

Solute–Solvent Interactions From Gas Chromatographic Activity Coefficients and the Solvation Parameter Model for Nitrogen-Containing Stationary Phases

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Abstract

Infinite dilution gas–liquid chromatographic activity coefficients (γ) and excess thermodynamic molar partial magnitudes [Gibbs energy (G^E), enthalpy (H^E), and entropy (S^E)] for 37 solutes of varied polarity on four stationary phases with –NH groups are obtained from partition coefficients taken from literature. Relationships between G^E and S^E with the 37 solutes' structure in terms of the molecular connectivity index ($^1\chi^v$) are investigated. Correlations of solute–solvent interactions calculated in light of the solvation parameter model for selected solutes and stationary phases are tested. The effect of the solute's structure, expressed as the molecular connectivity index, on the nonpolar (cavity formation and dispersion interaction) [$c+I \cdot \log L(16)$] and the effect of the dipole moment and of the activity coefficient on the dipolarity–polarizability interaction ($\pi\pi^{\frac{1}{2}}$) are studied. The correlation between the nonpolar interaction with the athermal activity coefficient on the nonpolymeric stationary phases is also attempted. In addition, the influence of the stationary phase polarity on the solute–stationary phase interactions for a series of solutes is studied.

Introduction

Gas–liquid chromatographic (GLC) activity coefficients, easily determined from retention data (retention time, specific retention volume, partition coefficient, etc.), have been extensively studied (1–8). The values obtained are considered to be as accurate as those achieved by other techniques and are attainable with much less effort (9). It is well established that the energy (excess Gibbs energy of solvation, enthalpy, and entropy) released in the retention processes plays an important role in the elucidation of the interactions between an analyte injected into a gas chromatographic (GC) stationary phase (SP). The solvation parameter model propounded by Abraham

(10), Poole (11), and Carr (12) is the most widespread modern approach to the above interactions in which chromatography shows itself to be a valuable analytical technique of enormous power.

It therefore appears interesting to look for the existence of relationships between the different polar and nonpolar interactions predicted by the solvation model with the activity coefficients. In other words, it is suggestive to find answers to questions such as whether the solvent model and the GLC activity coefficients method are related and, if so, to what extent. For this reason the goals of this work are, first, the calculation of the infinite dilution molar fraction activity coefficients of a series of solutes on four stationary phases characterized in the literature (13) from the partition coefficients at 393 K, and then the study of the following relationships: (a) activity coefficients, derived solvation excess Gibbs energies, enthalpies, and entropies versus the structure of the analytes; (b) the dipole interaction predicted by the solvation parameter model versus the solute dipole moment; (c) the nonpolar interaction predicted by the same model versus the structure and athermal activity coefficient for the three stationary phases of known molecular weight; and (d) the stationary phase polarity versus the different specific individual interactions calculated in light of the solvation model's equation.

Methods

GLC activity coefficients are related to the specific retention volumes by the following equation (14,15):

$$\gamma = 273.15R/p_0M_S V_g \quad \text{Eq. 1}$$

where p_0 is the solute vapor partial pressure (Torr), M_S is the

stationary phase molecular mass (g/mol), R is the gas constant (taken as 62362.7 Torr.cm³.mol⁻¹.K⁻¹ throughout this paper), and V_g is the specific retention volume (cm³/g).

The specific retention volume, perhaps the most important retention data in GC, is defined as (16):

$$V_g = jF/W_s [1 - P_w/P_a] T/T_0 (t_R - t_M) \quad \text{Eq. 2}$$

where j is the James and Martin compressibility factor when the pressure is averaged over the column length; F is the carrier gas flow rate at the end of the column at ambient temperature T_0 and ambient pressure P_a ; P_w is the partial pressure of saturated water vapor at ambient temperature; t_R is the retention time (min); t_M is the hold-up time of an unretained substance; W_s is the mass of stationary phase present in the column; and T is the column temperature (in degrees Kelvin).

The relationship between specific retention volume (V_g) and the partition coefficient is given by:

$$V_g = 273.15K_L/r_S T \quad \text{Eq. 3}$$

where K_L stands for the partition coefficient and r_S stands for the stationary phase density at temperature T .

By substituting K_L from equation 3 into equation 1, the relationship between activity coefficients and partition coefficients is obtained by:

$$\gamma = r_S RT / K_L p_0 M_S \quad \text{Eq. 4}$$

where the solute vapor partial pressure (p_0) is obtained from Antoine-type equations with the form:

$$\log p_0 = A - B/(t + C) \quad \text{Eq. 5}$$

Here, t (the column temperature in degrees Celsius) and A , B , and C (the constants for every solute at the given temperature) were taken from the literature (17–19). Therefore, the activity coefficient values depend mainly on the solute vapor pressure and the partition coefficient because the density of the stationary phase is a number close to unity, and therefore of a comparatively minor influence.

Excess partial molar Gibbs energies of solvation (G), enthalpies (H), and entropies (S) were evaluated, respectively, with the following equations:

$$G^E = RT \ln \gamma \quad \text{Eq. 6}$$

$$H^E = RT \ln \gamma_{th} \quad \text{Eq. 7}$$

$$S^E = (H^E - G^E)/T = -R \ln \gamma_{at} \quad \text{Eq. 8}$$

whose units were determined by those of the gas constant (R). Here, $R = 62,362.7$ Torr. × cm³/mol/K, G^E and H^E are given in J/mol, and S^E in J.mol⁻¹.K⁻¹.

Prior to the application of equation 8, the athermal activity coefficients were calculated according to the theoretical treatment of Flory–Huggins (20–22), in which the activity coefficient can be divided into two contributions: one that is

temperature-independent (athermal) and the other is temperature-dependent (thermal):

$$\gamma = \gamma_{at} \cdot \gamma_{th} \quad \text{Eq. 9}$$

The athermal activity coefficient can be calculated as:

$$\gamma_{at} = 1/m \exp(1-1/m) \quad \text{Eq. 10}$$

where m , the solute to stationary phase “size ratio”, is given by the following:

$$m = V_{m2}/V_{mS} = M_2 r_S / M_S r_2 \quad \text{Eq. 11}$$

where V_{m2} , M_2 , and r_2 , are the solute’s molar volume, molecular weight, and density, respectively. V_{mS} , M_S , and r_S are the stationary phase’s molar volume (cm³/mol), molecular weight (g/mol), and solute density (g/cm³), respectively. The m value can be calculated exactly for the three nonpolymeric stationary phases [Quadrol, triethanolamine (TEA), and tetraethylene-pentamine (TEP)] because their molecular weight (M_S) is known, and therefore the solute infinite dilution molar fraction athermal activity coefficient (γ_{at}) can be evaluated with equation 10. However, this is not the case for the phenyl-diethanolamine succinate (PDAS) polymer ($M_S \approx 20,000$), for which infinite dilution weight fraction activity coefficients (ω) (23,24) have to be used:

$$\omega = RT r_S / p_0 M_2 K_L \quad \text{Eq. 12}$$

In returning to the molar fraction activity coefficients, once γ_{at} is calculated, the thermal contribution to the activity coefficient is determined with equation 10. H^E is then calculated with equation 7 or by adding G^E and TS^E .

Abraham (10,25) propounds the following equation for the solute–stationary phase retention interactions at a given temperature:

$$\log K_L = (rR_2 + s\pi_2^H + a\Sigma a_2^H + b\Sigma \beta_2^H) + l \cdot \log L(16) + c \quad \text{Eq. 13}$$

where the sum in the parenthesis is composed of the different polar solute–stationary phase interactions, and the other two terms constitute the nonpolar solute–stationary phase interaction.

The characteristic stationary phase constants [also called specific or system constants (25)], r , s , a , b , and l are obtained by applying multiple linear regression analysis to the experimental retention data of the GLC system and the 37 solutes of the pertinent stationary phase. They include the following: r , the ability of the stationary phase to interact with π - and n -electron pairs of solutes; s , the tendency of the stationary phase to interact with solute dipoles; a , the capacity of the stationary phase (basicity) to interact with acid solutes; b , the capacity of the stationary phases (acidity) to interact with basic solutes; and l , which is considered to be the cavity formation and dispersion interaction contribution of the stationary phase. The c constant is a regression term whose role has been considered

unimportant in solvation. It may contain contributions related to the lack of fit to the model (26), and when using retention factors as retention magnitude, this might incorporate the value of the column-phase ratio (27). In addition, c may account for the temperature differences between the GC retention data and that used to determine solvation parameters, especially l (28–30). The homologous contributions of the solutes are: R , excess molar refraction; π_2^H , the dipolarity–polarizability; $\Sigma\alpha_2^H$, the hydrogen donor or solute acidity; $\Sigma\beta_2^H$, the hydrogen acceptor or solute basicity; and $\log L(16)$, the Ostwald solubility coefficient (or gas–liquid partition coefficient K_L = solute concentration in hexadecane–solute concentration in gas phase) at 298 K, in which 16 stand for the carbon atom number of this hydrocarbon (31).

The solute–solvent interactions are given by the product of the complementary terms: rR_2 , $s\pi_2^H$, $a\Sigma\alpha_2^H$, $b\Sigma\beta_2^H$, and $l.\log L(16)$. rR_2 is the lone electron pair solute–stationary phase interactions, $s\pi_2^H$ is the dipole nature solute–stationary phase interactions, $a\Sigma\alpha_2^H$ is the acid solute–basic stationary phase interactions, $b\Sigma\beta_2^H$ is the base solute–acid stationary phase interaction, and $l.\log L(16)$ is the cavity formation and dispersion interactions.

Experimental

The amine group containing stationary phases used in this work (13) included: Quadrol, N,N,N',N' -tetrakis(2-hydroxypropyl) ethylenediamine, $C_{14}H_{32}N_2O_4$, $M_S = 292.4$ g/mol, $r_S = 0.974$ g/cm³; TEP, $C_6H_{13}O_3$, $M_S \approx 189.3$ g/mol, $\rho_S = 0.922$ g/cm³; TEA, $C_6H_{15}NO_3$, $M_S = 149.2$ g/mol, $r_S = 1.056$ g/cm³; and the PDAS polymer, $M_S \approx 20,000$ g/mol, $r_S = 1.726$ g/cm³.

The stationary phase polarity was evaluated from the retention data by applying the Kováts coefficient definition (32) (see equation 16). The K_c values obtained were: 246.1, 355.2, 231.6, and 161.4, [$\log(\text{cm}^3\text{He/g stationary phase})$]. This polarity criterion gives the stationary phase polarity in the order: PDAS < TEA < Quadrol < TEP.

The carrier gas was helium, inlet pressure was 27–30 psi, and flow rate was 30 cm³/min. T was 393.15 K. Loadings included: 12% of Quadrol and PDAS, 13% of TEP, and from 12.5% to 14.5% TEA (13).

Thirty-seven solutes were used, which included six hydrocarbons, five alcohols, seven carbonylic compounds, four halo-compounds, ten nitrogenated compounds, and five ethers. Pierotti et al. (33) related the activity coefficients and solute–solvent structure by a semiempirical method in which G^E is the sum of the individual G^E values of the different structural groups. In this work, topological indices have been used. First order connectivity indices of Randić (34) have been used for hydrocarbons:

$${}^1x = \sum_i^j (1/\sqrt{\delta_i\delta_j}) \quad \text{Eq. 14}$$

where δ_i and δ_j stand for the free valences of the carbon atom of each vertex (i) with the neighbor (j) discounting the hydrogen atom (by definition the molecule graph is built

without them). For the other triatomic heteroatoms, the refinements of Hall and Kier (35,36), which led to the term “molecular valence connectivity index” (${}^1\chi^v$) were used. And this was basically equal to ${}^1\chi$, with the exception of the free valence, which is also called “delta valence”, and is now given by:

$${}^1\delta^v = Z^v - h \quad \text{Eq. 15}$$

where Z^v is the heteroatom valence electron number and h is the hydrogen atom number bonded to the heteroatom.

Kováts coefficients were used to evaluate the stationary phase polarity (32):

$$K_c = 100[z - \log K_{L,z}/q] \quad \text{Eq. 16}$$

where q is the slope of the least mean squares regression (LMSR) of the plots of $\log K$ versus the carbon atom number for n -alkanes (z), which is described by:

$$q = (\log K_{L,z+n} - \log K_{L,z})/n \quad \text{Eq. 17}$$

where $z+n$ and z are two n -alkanes of $z+n$ and z carbon atoms.

Data were extrapolated to 393.15 K for TEA. Solute descriptors were taken from Abraham’s compilations (37), and the specific characteristic constants [taken from the literature (13)] of the stationary phases used in this work were: for Quadrol, $r = 0.037$, $s = 0.943$, $a = 1.78$, $b = 0.311$, $l = 0.430$, and $c = -0.184$; for TEP, $r = 0.155$, $s = 0.931$, $a = 2.80$, $b = 0.016$, $l = 0.448$, and $c = -0.282$; for TEA, $r = 0.135$, $s = 0.800$, $a = 1.654$, $b = 0.343$, $l = 0.178$, and $c = -0.203$; and for PDAS, $r = -0.387$, $s = 1.069$, $a = 1.13$, $b = 0.099$, $l = 0.364$, and $c = 0.280$. Calculations were carried out using the Excel utility in a personal computer, and the graphs and regression equations were obtained with the Microcal Origin 6.0 program.

Results and Discussion

Activity coefficients and solute–stationary phase interactions

The stationary phases used for this study contained amino groups and, therefore, showed strong selectivity, which tended to form hydrogen-bond bridges. The additional presence of –OH groups in Quadrol and TEA increased this tendency. Specific characteristic-phase constants seemed to agree with this. Constant a (stationary phases’ hydrogen-bond acidity specific constant) was dominant but s was also considerable, and b was as significant as r but far less important than a .

Table I lists the molecular connectivity indices, dipole moments, infinite dilution molar fraction activity coefficients (γ), and athermal components (γ_{at}) of 37 solutes on three of the nonpolymer nitrogen-containing stationary phases studied in this work (13) at 393.15 K. It also lists the infinite dilution weight fraction activity coefficients (ω) on PDAS.

As Langer and Purnell (38) stated, the smaller the activity coefficient is, the larger the solute-stationary phase interaction

will be, and the reverse is true as well. In fact, the lowest values of γ obtained for the alcohols (ranking 0.44–0.97), amines (ranking 0.52–0.85), and amides (0.5) hinted at strong interactions of these chemical series with Quadrol, for which the constants a and s are the more important ones ($a \approx 2s \approx 1.78$). For alcohols and amines with large $\Sigma\alpha_2^H$ values, the base stationary phase–acid solute interactions are important, though they are not important for aldehydes and ketones because the corresponding solute descriptor is negligible. The same can be said of TEP, although with somewhat larger activity coefficient values. But it was confirmed that these functions had smaller activity coefficients and, therefore, stronger interactions. The same applies for the stationary phase TEA, for which the γ values were still somewhat larger. Also, low weight fraction activity coefficients for amines and alcohols on PDAS were obtained. In contrast, for all the sta-

tionary phases, the hydrocarbons had the largest activity coefficients, which showed a weak interaction with the stationary phases studied.

In a homologous series, γ increases as z (the carbon atom number) increases. And γ_{at} seems to increase following the same trend as γ . The athermal contribution to the activity coefficient takes a maximum value of 1.0 for TEP and TEA, and a small values for alcohols, ketones, aldehydes, halocompounds, amines, amides (especially nitromethane and acetonitrile), and values close to unit for hydrocarbons. With these values the logarithm was negative and, therefore, the excess entropy was mostly positive in all cases (see equation 8). For Quadrol (in Table I), γ was less than 1 for alcohols, acetone, amines (except triethylamine), amides, and ethers (except dibutylether and anisole). Therefore G^E was less than 0 for these compounds. Only alcohols and aniline showed $\gamma < 1$

Table I. Molecular Connectivity Indices, Dipole Moments, and Activity Coefficients of 37 Solutes on Amine Stationary Phases at 393.15 K

Solute	Quadrol				TEP		TEA		PDAS
	${}^1\chi_v$	μ_m	γ	γ_{at}	γ	γ_{at}	γ	γ_{at}	ω
<i>n</i> -Heptane	3.414	0	3.03	0.81	5.24	0.98	17.72	0.98	7.76
<i>n</i> -Decane	4.914	0	8.67	0.90	14.0	0.999	116.2	0.95	24.17
<i>n</i> -Dodecane	5.914	0	13.01	0.93	17.99	1.00	284.68	0.93	37.95
Cyclohexane	2.982	0	1.68	0.40	3.54	0.79	9.89	0.97	5.18
Benzene	3.000	0	1.06	0.42	1.64	0.76	5.03	0.94	2.51
Toluene	3.366	0.36	1.57	0.44	2.22	0.75	8.60	0.95	3.13
Methanol	0.447	1.70	0.44	0.03	0.40	0.15	0.85	0.40	5.07
Ethanol	1.023	1.69	0.54	0.12	0.53	0.25	1.18	0.66	4.19
Isobutanol	1.412	1.58	0.60	0.30	0.66	0.61	1.57	0.88	3.79
<i>n</i> -Butanol	2.023	1.75	0.73	0.44	0.62	0.75		0.95	4.33
<i>n</i> -Hexanol	3.023	1.55	0.97	0.67	0.81	0.91		1.00	5.09
Acetone	1.204	3.88	0.63	0.30		0.61	2.16	0.87	2.37
Butanone	1.765	2.76	1.50	0.44	3.22	0.75	5.53	0.95	4.69
Ethyl acetate	1.904	1.78	1.01	0.53	1.88	0.82	4.31	0.98	2.54
Isobutanal	1.724	2.58	1.13	0.33		0.65		0.90	3.37
Heptanal	3.351	3.14	1.83	0.63	2.39	0.90		1.0	4.16
Benzaldehyde	3.932	2.77	1.23	0.75		0.95		1.0	1.73
Acetophenone	2.864	3.02	1.34	0.53		0.82		0.98	1.86
Trichloromethane	2.085	1.01	1.46	0.34	1.44	0.65	6.55	0.90	2.67
1,2-Dichloroethane	2.903	2.06	1.25	0.38	1.58	0.69	5.15	0.92	2.19
Chlorobenzene	3.366	1.69	1.37	0.50	1.81	0.80	8.33	0.97	2.15
1-Bromopropane	3.139	2.18	2.00	0.33	4.61	0.64	10.71	0.89	3.37
<i>n</i> -Butylamine	2.115	1.37	0.52	0.70	1.39	0.81		0.97	
<i>n</i> -Hexylamine	3.115	1.04	0.85	0.82	1.82	0.94		1.00	
Triethylamine	3.070	0.66	1.78	0.75	3.96	0.86	8.48	0.93	
Aniline	3.155	1.53	0.71	0.65	0.69	0.72		0.96	1.36
Benzylamine	2.671	1.50	0.84	0.69	1.35	0.78		0.89	
Pyridine	1.850	2.19	0.62	0.60	1.36	0.64		0.86	1.51
Dimethylformamide	1.649	3.82	0.59	0.58	1.88	0.59		0.94	1.95
Dimethylacetamide	2.148	3.72	0.54	0.66	2.06	0.73		0.62	1.75
Nitromethane	0.742	3.46	1.22	0.45	1.92	0.32		0.51	3.08
Acetonitrile	0.724	3.92	1.45	0.40	2.58	0.22	3.61	0.95	7.66
Diethylether	1.991	1.15	0.68	0.67	1.58	0.75	2.40	0.95	
Dibutylether	3.991	1.17	3.88	0.88		0.99		0.98	9.17
Tetrahydrofuran	2.077	1.63	0.63	0.59	1.26	0.62	2.43	0.88	1.99
1,4-Dioxane	2.155	0	0.88	0.63	1.56	0.68	2.69	0.82	1.75
Anisole	2.523	1.38	1.58	0.73	2.05	0.84		0.89	2.25

values ($G^E < 0$) on TEP, and only methanol yielded $\gamma < 1$ and $G^E < 0$ for TEA.

Table II lists the excess Gibbs energy, enthalpy, and entropy of nine solutes of varied polarity on the three nonpolymeric stationary phases calculated with equations 6, 7, and 8. The lowest G^E values corresponded to Quadrol, and the largest ones to TEA for a given solute. According to Table I, G^E was negative for butanol and benzylamine on Quadrol; negative for butanol on TEP, and positive for all solutes on TEA. Trends for enthalpies and entropies were different: H^E followed the same trend as G^E , and S^E took the lowest values for TEA.

Figure 1 is the plot of the entropy of mixing S^E versus the molecular connectivity index of 37 solutes on Quadrol, TEP, and TEA. As it was established, all γ_{at} were less than 1 and, therefore, S^E was greater than 0 for all solutes on the three stationary phases. Descending hyperbolic curves were seen, and most solutes were located in a middle zone flanked by a top set of four points of small solutes (low connectivity index) and by a bottom set of two points of large solutes (high connectivity index). The results of the fitting with second-grade polynomials yielded correlation coefficients of $R^2 = 0.801$ for Quadrol, $R^2 = 0.798$ for TEP, and $R^2 = 0.788$ for TEA.

Plots of G^E versus ${}^1\chi^v$ for Quadrol, TEP, and TEA were also built. Discreet correlations for Quadrol and TEP ($R = 0.762$ and 0.700 for $N = 37$) were obtained, though a much better correlation ($R = 0.936$ for $N = 20$) for TEA was achieved.

If regressions for each chemical function were tried separately, the following would be given: for hydrocarbons, $R = 0.958$ ($N = 6$); alcohols, $R = 0.999$ ($N = 5$); nitrocompounds, $R = 0.748$ ($N = 7$); and ethers, $R = 0.966$ ($N = 9$). The group of carbonylic compounds yielded a worse correlation: $R = 0.58$.

Abraham's solvation model and solute-stationary phase interactions

Figure 2 shows the dependence of the dipole-polarizability interaction on the solute dipole moment of 37 solutes and 4 selected stationary phases. In all cases, $\sigma\pi^H_2$ increases with increasing dipole moment. Although correlation coefficients of $R = 0.673, 0.705, 0.707,$ and 0.708 , respectively, for (i) TEA, (ii) PDAS, (iii) TEP and (iv) Quadrol were rather poor, the mean slope $\approx 0.17 \pm 0.03$ of the straight lines showed that the dipole-polarizability interaction increased at the same rate for the four stationary phases.

The cavity formation and dispersion term, $[c+l.\log L(16)]$,

Table II. Excess Thermodynamic Magnitude Values for Selected Solutes and Stationary Phases

Solute	G^E (kJ/mol)			H^E (kJ/mol)			$S^E \times 10^3$ (kJ · mol ⁻¹ · K ⁻¹)		
	Quadrol	TEP	TEA	Quadrol	TEP	TEA	Quadrol	TEP	TEA
Benzene	0.20	1.61	5.27	3.06	2.65	5.47	7.27	2.65	0.51
Butanol-1	-1.04	-1.58	9.84	1.63	-0.64	10.01	6.80	2.40	0.42
Isobutanol	0.41	4.90	6.11	3.99	6.31	6.47	9.10	3.61	0.91
Butanone	1.32	3.83	5.59	4.00	4.77	5.75	6.83	2.41	0.42
Chlorobenzene	1.04	1.94	6.92	3.29	2.67	7.02	5.72	1.85	0.23
Benzylamine	-0.57	0.97	16.84	1.84	1.78	16.96	6.13	2.05	0.30
Nitromethane	0.64	2.14	9.03	8.23	5.88	10.57	19.3	9.50	3.93
Acetonitrile	1.21	3.09	4.19	10.66	7.97	6.38	24.0	12.4	5.56
Dibutylether	4.43	9.11	12.28	5.02	9.16	12.36	1.50	0.12	0.17

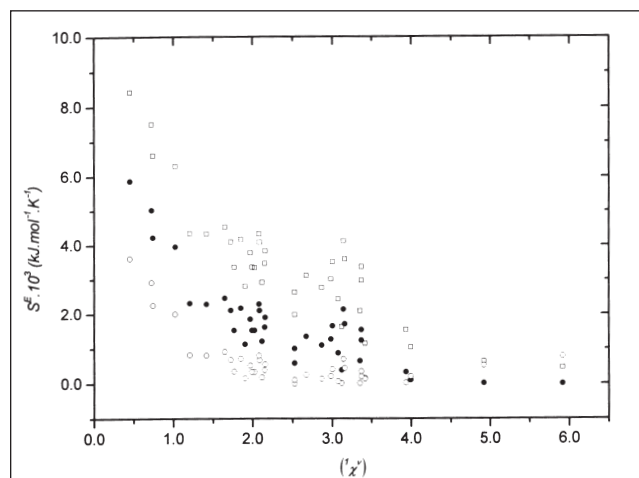


Figure 1. Plot of the excess entropy [$S^E \times 10^3$ (kJ · mol⁻¹ · K⁻¹)] versus the molecular connectivity index for 37 solutes on three amine stationary phases. $T = 393.15$ K. The stationary phases are TEA (●), TEP (○), and Quadrol (□).

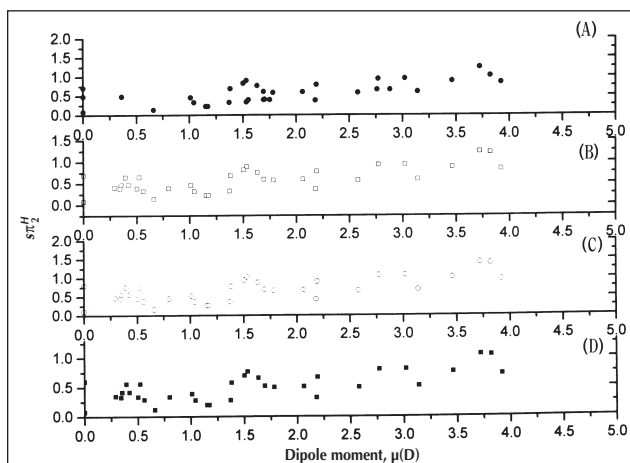


Figure 2. The variation of the dipolarity-polarizability ($\sigma\pi^H_2$) interaction with the solute dipole moment, $\mu(D)$. The stationary phases are TEP (A), Quadrol (B), PDAS (C), and TEA (D).

was also related to the molecular structure of solutes, expressed as the molecular connectivity indices (as seen in Figure 3). The corresponding LMSR gave straight lines with correlation coefficients of $R = 0.867$, 0.867 , 0.868 , and 0.866 for Quadrol, PDAS, TEP, and TEA, respectively.

Figure 4 is the plot of the nonpolar interactions versus the athermal activity coefficient (γ_{at}) for the three nonpolymeric stationary phases. Increasing straight lines were obtained for the three. Correlation coefficients of $R = 0.800$ for Quadrol, PDAS, and TEP, and $R = 0.790$ for TEA, were obtained ($N = 37$ in all cases).

Table III lists the individual solute–solvent interactions for six solutes on the four NH-containing stationary phases arranged by increasing polarity. As already found, rR_2 interactions were small with the exceptions of the amine, nitromethane, and the chlorocompound on PDAS. The

hydrogen-bond acidity stationary phase–base solute interactions were also small, with their largest values for TEA, specifically dichloroethane. The $l \cdot \log L(16)$ interaction reached its largest values for Quadrol and TEP, whereas the lowest ones corresponded to TEA. However, the prevalent interactions were the dipole ($s\pi_2^H$) and the hydrogen-bond base stationary phase–acid solute ($a\Sigma\alpha_2^H$). Maximum values for the dipole corresponded to aniline, nitromethane, and acetonitrile on PDAS not only because of the large value for the constant, but also because of the large dipole moment values. In contrast, minimum values seemed to correspond to TEA, mainly because of the low values of the s constant for this stationary phase. As for the hydrogen-bond base stationary phase–acid solute, the largest values (even those greater than 1) were found for *n*-butanol and ethyl acetate on TEP, and the lowest values were for nitromethane and acetonitrile on PDAS. The $a\Sigma\alpha_2^H$ interaction clearly increased with increasing stationary phase polarity in all cases. The same was found for $s\pi_2^H$, with the exception of TEA, which had unexpected low values of the constant s . As for the dispersive interactions $l \cdot \log L(16)$, the trend seemed to be the same: an increase from PDAS to TEP for all solutes when TEA was discarded. Quadrol and TEP had the same values for this interaction in spite of their polarity difference. Aniline again had the largest [$l \cdot \log L(16)$] values on PDAS, Quadrol, and TEP.

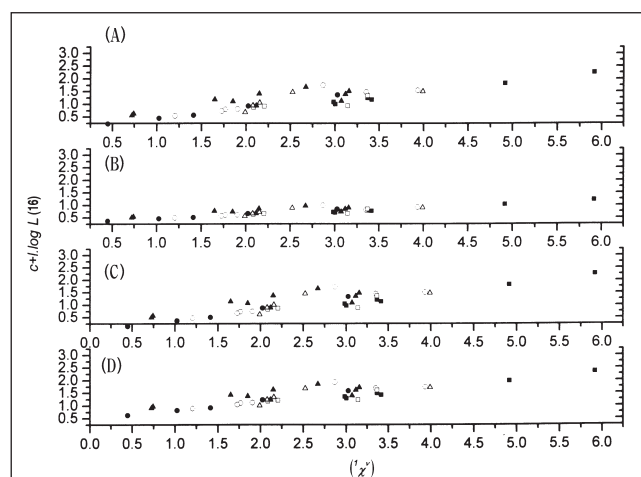


Figure 3. Plot of the cavity formation and dispersion–retention interactions with the structure of 37 solutes on 3 amine stationary phases. The stationary phases are PDAS (A), TEP (B), TEA (C), and Quadrol (D). The chemical functions are hydrocarbon (■), alcohols (●), carboxylic compounds (○), halogenated compounds (□), nitrogenated compounds (▲), and ethers (△).

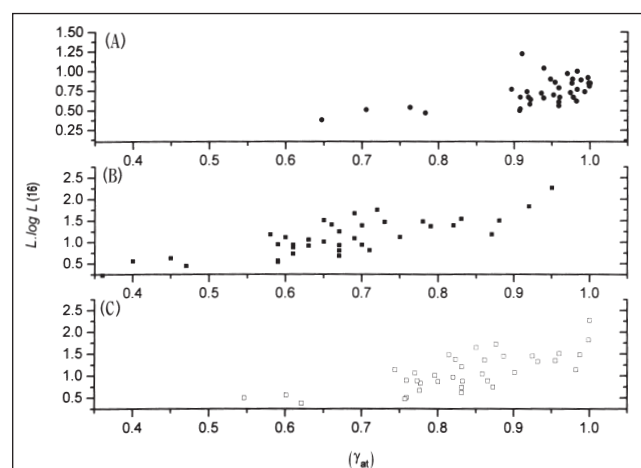


Figure 4. Dependence of the cavity formation and dispersion interaction on the infinite dilution molar fraction athermal activity coefficient for 37 solutes on 3 amine stationary phases. The stationary phases include TEP (A), Quadrol (B), and TEA (C).

Table III. Different Interactions Predicted by the Solvation Parameter Model for Six Solutes on Four NH₂-Containing Stationary Phases

Solute	Stationary phase	rR_2	$s\pi_2^H$	$a\Sigma\alpha_2^H$	$b\Sigma\beta_2^H$	$l \cdot \log L(16)$
Aniline	PDAS	0.370	1.03	0.29	0.041	1.430
	TEA	0.129	0.77	0.43	0.14	0.700
	Quadrol	0.035	0.90	0.46	0.127	1.692
	TEP	0.148	0.89	0.73	0.007	1.762
Butanol-1	PDAS	0.087	0.449	0.418	0.047	0.947
	TEA	0.030	0.336	0.612	0.165	0.463
	Quadrol	0.008	0.396	0.659	0.149	1.118
	TEP	0.035	0.391	1.036	0.008	1.165
Ethyl acetate	PDAS	0.041	0.663	0.509	0.045	0.842
	TEA	0.014	0.496	0.744	0.154	0.412
	Quadrol	0.004	0.585	0.801	0.140	0.995
	TEP	0.016	0.577	1.260	0.007	1.037
Nitromethane	PDAS	0.117	1.015	0.068	0.031	0.689
	TEA	0.041	0.76	0.099	0.106	0.337
	Quadrol	0.011	0.896	0.107	0.096	0.813
	TEP	0.047	0.884	0.168	0.005	0.848
Acetonitrile	PDAS	0.092	0.962	0.079	0.032	0.633
	TEA	0.032	0.72	0.116	0.110	0.309
	Quadrol	0.009	0.849	0.125	0.009	0.748
	TEP	0.037	0.838	0.196	0.005	0.779
Dichloroethane	PDAS	0.161	0.684	0.113	0.011	0.937
	TEA	0.011	0.937	0.056	0.512	0.165
	Quadrol	0.016	0.603	0.178	0.034	1.106
	TEP	0.064	0.596	0.28	0.002	1.153

Conclusion

Activity coefficients give information as valuable as that given by Abraham's formulation about solute-solvent interactions at a given temperature. The small values of γ for alcohols and amines agree with the large values of the $s\pi^{H_2}$ and $a\Sigma\alpha^{H_2}$ interactions that are predicted by Abraham's treatment. The γ values increase with increasing stationary phase polarity when TEA is disregarded. The nonpolar dispersion interaction [$c+l\log L(16)$] also grows as the polarity of the stationary phase increases.

Positive entropies of mixing are obtained for 37 solutes on the three nonpolymer stationary phases studied, decreasing with an increasing molecular connectivity index. Correlation coefficients of $R \approx 0.80$ for the parabolic fits are found in all cases. Negative Gibbs energy and enthalpy of mixing are obtained, especially for alcohols, amines, and some ethers.

Among the prevailing solute-stationary phase interactions reported by Ballantine et al. (13) (such as $s\pi^{H_2}$ and $a\Sigma\alpha^{H_2}$), the correlation found between $s\pi^{H_2}$ and the solute dipole moment has been demonstrated by the increasing straight lines obtained for every stationary phase (with correlation coefficients near 70% for all cases), and $s\pi^{H_2}$ correlates with $\ln \gamma$, with $R = 0.77-0.80$ for PDAS, Quadrol, and TEP. R was worse for TEA, perhaps because there are fewer solutes for this column.

The cavity formation and dispersion interaction [$c+l\log L(16)$] correlates fairly well with the molecular connectivity index of the 37 solutes ($R \approx 0.87$ in all cases). It is therefore the best fit obtained in this study. Taking the chemical functions separately, the correlation improves γ_{at} at up to 95% or better. Cavity formation and dispersion versus plots gives discreet straight lines with correlation coefficients of $R \approx 0.70$ for all of the amine stationary phases.

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