interactions term is much more important in the solution behavior of polar compounds in polar stationary phases where it approaches or exceeds in magnitude the contribution to the total free energy of solution from the cavity–dispersion term. In the general case it is only weakly temperature dependent in the temperature range investigated. By principal component analysis it was shown that three contributing factors are required to analyze the properties of the polar interactions term as a function of temperature. The major component (PC-1) was identified with the capacity of the stationary phase for orientation and induction interactions and, with the exception of QPTS, was only weakly temperature dependent. The second and third principal components were tentatively identified with the capacity of the stationary phase to form hydrogen bond and π -electron complexation interactions. These interactions were most important in characterizing the properties of QF-1 and QPTS and were moderately temperature dependent being less effective at higher temperatures in influencing the solvation behavior of compounds with the necessary complementary properties for the interactions specified.

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