A Study of Solid Surface Polarity Using Inverse Gas Chromatographic Retention Data

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Key Words

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Summary

Sensitivities of a solid surface to dispersive and nondispersive (polar) interactions can be readily estimated by a multiple regression analysis of inverse gas chromatographic retention data of a set of probe solutes. This analysis is based on linear free energy relationships (LFERs). The sensitivity to the latter type of interactions can be used as a measure of the surface polarity of the solid. This has been shown in the case of a graphitized carbon fiber and the method is also applicable to other solids.

Introduction

Inverse gas chromatography (IGC) has been employed extensively to characterize the surface properties of fibers and allows the measurement of the surface energies of fibers [1]. The surface energy has been assumed to be the sum of two components: a London's dispersive component and non-dispersive (polar) component which includes induction, orientation and acid-base interaction forces. A method for the study of surface polarity is based upon the estimation of the non-dispersive energies of probe solutes, which are obtained by subtracting the dispersive energies from the total adsorption energies obtained by IGC. One of us recently proposed a method to study the solid surface polarity of carbon fibers [1]. The method was based on the estimation of the dispersive interaction energies as a function of molar deformation polarization of molecules. It has been shown that the method can provide reasonable estimates of both the dispersive and polar components of adsorption energies.

In the present work we show that multiple regression analyses based on linear free energy relationships [2, 3] can readily estimate both components of the surface energy for a given solute-adsorbent pair using the molar volume and a solvatochromic parameter [4] for the test solute. Dispersive interaction energies for some solutes obtained in this study are in good agreement with the values obtained by our theoretical approach [1].

Over the past decade Kamlet, Taft and their coworkers have developed a methodology based on the linear free energy relationships (LFERs) [2, 3] and their solvatochromic parameters [5] for quantifying interactions and the influence of pure bulk solvents on a wide variety of solution phase processes. Kamlet et al. have applied these measurements of interaction strength to some 600 processes [2, 3] including a large number of systems of immediate relevance to chromatography, including Rohrschneider's gas-liquid partition coefficients [6], retention of McReynolds solutes on polymeric silicone oil gas chromatographic phases [7], and reversed phase liquid chromatography [8–12]. As originally developed by Kamlet and Taft the solvatochromic parameters are properties of the bulk liquid. Thus it would seem that they should not be used to characterize a species when it is a solute nor to characterize heterogeneous interactions between solvent or solute vapor and a surface. It has been shown recently that the LFER with the solvatochromic parameters can be used to rationalize these types of processes such as gas-solid adsorption coefficients [13] and Snyder's solvent strength parameter, ε^0 [14].

When LFER is applied to phase-transfer processes, a general solute or solvent property (SP) can be correlated via the use of three types of terms as follows [2, 3]:

$$\text{SP} = \text{C} + \text{cavity term} + \text{dipolar term} + \text{hydrogen bonding term(s)} \tag{1}$$

The constant C denotes the value of SP when all the three terms in the equation are zero. The cavity term is usually taken as the product of the solute van der Waals molar volume (V_I) and the square of the Hildebrand solubility parameter (δ_H) of the solvent. The dipolar term is the product of the solute π^* and the solvent π^*. The π^* parameter measures a combination of dipolarity/polarizability of a compound. The hydrogen bonding (HB) terms are written as a cross product of the solute α and the solvent β (type B HB) and the product of the solute β and the solvent α (type A HB). The parameters α and β measure HB donor

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acidity and HB acceptor basicity of the compound, respectively. In the case of the chromatographic retention, SP in the equation below denotes a retention parameter such as k' or V_N and the subscript 2 designates a solute property. The subscripts s and m denote the stationary and mobile phases, respectively.

$$\log(k' \text{ or } V_N) = C + M(\delta_s^2 - \delta_m^2)V_{I,2}/100 + S(\pi_s^* - \pi_m^*)\pi_2^* + B(\alpha_s - \alpha_m)\beta_2 + A(\beta_s - \beta_m)\alpha_2 \quad (2)$$

The coefficients *M, S, B,* and *A* are the fitting parameters. $V_{I,2}/100$ is used so that the parameter covers roughly the same range as the solvatochromic parameters, which makes easier the evaluation of the contributions of the various terms to the properties studied.

When a system with a fixed pair of mobile and stationary phases is considered, Eq. (2) is reduced to

$$\log(k' \text{ or } V_N) = C + m\, V_{I,2}/100 + s\,\pi_2^* + b\,\beta_2 + a\,\alpha_2 \quad (3)$$

The coefficients *m, s, a,* and *b* are obtained by a multiple linear regression of log (k' or V_N) vs. the solute parameters. In gas-solid adsorption chromatography such as IGC, the cavity term is, in fact, not necessary since the system does not involve a liquid in which a cavity for the solute is to be made. The term $(\delta_s^2 - \delta_m^2)$ in Eq. (2) is simply non-existing in the gas-solid adsorption processes. The term $mV_{I,2}/100$ in Eq. (3) approximates an increase in dispersive interactions between the adsorbent and the solute as the solutes increase in size and hence polarizability [14]. Indeed, a good linear correlation was observed between $V_{I,2}/100$ and molar deformation polarization of molecules, P_D ($P_D = -2.49\ (\pm 1.77) + 50.42\ (\pm 3.28)\ V_{I,2}/100$, n = 12, r = 0.980, S.D. = 1.79). In GC the mobile phase is an inert gas and the interactions between the solute vapor and the carrier gas are negligible at the pressures normally used. The values of π_m^*, α_m and β_m in Eq. (2) are equal to zero. Then the sign and magnitude of the coefficients measure the direction and relative strength of different types of solute-adsorbent interactions affecting retention on a given solid. Thus, differences in these coefficients for retention parameters, for a given solute set measured on different solids, indicate the contributions from various adsorbate-adsorbent interactions to retention on the solids. The size of the coefficients *s, a,* and/or *b* can be used to estimate the relative polarity of various solids under study.

Experimental

Details of the chromatographic apparatus and measurement procedure have been described elsewhere [15]. Retention data for ten probe solutes including three n-alkanes on a column packed with a graphitized carbon fiber (designated as Fiber E) at four different column temperatures are given in Table I.

Results and Discussion

The thermodynamic function relating the retention process in IGC can be expressed by the adsorption free energy ΔG_A for one mole of solute vapor from a reference state [1]:

$$\Delta G_A = -RT \ln [V_N P_0/(S_p\, w\, \pi_0)] \quad (4)$$

where V_N, P_0, π_0, S_p, and w are the net retention volume, the pressure, the bidimensional spreading pressure of the solute, the specific surface area and the weight of the solid in the column, respectively. Since the choice of the reference state is arbitrary, Eq. (4) can be rewritten as:

$$\Delta G_A = -[RT \ln V_N + C] \quad (5)$$

C being a constant depending on the chosen reference state for a given column. At a given temperature the quantity RT ln V_N depends only on the nature of the solute injected and in turn is a measure of the adsorbate-adsorbent interactions. It is generally assumed that these interactions are composed of two types of interactions (dispersive and polar) and that these two types of interactions are inde-

Table I. Properties and net retention volume of the probe solutes on Fiber E over a range of temperatures.

				V_N (mL) at T (°C)			
Solute	P_D^a	$V_I/100^b$	π^{*b}	20.8	29.6	34.6	39.9
n-pentane	25.3	0.553	−0.08	5.109	3.387	2.723	2.210
n-hexane	29.9	0.648	−0.04	30.41	18.12	13.83	10.64
n-heptane	35.5	0.745	−0.02	182.9	97.96	72.39	52.46
chloroform	21.5	0.427	0.58	6.076	4.006	3.336	2.732
benzene	26.2	0.491	0.59	17.38	10.99	8.619	6.847
nitromethane	12.5	0.348	0.85	3.882	3.255	3.112	2.871
acetonitrile	11.1	0.271	0.75	4.358	3.004	2.778	2.603
acetone	16.2	0.380	0.71	3.507	2.047	1.616	0.967
ethyl acetate	22.3	0.521	0.55	14.12	7.924	6.209	4.974
tetrahydrofuran	19.9	0.455	0.58	9.785	5.523	4.593	3.746
ethyl ether	22.5	0.505	0.27	3.997	2.592	2.109	1.842

a. $P_D \approx (4/3)\pi N \alpha_e = V(n^2 - 1)/(n^2 + 2)$ (in cm^3/mole), where V = molar volume and n = refractive index of the solute.

b. Data from ref. [4].

pendent of each other and are additive. Eq. (5) can be thus expressed as:

$$\mathrm{RT}\ln V_N + C = (-\Delta G_A^D) + (-\Delta G_A^P) \tag{6}$$

where the superscripts D and P refer to the dispersive and polar interactions including orientation, induction and hydrogen-bonding (HB), respectively.

The LFER approach with solvatochromic parameters can readily provide estimates of interaction energies on carbon fiber. Carbon fiber does not possess strong dipolar or hydrogen bonding functionalities and thus the interactions that can take place between the polar solute and carbon fiber comprise only dispersive interactions and induction interactions between the dipole of the polar solute and the induced dipole on the fiber, with the former playing a major role. Since the interactions that can take place on carbon fiber with the probe solutes comprise mainly dispersive and induction interactions, the first two terms in Eq. (3) are only necessary to describe adsorption processes of the probe solutes onto the carbon fiber.

$$\mathrm{RT}\ln V_N = C + m\,V_I/100 + s\,\pi^* \tag{7}$$

The term, $m\,V_I/100$, estimates the dispersive interaction energies, $(-\Delta G_A^D)$, and the term, $s\,\pi^*$, the induction interaction energies, $(-\Delta G_A^P)$. The coefficient s then measures the sensitivity of the carbon fiber to induction interactions and the coefficient m measures the sensitivity of the fiber to dispersive interactions with the probe solutes. Result of a regression using the above two-parameter LFER equation for RT ln V_N data at 20.8 °C is given below:

$$\begin{aligned}\mathrm{RT}\ln V_N = &-18.73\,(\pm 2.69) + \\ &+ 41.89\,(\pm 4.23)\,V_I/100 + \\ &+ 8.28\,(\pm 1.50)\,\pi^* \\ &n = 10,\ r = 0.975,\ \mathrm{S.D.} = 0.75\end{aligned} \tag{8}$$

Fiber E is a graphitized fiber treated at 2500–2700 °C and may possess some active surface oxygen atoms which can act as hydrogen bond acceptor sites. It may then necessary to include in the LFER equation a hydrogen bonding term ($a\,\alpha_2$) in order to account for HB interactions between the solute as HB donor and the fiber as HB acceptor. Regression using the three-parameter LFER equation gives the following:

$$\begin{aligned}\mathrm{RT}\ln V_N = &-19.41\,(\pm 2.76) + \\ &+ 42.99\,(\pm 4.35)\,V_I/100 + \\ &+ 8.23\,(\pm 1.49)\,\pi^* + 2.50\,(\pm 2.42)\,\alpha \\ &n = 10,\ r = 0.979,\ \mathrm{S.D.} = 0.75\end{aligned} \tag{9}$$

We find no improvement in the goodness of the fit and the coefficient a is statistically insignificant. We used the Ehrenson test [16] to determine confidence level (CL %) whether the double regression should be rejected in favor of the triple regression. Only when CL % for the additional variable is greater than 90 % is the multiple regression with a greater number of explanatory variables justified. The Ehrenson test also shows that the $a\alpha$ term is not significant. It should, however, be noted that the data set does not include any stronger HB donor solute than chloroform ($\alpha = 0.20$ [17]), so that the dependence on HB donor acidity remains uncertain. The carbon fiber may contain active HB donor sites on the surface and we would then expect to see a significant dependence of RT ln V_N on the solute basicity. When the three parameter regression including the solute HB acceptor basicity parameter (β) was performed, we found there was a slight improvement in the goodness of the fit. However, the b coefficient was very small compared to the s coefficient and CL % was only 75 %. The above results indicate that the carbon fiber does not possess strong HB acceptor or donor sites. The fiber may contain weak HB donor sites but their presence is not significant in determining the solute adsorption energy. Thus the α and β parameters were not incorporated in the further regressions.

The results of regressions of RT ln V_N on the carbon fiber vs. the solutes' $V_I/100$ and π^* parameters are given in Table II. Data for chloroform at all temperatures and that for acetone at 39.9 °C turned out to be outliers based on Cook's distance and Student's t-test [18] and thus were not used in the regressions. Correlation coefficients are all reasonably good and standard errors of the fits are quite small. The quality of the fit is demonstrated in Figure 1. Abraham et al. [19, 20] suggested that logarithm of hexadecane-gas partition coefficient (log L_{16}) be a better measure of strength of dispersive interactions and recommend-

Table II. Coefficient estimates in multiple regression equations of RT ln V_N on Fiber E vs. $V_I/100$ and π^* of the probe solutes[a].

Temp. (°C)	C	m	s	r[b]	S.D.[c]	n[d]
20.8	− 18.73 (2.69)	41.89 (4.23)	8.28 (1.50)	0.975	0.75	10
29.6	− 18.30 (3.13)	40.27 (4.92)	7.97 (1.74)	0.965	0.87	10
34.6	− 18.94 (3.44)	39.59 (5.41)	8.03 (1.91)	0.955	0.86	10
39.9	− 18.29 (3.67)	37.64 (5.78)	7.93 (2.00)	0.947	1.00	9

a. Standard deviations in the coefficient estimates are in parentheses.
b. Correlation coefficient.
c. Standard error of the fit.
d. Number of test solutes included in regressions.

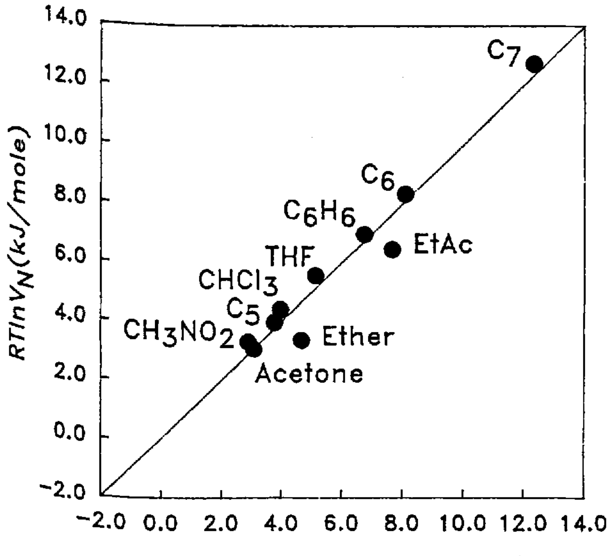

Figure 1
Plot of measured RT ln V_N at 20.8 °C vs. calculated values by Eq. (8).

Table III. Estimated contributions to total interaction energy (RT ln V_N) from dispersive and induction interactions for some solutes on Fiber E based on the LFER at 20.8 °C (kJ/mole).

Solutes	RT ln V_N (D)^a	RT ln VN (P)^b
n-pentane	23.17 (21.61)^c	0.00 (0.00)^c
n-hexane	27.15 (25.53)	0.00 (0.00)
n-heptane	31.22 (26.67)	0.00 (0.00)
chloroform	17.89 (18.36)	4.81 (3.52)
benzene	20.57 (22.38)	4.90 (2.07)
nitromethane	14.58 (10.68)	7.06 (10.12)
acetone	15.92 (13.84)	5.89 (6.08)
ethyl acetate	21.83 (19.04)	4.57 (4.90)
tetrahydrofuran	19.06 (17.00)	4.81 (6.50)
ethyl ether	21.16 (19.22)	2.24 (1.64)

a. Computed from the dispersive interaction term, 41.89 $V_I/100$.
b. Computed from the dispersive interaction term, 8.28 π^*.
c. In parentheses are values estimated by the theoretical approach based on P_D [1].

ed that log L_{16} be used when dealing with gas-condensed phase processes. Li et al. [21] also followed a similar approach in their characterization of GC liquid stationary phases. We tried log L_{16} in place of $V_I/100$ in regressions but the fit was even poorer. For example, regression of RT ln V_N at 20.8 °C vs. log L_{16} and π^* gave the following result.

$$\begin{aligned}\mathrm{RT}\ln V_N &= -7.62\ (\pm 3.18) + \\ &+ 5.82\ (\pm 1.19) \log L_{16} - 1.23\ (\pm 1.51)\ \pi^* \qquad (10)\\ &n = 10,\ r = 0.914,\ \mathrm{S.D.} = 1.37\end{aligned}$$

The coefficient *s* in Eq. (10) is statistically zero, indicating that induction interactions are not involved in the adsorption process at all. This is obviously incorrect. Simple regression vs. log L_{16} alone gave a correlation coefficient of 0.873. The F-test [22] also indicates that the regression using $V_I/100$ and π^* is significantly better than that using only log L_{16} (F_R = 67 vs. 29). While the use of log L_{16} provides better correlation for gas-liquid transfer processes than the use of V_I, it seems that this may not be the case in the case of gas-solid adsorption processes.

Table II indicates that the *m* coefficients are much greater than the *s* coefficients. This is in agreement with the fact that there is a much greater contribution to solute retention on the carbon fiber from dispersive interactions than induction interactions since the fiber does not possess strong dipolar functionalities. Table III lists the contributions of the two types of interactions estimated by LFER to the total adsorption energies of some polar solutes on the carbon fiber. Values in parentheses are estimated by theoretical analysis [1]. The two sets of values are in reasonably good agreement with each other. Meyer et al. reported the contribution of different types of interaction energies to total cohesion of several homologous series of liquids [23–26]. The estimated value of dispersive interaction energies for acetone and ethyl acetate by the LFER approach are 16 and 22 kJ/mole, which are in reasonably good agreement with the literature value (21 and 30 kJ/mole) for dispersive interaction energies in each liquid [23, 26], although the comparison of data for intractions between unlike molecules with those for like molecules may not be entirely rigorous. The size of both the *m* and *s* coefficients in general decrease with temperature, which is in agreement with the fact that the strength of intermolecular interactions decreases with temperature.

The results shown above demonstrate that the LFER approach can give reasonable estimates of different types of interaction energies contributing to the total adsorption energy on a solid surface. By performing similar analyses for IGC retention data obtained on various solids with the same set of probes and simply comparing the size of the coefficient *s*, one can readily determine the relative polarity of the solids. Obviously the LFER approach is applicable to other solids having both dipolar and hydrogen bonding functionalities by performing similar analyses using LFER equations with the hydrogen bonding terms included.

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