# INTERPRETATION OF NORMAL-PHASE SOLVENT STRENGTH SCALES BASED ON LINEAR SOLVATION ENERGY RELATIONSHIPS USING THE SOLVATOCHROMIC PARAMETERS $\pi^*$, $\alpha$ AND $\beta$

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SUMMARY

An analysis of normal-phase solvent eluotropic strength ($\varepsilon^0$) and solute adsorption energy ($S^0$) was carried out by use of linear solvation energy relationships using solvatochromically based measurements of molecular dipolarity/polarizability ($\pi^*$), hydrogen bond acidity ($\alpha$) and hydrogen bond basicity ($\beta$). It is demonstrated that in normal-phase chromatography acceptable regressions of the $\varepsilon^0$ parameter *vs.* the solvatochromic parameters ($\pi^*$, $\alpha$, $\beta$) are obtained. The dependence of $\varepsilon^0$ on the solvatochromic parameters indicates that silica and alumina are virtually equally retentive towards dipoles, whereas silica surfaces are definitely stronger hydrogen bond donors than are alumina surfaces. In contrast, the surface of alumina is a stronger hydrogen bond base than is that of silica. Unlike reversed-phase liquid chromatography, where the dominant solute properties are cavity formation and a solvent (as acid) to solute (as base) hydrogen bond interaction, normal-phase processes are sensitive to dipole–dipole interactions and to hydrogen bond formation to the solvent acting as both an acid and a base.

INTRODUCTION

A knowledge of the eluotropic strength of a pure or mixed solvent is vital in all forms of liquid chromatography in order to establish the initial separation conditions and to optimize the final separation[1]. Normal-phase adsorption chromatography, which is most often implemented using silica or alumina as the adsorbent, unquestionably entails the use of a much wider range of solvent classes than does reversed-phase liquid chromatography. Solvents varying in strength and type from exceedingly non-polar, non-polarizable perfluorinated alkanes to highly dipolar hydrogen bond acceptor/donor alcohols are in common use in normal-phase chromatography. The parameter $\varepsilon^0$ was developed by Snyder[2,3] to quantify the overall strength of a solvent on a particular adsorbent. This parameter is related to the adsorption energy of a solvent molecule per unit area occupied by that molecule on

a specified adsorbent of standard activity. It can be shown, based on the assumption of a displacement mechanism[3,4], that the adsorption coefficient, *i.e.*, the equilibrium constant ($K_{ads}$) for the process defined by eqn. 1, is given by eqn. 2.

$$X_n + nM_a \rightleftharpoons X_a + nM_n \tag{1}$$

$$\log K_{ads} = \log V_a + \alpha(S^0 - A_s \varepsilon^0) \tag{2}$$

where X and M denote the solute and solvent molecules and the subscripts n and a refer to a molecule of either type (X or M) in the non-adsorbed and adsorbed states, respectively; $V_a$ is the adsorbent surface volume (*i.e.*, the volume of an adsorbed solvent monolayer per gram of adsorbent) and $\alpha$ is the surface activity which varies with the condition of the surface, *i.e.*, how it is thermally and chemically precon-ditioned with water or some other deactivating agent. In principle, both $V_a$ and $\alpha$ are properties of the adsorbent and are not related to the solvent or the solute. Hence they are of no further interest in this work. The term $S^0$ is the dimensionless free energy of adsorption of the solute molecule on to a surface of unit activity using pentane as the mobile phase and $A_s$ is the surface area occupied by a solute molecule.

It is most important to note that eqn. 2 is based on the simplifying assumption that mobile phase interactions between the solute and the solvent can be neglected[2]. This condition will obtain when solute–solvent and solvent–solvent interactions are inherently small compared with the energies of adsorption. Eqn. 2 will also be accurate when the energy gained by the formation of the solute–solvent interactions, on displacement of the solute from the adsorbed state, is cancelled by the corresponding solvent–solvent interactions which are lost. Related work involving solubility parameter-based models of liquid chromatographic processes indicate that this approximation is likely to be most realistic when the solute and solvent are unable to interact significantly via hydrogen bonding[5].

With the above assumptions, the $\varepsilon^0$ scale is independent of the solute and of the specific activity of the surface ($\alpha$); $\varepsilon^0$ does depend on the chemical nature of the surface. Therefore, values of $\varepsilon_0$ for a particular solvent, *e.g.*, methanol, will be different for different adsorbents such as silica, alumina and activated carbon. The sequence of solvents in order of their $\varepsilon^0$ values is termed an eluotropic series. The most recent comprehensive collection of eluotropic data for a number of adsorbents is given in ref. 3. The major thrust of this work is to explore the chemical and physical differences between silica and alumina as normal-phase adsorbents and determine how these differences influence the solvent (and secondly the solute) adsorption energy.

Experimentally $\varepsilon^0$ cannot be separated from the test solutes used to establish it. Eqn. 2 indicates that for non-localizing solutes a plot of $\log k'$ ($k'$ = capacity factor) *vs.* $\varepsilon^0$ will be independent of the solute adsorption energy but dependent on solute size ($A_s$) for non-localizing solutes. This has been demonstrated repeatedly. Snyder and Schunk[6] did so using an amino-bonded phase as the column packing. The validity of eqn. 2 was further substantiated by Snyder and Glajch[7], who have shown that for a non-localizing solvent mixture the measured $\varepsilon^0$ value of the strong solvent is independent of both the eluent composition (volume percent) and of the solute. This is not the case when the eluent contains a localizing component. In essence, $\varepsilon^0$ is an

empirical parameter obtained by measuring the $k'$ value of a solute in a series of solvents on an adsorbent of known activity with a solute of known size. Eqn. 2 yields the following relationship which is used to calculate $\varepsilon_2^0$:

$$\log k_1'/k_2' = \alpha A_s(\varepsilon_2^0 - \varepsilon_1^0) \tag{3}$$

In order to calculate $\varepsilon_2^0$ it is necessary to define arbitrarily the $\varepsilon^0$ value of some solvent. For this purpose the value of $\varepsilon^0$ of *n*-pentane was defined as zero[2].

It should be evident from the above discussion that with a typical normal-phase adsorbent the chief properties which establish the strength of the interaction of a molecule with an adsorbent are its dipolarity and hydrogen bonding donor (acidity) and acceptor (basicity) strength.

Over the past decade Kamlet, Taft and co-workers have developed a methodology for quantifying such interactions and the influence of pure bulk solvents on a wide variety of solution-phase processes. They have made use of the phenomena of solvatochromism[8-10], that is, the effect of a solvent on a spectroscopic property, to establish three carefully constructed scales representing solvent dipolarity ($\pi^*$) and hydrogen bond acidity ($\alpha$) and basicity ($\beta$). Most of these parameters have been measured for over 200 solvents[11].

Taft and co-workers[12,13] have applied these measures of interaction strength to about 600 processes, including a large number of systems of immediate relevance to chromatography. For example, Rohrschneider's gas–liquid partition coefficients[14], retention of McReynold's solutes on polymeric silicone oil gas chromatographic phases[15] and reversed-phase liquid chromatography[16,17] have been studied. As originally developed by Taft and co-workers, $\pi^*$, $\alpha$ and $\beta$ are properties of the bulk liquid. Therefore, it would seem that they should not be used to characterize a species when it is a solute or to characterize a solvent–surface interaction as is proposed here. Recent work has shown that for species which self-associate (*e.g.*, alcohols) in the bulk liquid state the values of $\alpha$ and $\beta$ require modification[18]. In this work we rationalize the use of these parameters based on the findings of Abraham *et al.*[19] that gas–solid adsorption coefficients on several types of carbon can be rationalized based on the solvatochromic properties of the adsorbate.

In this work we examined the $\varepsilon^0$ scale and solute retention in normal-phase liquid chromatography by use of linear solvation energy relationships (LSER) based on the above-mentioned parameters. In previous studies of solvent effects on chemical and physical properties of a solute we considered a free energy parameter with a linear combination of the solvent cohesiveness as measured by the Hildebrand solubility parameter ($\delta_H^2$), the solvent polarizability-dipolarity parameter ($\pi_1^*$), hydrogen bonding acidity ($\alpha_1$) and hydrogen bonding basicity ($\beta_1$). For several reasons which will be given below we believed that the eluotropic strength ($\varepsilon^0$) for normal-phase chromatography would not depend on the solvent's solubility parameter, so an equation of the following form was used:

*Solvent studies:*

$$\varepsilon_1^0 = \varepsilon_0^0 + s(\pi_1^* + d\delta) + a\alpha_1 + b\beta_1 \tag{4}$$

where $\delta$ is a polarizability correction term[20] ($d = -0.2$, $\delta = 0.00$ for non-chlorinated

aliphatic solvents, 0.50 for polychlorinated aliphatics and 1.00 for aromatics), the subscript 1 denotes a solvent property and $\varepsilon_0{}^0$ is the intercept of the regression.

Similarly in the past we represented the variation of a free energy property with solute type by a linear equation which depended on the solute size as measured by its molar volume, in addition to its dipolarity ($\pi^*$), and for solutes which self-associate in the pure liquid state on their monomer hydrogen bond acidity ($\alpha_m$) and basicity ($\beta_m$). Because we felt that cavity formation would not be a significant factor in normal-phase chromatography, we delete the dependence on solute size to give an equation of the following form:

*Solute studies:*

$$S_2 = S_0 + s\pi_2^* + a(\alpha_m)_2 + b(\beta_m)_2 \tag{5}$$

were $S$ is the solute adsorption energy, subscript 2 denotes the solute and the additional subscripts indicate the use of the monomer value for the solute as explained previously[16,17]. The terms $\alpha_m$ and $\beta_m$ indicate the $\alpha$ and $\beta$ values of a substance when it acts as a monomer. For all but non-associating solutes $\alpha_m = \alpha$ and $\beta_m = \beta$. When a compound self-associates, owing to strong intermolecular hydrogen bond formation, $\alpha_m$ is less than $\alpha$ and $\beta_m$ is less than $\beta$. This is based on the experimental findings of Abboud *et al.*[18], who have shown convincingly that dimeric alcohols are both stronger hydrogen bond acids and bases than are the monomers.

## RESULTS AND DISCUSSION

All the solvent parameters used here are given in Table I. These were taken from the most recent compilations of both types of parameters[3].

As the outset it should be understood that the solvent strength scale on alumina is closely related to that on silica (see Fig. 1). A linear regression shows that

$$\varepsilon_{\text{alumina}}^0 = -0.003\ (\pm 0.06) + 1.19(\pm 0.09)\ \varepsilon_{\text{silica}}^0 \tag{6}$$

$$n = 19;\ r = 0.958;\ sd = 0.07$$

where $n$ is the number of solvents tested, $r$ is the correlation coefficient and $sd$ is the average residual of the fit. This is not a particularly good regression relative to what we have been able to obtain regularly when other solvent properties were correlated with the solvatochromic parameters and indicates that there may be chemical differences in the interactions of silica and alumina with the set of solvents included in the regression. Clearly the eluotropic strength scale on silica is compressed relative to alumina.

*Solvatochromic study of silica*

Based on previous experiences, it is important to build up the regression in a stepwise fashion in order to avoid addition of unnecessary parameters. For all available solvents we obtain

$$\varepsilon_{\text{silica}}^0 = 0.08(\pm 0.06) + 0.62(\pm 0.13)\ (\pi^* - 0.2\delta) \tag{7}$$

$$n = 19;\ r = 0.753;\ sd = 0.13$$

TABLE I

SOLVENT PARAMETERS FOR LIQUID–SOLID CHROMATOGRAPHY

| Solvent[a] | $\varepsilon^0_{alumina}$ [b] | $\varepsilon^0_{silica}$ [b] | $\pi^{*c}$ | $\alpha^c$ | $\beta^c$ |
|---|---|---|---|---|---|
| Hexane (S) | 0 | 0 | −0.04 | 0 | 0 |
| Heptane (S) | 0 | 0 | −0.05 | 0 | 0 |
| Tetrachloromethane | 0.17 | 0.11 | 0.29 | 0 | 0 |
| Diisopropyl ether (S) | 0.28 | 0.32 | 0.27 | 0 | 0.49 |
| Isopropyl chloride (S) | 0.31 | 0.28 | 0.37 | 0 | 0 |
| Toluene | 0.30 | 0.22 | 0.55 | 0 | 0.11 |
| $n$-Propyl chloride (S) | 0.31 | 0.28 | 0.37 | 0 | 0 |
| Chlorobenzene | 0.31 | — | 0.71 | 0 | 0.07 |
| Benzene | 0.32 | 0.25 | 0.59 | 0 | 0.10 |
| Bromoethane | 0.34 | — | 0.60 | 0 | 0 |
| Triethylamine | 0.36 | — | 0.14 | 0 | 0.71 |
| Diethyl ether (S) | 0.38 | 0.43 | 0.27 | 0 | 0.47 |
| Chloroform | 0.36 | 0.26 | 0.58 | 0.44 | 0 |
| Dichloromethane | 0.40 | 0.30 | 0.82 | 0.30 | 0 |
| Tetrahydrofuran (S) | 0.51 | 0.53 | 0.58 | 0 | 0.55 |
| 1,2-Dichloroethane | 0.44 | 0.34 | 0.81 | 0 | 0 |
| Acetone (S) | 0.58 | 0.53 | 0.72 | 0.08 | 0.48 |
| $p$-Dioxane | 0.61 | 0.51 | 0.55 | 0 | 0.37 |
| Ethyl acetate (S) | 0.60 | 0.48 | 0.55 | 0 | 0.45 |
| Acetonitrile (S) | 0.55 | 0.52 | 0.75 | 0.19 | 0.31 |
| Pyridine | 0.70 | — | 0.87 | 0 | 0.64 |
| Isopropyl alcohol | 0.82 | 0.60 | 0.48 | 0.76 | 0.95 |
| Methanol | 0.95 | 0.70 | 0.60 | 0.93 | 0.62 |

[a] S denotes select solvents.

[b] Data from ref. 3.

[c] Data from ref. 11.
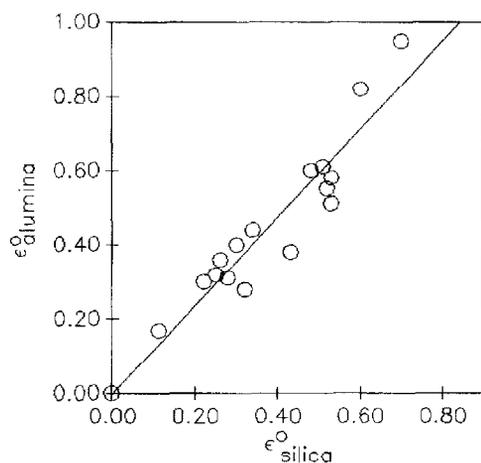


Fig. 1. Plot of $\varepsilon^0_{alumina}$ vs. $\varepsilon^0_{silica}$. The straight line indicates the least-squares line. For data see Table I.

By any standard this is an extremely poor result. It is the expected result as this regression equation completely omitted any solvatochromic representation of hydrogen bonding interactions, which are known to be important owing to the presence of hydrogen-bond active silanol groups on the surface of silica[2].

The original list of 23 solvents contains twelve 'select' solvents. Select solvents are defined as aliphatic, monofunctional, non-polyhalogenated, aprotic solvents and are denoted in Table I with an S in parentheses following the solvent name. For the select solvents:

$$\varepsilon_{silica}^0 = 0.08(\pm 0.04) + 0.67(\pm 0.10)\,(\pi^* - 0.2\delta) \tag{8}$$

$$n = 10; r = 0.928; d = 0.08$$

This is clearly an improvement over eqn. 7. Although the select solvents are by definition aprotic and therefore have no acidity, the select solvent set does contain many strong hydrogen bond bases ($\beta > 0$), so we now include the solvatochromic hydrogen bond basicity parameter ($\beta$) and carry out a two-parameter regression:

$$\varepsilon_{silica}^0 = 0.06(\pm 0.03) + 0.51(\pm 0.07)\,(\pi^* - 0.2\delta) + 0.32(\pm 0.08)\beta \tag{9}$$

$$n = 10; r = 0.979; sd = 0.05$$

Incorporation of a solvatochromic representation of HB basicity obviously improves the regression very considerably. The Ehrenson test[21] indicates that the $\beta$ parameter is significant at the 99% confidence level. The entire data set, including the hydrogen bond donor solvents, is now examined and we obtain

$$\varepsilon_{silica}^0 = 0.04(\pm 0.03) + 0.46(\pm 0.06)\,(\pi^* - 0.2\delta) + 0.43(\pm 0.05)\beta \tag{10}$$

$$n = 19; r = 0.963; sd = 0.06$$

When the solvent hydrogen bond acidity parameter ($\alpha$) is incorporated in the regression, we find there is no improvement in the goodness of the fit and the $a$ coefficient is very small (statistically zero):

$$\varepsilon_{silica}^0 = 0.04(\pm 0.03) + 0.45(\pm 0.06)\,(\pi^* - 0.2\delta) + 0.03(\pm 0.06)\alpha +$$
$$+ 0.41(\pm 0.05)\beta \tag{11}$$

$$n = 19; r = 0.964; sd = 0.06$$

If the surface of silica were substantially basic, that is, able to accept a hydrogen bond from an acidic solvent, then we could expect to see a significant dependence of $\varepsilon^0$ on the solvent acidity ($\alpha$). As this does not occur (the coefficient of $\alpha$ in eqn. 11 is trivial), we conclude that the surface of silica is not a good hydrogen bond base.

The quality of the fit is demonstrated in Fig. 2. First, as expected, the intercept term in the final regression (eqn. 11) is extremely small. Based on the definition of $\varepsilon^0$ as 0.00 for $n$-pentane and the very small $\pi^*$ value ($-0.087$) for this solvent[22], the
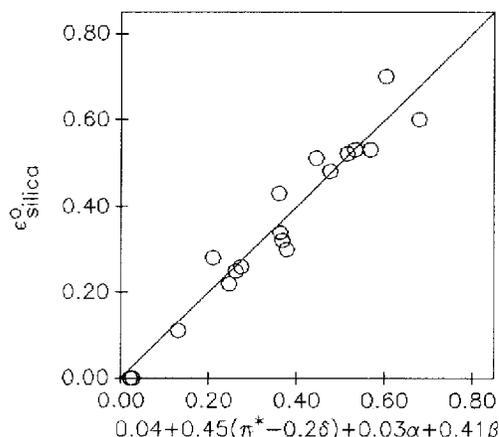
Fig. 2. Plot of $\varepsilon^0_{\text{silica,expt}}$ vs. $\varepsilon^0_{\text{silica,calcd}}$. Results calculated from eqn. 11.

calculated value of $\varepsilon^0$ for *n*-pentane is 0.009, which is well within the standard deviation of the fit. Second, the two factors, *viz.*, dipolarity and HB basicity, lead to an increase in solvent strength on silica. All of these results are in good agreement with the chemistry of silica, *i.e.*, it is known to be a very strong hydrogen bond acid and therefore should interact strongly with hydrogen bond bases. Basic solvents are known to be very strong displacing agents on silica.

In general, we prefer to deal with data sets in which there are a minimum of four or five data points per parameter, including the intercept. The paucity of solvents for which a set of $\varepsilon^0$ values is available on both silica and alumina is a real impediment to achieving precise regressions in this work, particularly as $\varepsilon^0$ values of the more polar solvents are certainly not more precise than $\pm 0.02$ units. Nonetheless, the regression results are reasonably robust, that is, the coefficients are insensitive to the data set within the standard deviation of the coefficients. This is shown most clearly in comparing the *s* and *b* coefficients in eqns. 9, 10 and 11. It is incorrect to compare the coefficients in eqns. 7 and 8 with those in eqns. 9, 10 and 11 as the models used in eqns. 7 and 8 are incomplete owing to the lack of a $\beta$ term and the inclusion of basic solvents in the data set.

## Alumina

A similar set of correlations were carried out for alumina. For all solvents:

$$\varepsilon^0_{\text{alumina}} = 0.11 \ (\pm 0.07) + 0.68(\pm 0.14) \ (\pi^* - 0.2\delta) \tag{12}$$

$$n = 23; \ r = 0.722; \ sd = 0.16$$

For just the select solvents:

$$\varepsilon^0_{\text{alumina}} = 0.11(\pm 0.05) + 0.65(\pm 0.11) \ (\pi^* - 0.2\delta) \tag{13}$$

$$n = 12; \ r = 0.882; \ sd = 0.10$$

For the same solvents including a $\beta$ dependence:

$$\varepsilon^0_{alumina} = 0.05(\pm0.03) + 0.57(\pm0.06)\,(\pi^* - 0.2\delta) + 0.30(\pm0.06)\beta \qquad (14)$$

$$n = 12;\, r = 0.967;\, sd = 0.06$$

The entire data set is examined incorporating $\pi^*$ and an HB acidity term instead of a HB basicity term:

$$\varepsilon^0_{alumina} = 0.11(\pm0.05) + 0.57(\pm0.11)\,(\pi^* - 0.2\delta) + 0.43(\pm0.10)\alpha \qquad (15)$$

$$n = 23;\, r = 0.860;\, sd = 0.12$$

There is a significant improvement in the goodness of the fit relative to the regression incorporating only $\pi^*$ term (eqn. 12). This indicates that the HB basicity of alumina is important. For the same solvents incorporating $\pi^*$ and a HB basicity term, the resulting regression equation is:

$$\varepsilon^0_{alumina} = 0.04(\pm0.04) + 0.55(\pm0.08)\,(\pi^* - 0.2\delta) + 0.45(\pm0.07)\beta \qquad (16)$$

$$n = 23;\, r = 0.919;\, sd = 0.09$$

There is also a significant improvement in the goodness of the fit relative to the regression incorporating only $\pi^*$ term (eqn. 12). This indicates that the HB acidity of alumina is important. For the regression including all three terms we obtain

$$\varepsilon^0_{alumina} = 0.06(\pm0.03) + 0.51(\pm0.06)\,(\pi^* - 0.2\delta) + 0.28(\pm0.06)\alpha + \\ + 0.37(\pm0.05)\beta \qquad (17)$$

$$n = 23;\, r = 0.961;\, sd = 0.07$$
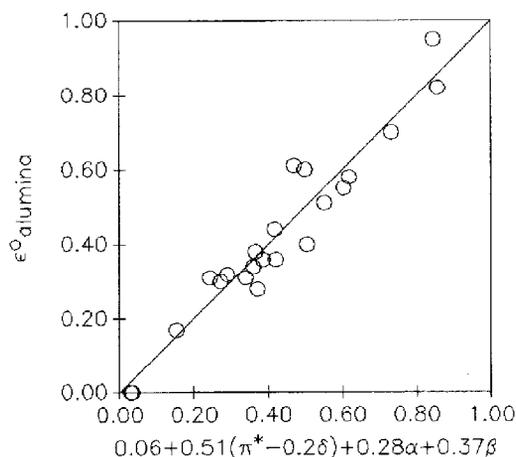


Fig. 3. Plot of $\varepsilon^0_{alumina,expt}$ vs. $\varepsilon^0_{alumin,calcd}$. Results calculated from eqn. 17.

The triple regression equation (eqn. 17) is an improvement over both eqns. 15 and 16 at the 99% confidence level according to the Ehrenson test[21]. The quality of the fit is demonstrated in Fig. 3. We again note that the intercept is small, as predicted from the $\pi^*$ value for $n$-pentane, and an increase in any of the solvatochromic parameters correctly leads to an increase in eluotropic strength.

Despite the poor robustness of the results on alumina, it is clear that a complete description of an alumina surface requires the presence of both an $\alpha$ and a $\beta$ term. We conclude that the surfaces of alumina and silica are acidic but alumina is a considerably stronger HB base than silica.

In this context it should be noted that previous discussions of the acid–base chemistry of these surfaces has focused primarily on their Brønsted acidity and basicity[23]. While there is often a parallelism between proton transfer strength and proton sharing strength, the relationships are by no means general. In some instances an inverse relationship exists. Further, there are enormous medium effects on Brønsted basicity such that a complete change in sequence of basicity between solution and gas phase process is common[24].

Many other correlations of $\varepsilon^0$ parameters with solvatochromic and non-solvatochromic parameters have been reported. Some time ago Keller and Snyder[25] showed the existence of a rough correlation between $\varepsilon^0$ for both alumina and silica and the Hildebrand solubility parameter of the solvent ($\delta_H$). Their correlations explained about only 65–70% of the variation in $\varepsilon^0$. As discussed in their paper, this results because the Hildebrand parameter is roughly proportional to the ability of the solvent molecule to interact with surrounding molecules of any type. An increase in $\delta_H$ would lead to an increase in the strength of a solvent's interaction with any neighboring molecule or surface group and therefore would be subject to preferential adsorption of materials with large $\delta_H$ values.

In our view this is not entirely correct. It is well known that the Hildebrand solubility parameter can be profitably subdivided into component parts. Karger *et al.*[5] expressed the total solubility parameter as the following sum of four distinct types of interactions:

$$\delta_H^2 = \delta_d^2 + \delta_0^2 + \delta_{in}\delta_d + \delta_a\delta_b \tag{18}$$

where the subscripts d, o, in, a and b denote dispersive, orientational, inductive, hydrogen bond acid and hydrogen bond base contributions, respectively. Karger *et al.*[5] reported a multi-variable regression of $\varepsilon^0$ for alumina *vs.* the expanded solubility parameters with a much improved correlation. We believe that the relative weightings of the contributions of the various physical processes represented in eqn. 18 probably differ depending on whether one is considering the total solubility parameter or the eluotropic strength. Although it is possible to arrive at measures of the component solubility parameters by various schemes, *e.g.*, based on the use of homologs[26], the solvatochromic methodologies which provide the values of $\pi^*$, $\alpha$ and $\beta$ are far more accurate measures of the relative dipolarity and hydrogen bonding properties. However, it should be mentioned that Karger *et al.*[5] reported a fairly good correlation of $\varepsilon^0$ for alumina with the component solubility parameters of solvents.

We opted not to include any correlations between $\varepsilon^0$, $\delta_H$ and the solvatochromic parameters here because $\delta_H$ is strongly correlated by a multi-variable equation with the

solvatochromic parameters, $\pi^*$ and $\alpha$. Inclusion of two strongly correlated explanatory parameters in a regression must lead to variance inflation and can generate regression coefficients which are entirely deceptive.

Finally, we must mention that Krygowski et al.[27] reported a multi-variable regression of $\varepsilon^0$ for alumina vs. the normalized $E_T(30)$ parameter of Dimroth and Reichardt[28] and a modified $\beta$ parameter. We do not report related correlations here for the same reason as stated above, ie., $E_T$ is demonstrably very strongly correlated with a linear combination of $\pi^*$ and $\alpha$, so it is not truly a measure of a single specific solvent characteristic.

The above results focus on interpreting the solvent strength parameter on very polar adsorbents in order to understand the surface chemistry better. We can, of course, gain an insight into the chemical factors which control intermolecular interactions by examining solute retention processes. This approach is very similar to that used in our previously reported studies of reversed-phase liquid chromatography[16]. Further, the $\varepsilon^0$ parameter is actually the energy of adsorption per unit area occupied (see eqn. 2), whereas the solute parameter ($S^0$) is an adsorption energy parameter per se. Snyder[2] showed that $S^0$ results from the sum of the interactions between all of the functional groups ($i$) in a solute molecule with the surface and presented an extensive set of group interaction parameters ($Q_i$):

$$S^0 = \Sigma Q_i \tag{19}$$

His values of $Q_i$ were arrived at by averaging over data obtained with many different solutes, so in general $Q_i$ values are likely to be more reliable than a set of $S^0$ values for a series of solutes under one set of mobile phase conditions. In order to be specific we have generated a data set for a group of solutes on both alumina and silica using at least one compound for each functional group in Snyder's compilations[2]. These data, together with the appropriate solvatochromic parameters, are presented in Table II. In all instances the solvatochromic parameters are for the monomer form of the solute. In general $\alpha_m = \alpha$ and $\beta_m = \beta$, except for those compounds which self-associate in the pure liquid phase[18]. Although the database is overwhelmingly aromatic and polyhalogenated materials are not represented, the primary goal of this study was to examine the relative hydrogen bond acidity and basicity of silica and alumina. Addition of aliphatic and halogenated materials would be of little value.

As in previous solute studies[16,17], we found that the molar volume ($V_2$) must be included in the regression equation to obtain satisfactory correlations (see below). The following regression results were obtained:

$$S^0_{\text{alumina}} = -1.21(\pm 0.43) + 1.51(\pm 0.32)V_2/100 + 4.59(\pm 0.45)\pi^* + \\ + 8.22(\pm 0.68)\alpha_2 + 5.82(\pm 0.58)\beta_2 \tag{20}$$

$$n = 31; r = 0.993; sd = 0.27$$

$$S^0_{\text{silica}} = -1.06(\pm 0.58) + 0.95(\pm 0.43)V_2/100 + 3.96(\pm 0.61)\pi^* + \\ + 3.04(\pm 0.92)\alpha_2 + 8.05(\pm 0.78)\beta_2 \tag{21}$$

$$n = 31; r = 0.987; sd = 0.36$$

TABLE II

SOLUTE PARAMETERS FOR STUDY OF LIQUID–SOLID CHROMATOGRAPHY

| Solute | $S^0_{alumina}$ | $S^0_{silica}$ | $V_2/100$ | $\pi^*_m$ | $\alpha_m$ | $\beta_m$ |
|---|---|---|---|---|---|---|
| Benzene | 1.86 | 1.50 | 0.989 | 0.59 | 0 | 0.1 |
| Toluene | 1.92 | 1.61 | 1.163 | 0.54 | 0 | 0.11 |
| Ethylbenzene | 1.90 | 1.58 | 1.324 | 0.48 | 0 | 0.12 |
| Propylbenzene | 1.92 | 1.53 | 1.494 | 0.44 | 0 | 0.12 |
| Butylbenzene | 1.94 | 1.48 | 1.661 | 0.42 | 0 | 0.12 |
| tert.-Butylbenzene | 1.94 | 1.72 | 1.649 | 0.42 | 0 | 0.12 |
| m-Xylene | 1.98 | 1.72 | 1.328 | 0.47 | 0 | 0.13 |
| p-Xylene | 1.98 | 1.72 | 1.333 | 0.43 | 0 | 0.12 |
| Fluorobenzene | 1.97 | 1.35 | 1.039 | 0.62 | 0 | 0.07 |
| Bromobenzene | 2.19 | 1.33 | 1.150 | 0.79 | 0 | 0.06 |
| Chlorobenzene | 2.06 | 1.30 | 1.118 | 0.71 | 0 | 0.07 |
| Methoxybenzene | 3.60 | 3.40 | 1.186 | 0.73 | 0 | 0.22 |
| Ethoxybenzene | 3.62 | 3.41 | 1.364 | 0.69 | 0 | 0.30 |
| n-Propoxybenzene | 3.64 | 3.42 | 1.524 | 0.65 | 0 | 0.32 |
| Benzonitrile | 5.11 | 4.83 | 1.120 | 0.90 | 0 | 0.36 |
| Benzyl cyanide | 6.93 | 6.78 | 1.253 | 0.75 | 0 | 0.48 |
| 4-Methylbenzonitrile | 5.13 | 4.91 | 1.294 | 0.85 | 0 | 0.35 |
| Ethyl benzoate | 5.25 | 4.97 | 1.530 | 0.74 | 0 | 0.41 |
| Methyl benzoate | 5.23 | 5.02 | 1.351 | 0.76 | 0 | 0.39 |
| Benzyl acetate | 6.90 | 6.85 | 1.524 | 0.53 | 0 | 0.54 |
| Ethyl acetate | 4.96 | 5.36 | 0.978 | 0.55 | 0 | 0.45 |
| Ethyl propionate | 4.98 | 5.31 | 1.146 | 0.47 | 0 | 0.42 |
| Acetophenone | 5.57 | 6.26 | 1.269 | 0.90 | 0 | 0.48 |
| Ethyl phenyl ketone | 5.59 | 6.21 | 1.429 | 0.88 | 0 | 0.43 |
| Benzyl alcohol | 8.43 | 7.11 | 1.138 | 0.45 | 0.33 | 0.55 |
| 1-Propen-3-ol | 7.14 | 6.05 | 0.680 | 0.45 | 0.33 | 0.45 |
| 1-Phenylpropen-3-ol | 9.00 | 7.55 | 1.385 | 0.45 | 0.33 | 0.55 |
| Nitrobenzene | 4.61 | 4.27 | 1.129 | 1.01 | 0 | 0.25 |
| o-Nitrotoluene | 4.65 | 4.37 | 1.279 | 0.90 | 0 | 0.25 |
| Nitropropane | 5.41 | 5.68 | 0.896 | 0.75 | 0 | 0.25 |
| Benzaldehyde | 5.21 | 4.98 | 1.116 | 0.92 | 0 | 0.44 |

The results for all solutes and the input data are shown in Figs. 4 and 5. The necessity to include the molar volume dependence and the accuracy of the coefficients recovered by the regression can be checked to a limited extent by estimating the $S^0$ value of n-pentane ($V_2 = 115$ cm$^3$/mole, $\pi^* = -0.087$), which is defined as zero. The two regression equations lead to estimates of $S^0$ for n-pentane of 0.13 and $-0.19$ for alumina and silica, respectively. Given the standard deviations in the intercept, these are acceptable. In view of the fact that no solute for which $S^0$ is less than 1.3 is included for either adsorbent, the extrapolation involved is impressively accurate. Of course, this does not address the reliability of the hydrogen bonding terms, as $\alpha$ and $\beta$ are zero for n-alkanes.

The signs of all regression coefficients are as expected (see below for a discussion of the $V_2$ term), that is, as in the study of $\varepsilon^0$ an increase in $\pi^*$, $\alpha$ and $\beta$ increases $S^0$. In agreement with the study of $\varepsilon^0$, the coefficients of $\pi^*$ are similar for both adsorbents, so both are equally effective in retaining dipolar materials. The precision of the hydrogen
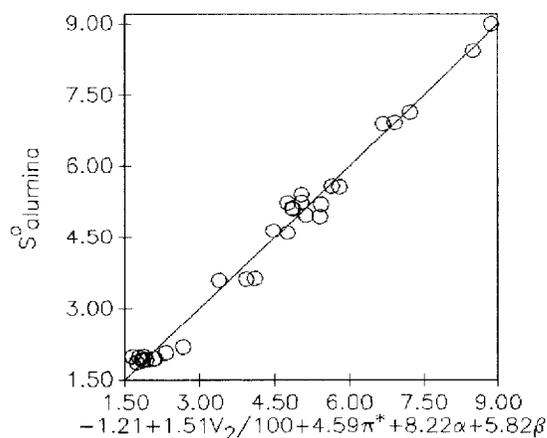
Fig. 4. Plot of $S^0_{\text{alumina,expt}}$ vs. $S^0_{\text{alumina,calcd}}$. Results calculated from eqn. 20.

bonding terms is good enough for us to state that alumina is decidedly more basic than silica ($a_{\text{alumina}} = 8.2$ vs. $a_{\text{silica}} = 3.0$), whereas silica is definitely more acidic than alumina ($b_{\text{silica}} = 8.0$ vs. $b_{\text{alumina}} = 5.8$). As no Brønsted acids or bases were included in the data sets, the basicity and acidity refer specifically to hydrogen bond interactions. From these results we may infer the practically sigificant result that silica will be a more selective adsorbent for the separation of materials which differ in their hydrogen bond basicity whereas alumina will be better able to discriminate between hydrogen bond acids. The above is predicted from the idea that the two solutes differ only in their hydrogen bond basicity. In practice, a change in a substituent alters all three of the solvatochromic parameters ($\pi^*$, $\alpha$ and $\beta$) and it is therefore not possible to predict whether silica or alumina will be more selective for a particular separation. We do believe that it is safe to say that if the two solutes have a significant difference in $\beta$ (0.2–0.3) then silica will produce a greater chromatographic selectivity.
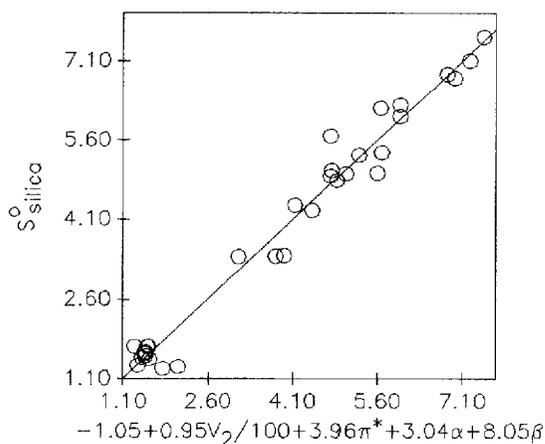


Fig. 5. Plot of $S^0_{\text{silica,expt}}$ vs. $S^0_{\text{silica,cald}}$. Results calculated from eqn. 21.

As a cautionary note, we point out that alumina manifests decidedly superior selectivity towards polynuclear aromatic solutes than does silica[29]. These solutes differ in their Lewis basicity, that is, in terms of the "soft" basicity, whereas hydrogen bond interactions are considered to be "hard" processes[30]. It is well known that normal-phase chromatography on solid surfaces such as silica and alumina is much more sensitive to solute structure than is liquid–liquid partition chromatography[1]. As Snyder[31] pointed out, alumina has a highly crystalline surface and consequently it has a high selectivity for linear molecules. It may be that the aromatic selectivity of alumina results from a combination of its Lewis acidity and its ordered surface.

The above regression equations can be compared with those obtained in many other studies. Before doing so, some comment on the term containing $V_2$ must be made. As expected, we found no necessity to incorporate a cavity term in analyzing the values of $\varepsilon^0$ as it is a pure solvent parameter. It seems that the cavity term is compensated for by the displaced solvent which forces the formation of a cavity of the same size, that is, it cancels out. In all previous solute studies we invariably needed a solute parameter which complements the measure of cavity formation energy in the solvent. As described, the displacement model of normal-phase chromatography neglects mobile phase solute–solvent interactions at the first level of analysis. Why, then, is the term $V_2$ required? In comparison with other studies, the magnitude of the coefficient of this term is much less important. For the present purpose we believe that this term crudely approximates an increase in dispersive interactions between the adsorbent and the solute as the solutes increase in size and hence polarizability[19]. Dipole–dipole and dipole–induced dipole interactions are reflected in the $\pi^*$ term.

In comparison with reversed-phase chromatography, the hydrogen bond acidity of the solute is important, as is its dipolarity. Hence the prediction of the retention of solutes in normal-phase chromatography will require far more accurate information than in reversed-phase chromatography, where a knowledge of solute size and hydrogen bond basicity suffices.

CONCLUSION

Based on the studies of $\varepsilon^0$ and $S^0$, alumina and silica are concluded to be similarly dipolar and both are reasonably strong hydrogen bond acids, silica being the stronger. In contrast, alumina is definitely a stronger hydrogen bond base than silica.

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