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SOLVENT STRENGTH OF MULTICOMPONENT MOBILE PHASES IN LIQUID–SOLID CHROMATOGRAPHY

BINARY-SOLVENT MIXTURES AND SOLVENT LOCALIZATION

L. R. SNYDER*
Technicon Instruments Corp., Tarrytown, NY 10591 (U.S.A.)
and
J. L. GLAJCH
Central Research and Development Department, E. I. du Pont de Nemours and Company, Wilmington, DE 19898 (U.S.A.)

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SUMMARY

The displacement model for the prediction of solvent strength in liquid–solid chromatography (LSC) has been summarized for the case of binary-solvent mobile phases. It is confirmed that a number of prior anomalies can be explained by the phenomenon of "solvent localization". Taking solvent localization into account leads to a simple, non-empirical procedure for the more accurate calculation of solvent strength. Application of this approach to literature data for silica and alumina as adsorbent shows agreement between calculated and experimental solvent strength values (ε^0) of 0.017 (1 standard deviation) for 93 binary-solvent mobile phases covering a range in solvent strength of $0.02 < \varepsilon^0 < 0.66$ ($r = 0.994$).

This means that more accurate predictions of solvent strength are now possible for binary-solvent LSC systems, for use in optimizing the separation of various samples. The only experimental system showing lack of correlation with the present model is isopropanol–pentane as mobile phase with alumina as adsorbent. It is believed that the behavior of alcohol solutions is more complex than can be described by the simple displacement model. Apart from the alcohols as mobile phases, however, the present study provides further verification of the physical correctness of the displacement model for mobile phases containing polar solvents.

INTRODUCTION

The choice of mobile phase in liquid–solid chromatography (LSC) is governed mainly by two considerations: (1) the need to maintain solute capacity factors k' within an optimum range of roughly $1 \leqslant k' \leqslant 5$; (2) the requirement that all adjacent bands have adequate separation factors α (*e.g.*, ref. 1). Optimum k' values are achieved by controlling the solvent strength ε^0 of the mobile phase, which usually involves varying the proportions of a weak solvent A and a strong solvent B in a binary-solvent mobile phase. Adequate α values are usually achieved by changing the B-solvent, *e.g.*, chloroform, methylene chloride. When a new B-solvent is selected, it is required to reoptimize the proportions of A- and B-solvents so as to maintain the correct solvent strength. This procedure is facilitated if it is possible to calculate ε^0 values for the mobile phase as a function of mobile phase composition. For a full discussion of this general approach to separation optimization, see ref. 1.

More recently (*e.g.*, refs. 2 and 3) there has been increased emphasis on the use of more complex mobile phases, for better "fine-tuning" of α values for samples that contain several components within a small range of k' values. Thus, the use of three-component (A–B–C) and four-component (A–B–C–D) mobile phases allows additional opportunities for optimizing the spacing of sample bands within a chromatogram. With such mobile phases it is possible to explore systematically mobile phase selectivity (α values) within the "selectivity triangle" described in ref. 4, while holding solvent strength constant (and optimum). This approach has already been illustrated for separations by reversed-phase chromatography[3], and the similar optimization of the mobile phase for LSC separation will be examined in following papers[5,6].

One approach to the prediction of solvent strength (ε^0) values in LSC has been described in refs. 7 and 8, for one- or two-component mobile phases. Other approaches for the prediction of binary-solvent mobile phase strength have been described by Soczewinski[9], Scott and Kucera[10], Jaroniec and Piotrowska[11], and Rozylo and co-workers[12,13].

The approaches taken by Soczewinski and by Scott and Kucera represent special cases of the more general treatment of Snyder[7], as discussed in refs. 8 and 14. In these studies the equations proposed for the solvent strength of a two-component mobile phase are derivable from the more general equations of ref. 7, but are limited to the case where the mole fraction of B-solvent in the mobile phase $N_B \gg 0$. The model used by the Polish workers[11–13] is more detailed than that of Snyder[7], in that certain physico-chemical effects are included to avoid approximations used in the treatment of Snyder. However, this approach is more complicated to use, and its value for practical predictions of solvent strength remains to be evaluated relative to the procedures described in ref. 7 and here.

In the present work we review the treatment of ref. 1 for predicting the solvent strength of binary mobile phases. More importantly, we propose approaches to improve these calculations for greater accuracy. The present work also provides further insight into the role of the mobile phase in affecting sample retention in LSC. In a following paper[15] we will extend the present approach to include the case of mobile phases that contain three or more solvent constituents.

THEORY

The first-approximation Snyder model

The treatment of Snyder[7] gives the effect of mobile phase composition on solute retention as:

$$\log (k_1/k_2) = \alpha' A_s (\varepsilon_2 - \varepsilon_1) \qquad (1)$$

Here, k_1 and k_2 refer to capacity factor values for a solute when using solvents 1 and 2, respectively, as mobile phases, ε_1 and ε_2 are solvent strength values (ε^0) for solvents 1 and 2 (which can be either pure or mixed solvents), A_s is the relative molecular area of the solute (area required by the solute when adsorbed onto the adsorbent surface) and α' is an adsorbent activity function (related to the ability of the adsorbent to interact with adjacent molecules of solute or solvent). The solvent strength ε_{AB} of a binary-solvent mobile phase can be related to the mole fraction of the stronger solvent B (N_B) in the mobile phase, the ε^0 values of the two pure solvents which constitute the mobile phase (ε_A and ε_B), and the area n_b required by a molecule of B-solvent on the adsorbent surface:

$$\varepsilon_{AB} = \varepsilon_A + \log \frac{(N_B 10^{\alpha' n_b(\varepsilon_B - \varepsilon_A)} + 1 - N_B)}{\alpha' \, n_b} \tag{2}$$

It is useful to review first the derivation of eqn. 2. It is assumed that the molecular areas of the two solvent components A and B are roughly equal, so that the adsorption equilibrium can be written as:

$$B_n + A_a \rightleftharpoons B_a + A_n \tag{3}$$

That is, adsorption of a molecule of B from the non-sorbed (mobile) phase, B_n, occurs by displacing one molecule of A (A_a) from the adsorbed (stationary) phase. Subscripts n and a refer here and elsewhere to non-sorbed and adsorbed phases, respectively. If the mole fractions of A and B in the mobile phases are N_A and N_B, respectively, and if the mole fractions in the stationary phase are θ_A and θ_B, then the equilibrium constant K for eqn. 3 is:

$$K = \theta_B \, N_A / \theta_A \, N_B \tag{4}$$

Eqn. 4 gives for θ_A and θ_B:

$$\theta_A = N_A/(N_A + KN_B) \tag{4a}$$

$$\theta_B = KN_B/(N_A + KN_B) \tag{4b}$$

The dimensionless free energy of adsorption of B (eqn. 3) is given as $\Delta E = -\Delta G^0/RT$ (R is the gas constant, and T is absolute temperature). This allows the derivation for K:

$$K = 10^{\Delta E} \tag{5}$$

The free energy ΔE can be related[7] to the molecular area of solvent B (n_b), and the dimensionless free energies of adsorption of solvents A and B from pentane (or hexane, isooctane, etc.) per unit area of adsorbent surface: $\alpha'\varepsilon_A$ and $\alpha'\varepsilon_B$:

$$\Delta E = \alpha' \, n_b \, (\varepsilon_B - \varepsilon_A) \tag{5a}$$

and

$$K = 10^{\alpha' n_b(\varepsilon_B - \varepsilon_A)} \tag{5b}$$

The solvent strength ε_{AB} of a solvent-binary A–B can be related to the capacity factor values k' of some solute in that mobile phase (k_{AB}) and in pure solvent A (k_A); see eqn. 1:

$$\varepsilon_{AB} = \varepsilon_A + \left(\frac{\log (k_A/k_{AB})}{\alpha' \ A_s}\right) \tag{6}$$

The quantity A_s, which is the molecular area of the solute, can have any value, so let it equal n_b:

$$\varepsilon_{AB} = \varepsilon_A + \left(\frac{\log (k_A/k_{AB})}{\alpha' \ n_b}\right) \tag{6a}$$

It is assumed that solution interactions between solvent and/or solute molecules are cancelled by corresponding interactions in the stationary phase. Therefore, the adsorption of solute can be visualized as occurring within separate surface regions covered by A (θ_A) or B (θ_B). If the solute k' values in pure solvents A and B are k_A and k_B, then k_{AB} will be given as:

$$k_{AB} = k_A \ \theta_A + k_B \ \theta_B \tag{7}$$

An expression similar to eqn. 6a is then given by:

$$\varepsilon_B = \varepsilon_A + \left(\frac{\log (k_A/k_B)}{\alpha' \ n_b}\right) \tag{7a}$$

which with eqn. 5b yields

$$k_A = Kk_B \tag{7b}$$

Eliminating k_B between eqns. 7 and 7b, followed by insertion of expressions for θ_A and θ_B (eqns. 4a, 4b) then gives

$$k_A/k_{AB} = N_A + KN_B \tag{7c}$$

Combining eqns. 6a and 1c gives the final expression for ε_{AB}:

$$\varepsilon_{AB} = [\log (KN_B + N_A)/\alpha' \ n_b] + \varepsilon_A \tag{8}$$

Insertion of eqn. 5b for K, and $(1 - N_B)$ for N_a, into eqn. 8 yields eqn. 2.

Eqn. 2 has been verified for a wide range of binary-solvent compositions, using data for alumina and silica, as summarized in Table I. These prior correlations of the data of Table I with eqn. 2 have assumed a constant (fixed) value of ε_B for each B-solvent.

TABLE I

SUMMARY OF BINARY-SOLVENT MOBILE-PHASE-STRENGTH DATA FOR LSC ON WATER-DEACTIVATED ALUMINA OR SILICA

Correlation of experimental ε^0 values with values calculated from eqn. 2. A-solvent is *n*.pentane.

No.	*B-solvent*	*Adsorbent*	*Binary composition (%, v/v, B)*	ε^0		n_b	n^*	*S.D.***	*Ref.*
				ε''_B	ε'_B				
1	Carbon tetrachloride	Alumina	5, 10, 25, 50, 100	0.17	0.17	5.0	5	0.007	16
2	Toluene	Alumina	30	0.30	0.30	6.8	1	–	18
3	1-Chloropropane	Alumina	10, 25, 50, 100	0.31	0.31	3.8	4	0.010	17
4	2-Chloropropane	Alumina	35, 60	0.31	0.31	3.8	2	–	18
5	Benzene	Alumina	1.5, 5, 15, 28, 30 50, 70, 80, 100	0.32	0.32	6.0	10	0.018	16, 18
		Silica	10, 25, 50, 100	0.25	0.25	6.0	4	0.001	19
6	Chlorobenzene	Alumina	30	0.31	0.31	6.7	1	–	18
7	Bromoethane	Alumina	40	0.34	0.34	3.8	1	–	18
8	Chloroform	Alumina	15, 30	0.36	0.36	5.0	2	–	18
9	Methylene chloride	Alumina	5, 10, 13, 23, 25, 35, 50, 60, 70, 100	0.40	0.40	4.1	11	0.027	16, 18
		Silica	5, 15, 40, 100	0.30	0.30	4.1	4	0.013	19
10	Isopropyl ether	Alumina	10, 25, 50, 100	0.28	0.31	5.1	4	0.006	17
11	Triethyl amine	Alumina	5	0.36***	0.85***	6.2	1	–	18
12	Ethyl ether	Alumina	2, 5, 9, 12, 19, 23, 29, 43, 61	0.38	0.50	4.5	11	0.025	17, 18
		Silica	2, 5, 15, 30, 60	0.43	0.78	4.5	5	0.008	20
13	Ethyl sulfide	Alumina	8, 10, 15, 30	0.39	0.43	5.0	4	0.015	17, 18
14	1,2-Dichloroethane	Alumina	15	0.44***	0.47***	4.8	1	–	18
15	Tetrahydrofuran	Alumina	2, 5	0.51	0.76	5.0	2	–	18
16	Acetonitrile	Alumina	0.1, 0.14, 0.3, 0.4, 0.6, 0.7	0.55	1.31	3.1	6	0.003	18
		Silica	5	0.6***	1.0***	3.1	1	–	20
17	Acetone	Alumina	0.2, 0.4, 0.6 0.8, 25, 50	0.58	1.01	4.2	6	0.005	17, 18
		Silica	5	0.5***	1.1***	4.2	1	–	20
18	Ethyl acetate	Alumina	1, 4, 100	0.60	0.77	5.2	3	0.007	17, 18
		Silica	5, 15, 30	0.48	0.94	5.2	3	0.010	20
19	Dioxane	Alumina	10, 25, 50, 100	0.61	0.79[§]	6.0	4	0.014	16
		Silica	5	0.6***	0.9***	6.0	1	–	20
20	Pyridine	Alumina	0.4, 1.4, 10, 25, 50	0.70	0.95	5.8	6	0.019	17
21	Diethyl amine	Alumina	5, 20, 50	0.71	1.8***	4.0	3	0.020	17

* Number of different binary compositions.

** Standard deviation of experimental ε^0 values *vs.* values from eqn. 2.

*** Approximate value, usually involving only one experimental value of ε_{AB}.

[§] Value from ternary solution[15].

Deviations from eqns. 1 and 2

In practice it is found that eqns. 1 and 2 are most reliable for less polar solvent and solute molecules, and ideally values of ε^0 or ε_{AB} will be measured for aromatic hydrocarbon solutes. The reasons for experimental deviation from eqn. 1 and/or 2 fall into two categories that have been discussed earlier[7,8,18]. First, hydrogen-bonding interactions between solute and solvent molecules in the adsorbed phase lead to so-called secondary-solvent effects. These give rise to an additional contribution to solute retention that must be corrected for in predicting the effect of different mobile phases on solute retention. At present it is possible to anticipate such effects and to use them for improving separation selectivity in LSC[1]. Work by us is underway to describe their quantitative prediction for silica as adsorbent and various solvents as mobile phase.

A second reason for experimental deviation from eqns. 1 and 2 is due to so-called localization of solvent and/or solute molecules in the adsorbed phase[7,14,18]. When an adsorbing molecule X (*e.g.*, CH_3CN) has a strongly polar substituent group within the molecule (*e.g.*, –CN), that polar group will attempt to adsorb directly on top of a corresponding polar adsorption site on the adsorbent surface (*e.g.*, –SiOH for silica). To the extent that such localization is possible, the energy of adsorption of X will be correspondingly increased. When both solute and solvent molecules compete for localized adsorption on the same surface sites, the relative adsorption of the solute will be decreased compared to the case of a non-localizing solvent or mobile phase. This effect gives rise to significant changes in solute retention that are not predicted by eqns. 1 and 2. However, as shown in ref. 18 for alumina, and will be further detailed in future work for silica, it is possible to predict these secondary retention effects with considerable precision.

An important further consequence of solvent localization is change in the apparent solvent ε_B value with change in θ_B. Thus localization of the B-solvent is possible, as long as $\theta_B < 0.75$ (see following section). For larger values of θ_B (corresponding to larger values of N_B for the mobile phase), however, the coverage of the remaining surface by B (as θ_B and $N_B \rightarrow 1$) must involve delocalized B-molecules (see discussion of Fig. 4 in ref. 14). That is, once most of the surface is covered by localized B-molecules, the remaining spaces on the surface are not able to accomodate B-molecules in the configuration and positioning required for the localization effect. Since the apparent solvent strength ε_B is directly related to the adsorption energy of B, and since this energy is less for delocalized molecules of B, the value of ε_B must therefore decrease when θ_B exceeds a certain value (about 0.75, as discussed later). This effect results in a failure of eqn. 2, if the value of ε_B is assumed constant for all values of N_B.

It is possible to correct empirically for this effect by assuming that n_b is larger than its true value calculated from the molecular dimensions of B[7,17,20]. However, a more fundamental approach to account for solvent localization is preferred, so as to be more reliable when a broad range of possible solvent compositions are considered. This is particularly true for the case of three- and four-solvent mobile phases which are discussed in the following paper[15]. Solvents which exhibit localization effects are also listed in Table I[10–21]; two values of ε_B are given in this instance: the value for large N_B (ε_B'') which usually applies over most of the A–B compositional range, and the value at small N_B (ε_B') where solvent localization takes place. For intermediate values of N_B, $\varepsilon_B'' < \varepsilon_B < \varepsilon_B'$.

Before further considering solvent localization as exemplified by the data cited in Table I, it should be noted when solvent localization is likely to be observed. First, localization is determined mainly by the polarity or adsorption energy Q_k^0 of the most strongly adsorbing functional group k within the solvent molecule. A function $f(Q_k^0)$

has been previously derived for application to localizing solvents (see Fig. 7 of ref. 17). The larger is Q_k^0 and f(Q_k^0), the greater is the possible localization of a solvent or solute. Therefore, solvent localization is observed only for stronger solvents with $\varepsilon_B > 0.3$. Second, solvent localization will be less important for the case of multifunctional B-molecules, *e.g.*, dioxane, pyridine. The reason is that such molecules have more than one polar or interacting functional group in the molecule, which generally precludes the simultaneous localization of both groups on two or more adsorbent sites (exact matching of the positions of surface and solvent groups is *a priori* unlikely). Also, groups k with a single heteroatom (*e.g.*, –O–, C=O) will be more strongly localized than multi-atomic groups k (*e.g.*, $-CO_2-$, $-NO_2$) for the same reason: difficulty in exact matching of positions of atoms in the B-molecule and surface. Finally, solvent localization occurs mainly at low values of N_B.

A fundamental model for solvent localization

As a first example of solvent delocalization which affects ε_{AB}, consider the data of Table II for acetonitrile(B)/pentane(A) as mobile phase. The second column of Table II lists experimental values of ε_{AB} for different values of N_B [or % (v/v) B].

TABLE II

SOLVENT LOCALIZATION AND SOLVENT STRENGTH

Acetonitrile–pentane as mobile phase, alumina (25% humidity) adsorbent[19].

Acetonitrile (%, v/v)	ε_{AB}				ε_B[§]	θ_B	$\%_{lc}$
	Expt.	*Calc.**	*Calc.***	*Calc.****			
0.0	0.000	0.000	0.000	0.000	(1.3)	0.000	(100)
0.1	0.122	0.009	0.122	0.115	1.28	0.41	97
0.14	0.146	0.012	0.146	0.138	1.26	0.47	94
0.3	0.208	0.026	0.204	0.204	1.20	0.59	85
0.4	0.235	0.034	0.228	0.219	1.18	0.64	82
0.6	0.253	0.049	0.262	0.248	1.11	0.66	71
0.7	0.263	0.056	0.274	0.260	1.09	0.68	68
100	0.65	0.65	0.65	0.65	0.65[§§]	1.00	0

* Eqn. 1, $n_b = 3.1$, $\varepsilon_B = 0.65$ (constant), $\varepsilon_A = 0.00$[7].

** Eqn. 1, $n_b = 7.6$, $\varepsilon_B = 0.65$ (constant), $\varepsilon_A = 0.00$.

*** Eqn. 1, $n_b = 3.1$, ε_B from eqn. 9 ($\varepsilon'_B = 1.3$, $\varepsilon''_B = 0.65$), $\varepsilon_A = 0.00$.

[§] Calculated from experimental ε_{AB} values and eqn. 2, with $n_b = 3.1$.

[§§] Value from ref. 7; present study suggests ε_B at large $N_B = 0.55$, but this is approximate because of extrapolation from large $\%_{lc}$ values (0.73–0.96) to a value of $\%_{lc} = 0$.

Using the ε_B value for pure B (0.65) it is possible from eqn. 2 and a calculated value of n_b (3.1) to calculate ε_{AB} values for these solutions. These values in column 3 show poor agreement with experimental values, being generally much smaller than the values of column 2. If n_b is artificially increased to a value of 7.6 (more than twice the actual value of 3.1), good agreement between calculated values (column 4) and experimental values results. The application of eqn. 2 to the experimental values of Table II allows us to calculate values of ε_B for each solvent composition ($n_b = 3.1$) and results in the data of column 6. These values are seen to vary from 1.31 for $N_B = 0.0$ to 0.65 for $N_B = 1.00$. The corresponding values of θ_B for each mobile phase can be calculated from eqns. 4 and 5. These values of θ_B are listed in the next-to-last column of Table II.

From Table II the localized-solvent value of ε_B (equal to ε'_B) for acetonitrile can be estimated to be 1.31 (by extrapolation to $N_B = 0$), and the delocalized value (ε'_B) for $\theta_B = 1.0$ is 0.65. The percent-localization $\%_{olc}$ for intermediate values of θ_B can be defined as:

$$\%_{olc} = (\varepsilon_B - \varepsilon''_B)/(\varepsilon'_B - \varepsilon''_B) \qquad (9)$$

and this function is plotted *vs.* θ_B in Fig. 1. Also shown in Fig. 1 are additional data for other B-solvents and for silica as well as alumina. These data fall close to a single curve, shown as the solid line; and $\%_{olc}$ is 50% for a value of θ_B (0.78) that is close to $\theta_B = 0.75$ (dashed vertical line in Fig. 1). That is, for $\theta_B < 0.75$, the B-solvent is largely localized, while for larger values of θ_B the B-solvent is mainly delocalized.

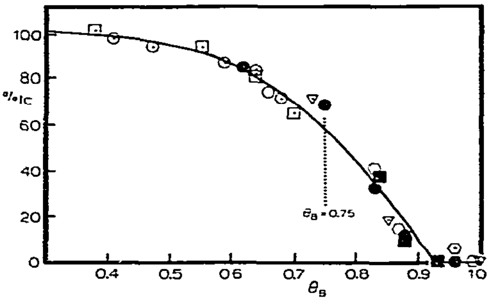

Fig. 1. Experimental values of the solvent-localization-function $\%_{olc}$ as a function of solvent mole fraction in the adsorbed phase θ_B, for class P solvents admixed with pentane. Alumina: ○, acetonitrile; □, acetone; ▽, ethyl acetate; ○, pyridine. Silica: ●, diethyl ether; ■, ethyl acetate.

The form of the solid curve of Fig. 1 appears conceptually reasonable. Thus, the data of ref. 21 for ethyl acetate–pentane and silica as adsorbent show that the completely localized B-solvent layer (ethyl acetate) occupies 0.097 g/g (the authors refer to this as the "first monolayer"; see discussion of ref. 14). Extrapolation of the isotherm data to $N_B = 1.0$ (Table III of ref. 14) gives a total monolayer uptake of 0.13 g/g, *i.e.*, the localized layer equals 75% of the total layer. From this, it is expected that the solvent will be mainly localized for $\theta_B < 0.75$, and mainly delocalized for $\theta_B > 0.75$, just as indicated in Fig. 1.

The use of the data of Fig. 1 is facilitated if the solid curve is expressed as a function of θ_B. By curve-fitting techniques, the empirical expression

$$\%_{olc} = (1 - \theta_B)\,[1/(1 - 0.94\,\theta_B) - 14.5\,\theta_B{}^9] \qquad (10)$$

was derived (least squares fit to the experimental data). Although this equation has no theoretical basis, it is a good approximation for calculating ε^0 values as in Appendix II. An estimate can be made of the fit of eqn. 10 to the experimental data of Fig. 1. A standard deviation (S.D.) of 6% is found, with 5% of this due to the scatter in the experimental data and 1% from statistical uncertainty in the coefficients of eqn. 10. Considering the variety of studies over 15 years[16–20] used to generate the data in Fig. 1, eqn. 10 appears to possess general applicability.

CALCULATION OF MOBILE PHASE ε_{AB} VALUES AND THE FURTHER VALIDATION OF THE SOLVENT-LOCALIZATION MODEL

Data of Table I

The solvent-localization model can be tested for the other B-solvents listed in Table I. The data used in Fig. 1 are for reported studies where several data points were available for each binary-solvent mobile phase. In most cases these data refer to the aromatic hydrocarbon solutes, so that solvent–solute hydrogen bonding and solute-localization effects are largely avoided as potential experimental complications. The data of Fig. 1 are also limited to systems where ε'_B is at least 0.15 units larger than ε''_B, since experimental values of $\%_{olc}$ are then measured more accurately. However, significant deviations in $\%_{olc}$ from the values of Fig. 1 have only a small effect on the accuracy of resulting ε_{AB} values from eqn. 2, when $(\varepsilon'_B - \varepsilon''_B) < 0.15$.

Having defined $\%_{olc}$ *vs.* θ_B as in Fig. 1, Table III or eqn. 10, it is possible to determine ε'_B and ε''_B, values for other B-solvents from this relationship. Only two experimental ε_{AB} values are required as measured for different values of N_B, preferably with a large difference in the corresponding values of $\%_{olc}$. Appendix I illustrates such a calculation for the solvent tetrahydrofuran with alumina as adsorbent.

TABLE III

SOLVENT DELOCALIZATION FUNCTION $\%_{olc}$ *VS.* θ_B

θ_B	$\%_{olc}$*
0.00	1.00
0.3	0.97
0.4	0.96
0.5	0.93
0.55	0.90
0.6	0.86
0.65	0.79
0.7	0.70
0.75	0.57
0.8	0.42
0.85	0.24
0.9	0.09
0.95	0.01
1.00	0.00

* Calculated using eqn. 10.

For those solvents of Table I where accurate values of ε'_B and ε''_B, can be determined (*i.e.*, $n \geqslant 2$), it is possible in turn to calculate values of ε_{AB} for any value of N_B, as described in Appendix II. Table I lists the resulting accuracy of such calculated values as the S.D. between experimental and calculated values for a given B-solvent. For the 93 different mobile phases in Table I for which accurate values of ε'_B and ε''_B, are known, the overall accuracy of calculated values of ε_{AB} is ± 0.017 units (1 S.D.). These 93 mobile phases comprise 13 different B-solvents and two adsorbents. Two or more individual retention measurements (values of k') were usually used for the determination of a given value of ε_{AB} from eqn. 1, so that the final correlation of the data in Table I involves several hundred different retention measurements. Since the range of experimental ε_{AB} values represented in Table I is 0.02–0.66, this overall accuracy further confirms the correctness of the model assumed in this work.

A precision of 0.017 units in calculated ε_{AB} values corresponds to an error in resulting k' values of about 1.3 to 1.7-fold (regardless of the value of ε_{AB}), since A_s values for various solutes are usually in the range of 10–20, and α' is normally equal to 0.6–0.7 for water-deactivated adsorbents. This level of precision is adequate for predicting the composition of new mobile phases for creating improved separation selectivity so that k' values for some sample will be maintained in the favorable range of $1 < k' < 5$. It has been observed also for the data in Table I that ε_{AB} values measured at any given time and with a particular batch of adsorbent show even better agreement with values from eqn. 2, providing that ε'_B and ε''_B, values for the B-solvent are redetermined for the particular adsorbent lot. This experimental approach can improve the general precision of calculated k' values to about ±10%.

Other literature data

Additional validation of the present approach is provided by other data from the literature. For large values of N_B, the function $\%_{lc}$ becomes zero, and eqns. 1 and 2 combine to give the simpler Soczewinski relationship[8,9]:

$$\log (k_2/k_1) = c \log (N_2/N_1) \tag{11}$$

Here, for binary mobile phases 1 and 2, k_1 and k_2 are solute k' values, and N_1 and N_2 are values of N_B for the two mobile phases. The constant c is equal to A_s/n_b. The above relationship has been shown to be accurate for a broad range of binary mobile phases and water-deactivated silica as adsorbent in thin-layer chromatography (*e.g.*, ref. 8).

Limited data for water-free mobile phases and silica as adsorbent have been reported by Scott and Kucera[22]. Most of the retention data reported by these authors involve hydroxyl-substituted solutes or solvents, and therefore, solute–solvent hydrogen bonding in the stationary phase is a probable complication. One LSC system from ref. 22 that is free of these effects is summarized in Table IV: 7.2–12.6% (w/v) ethyl acetate in heptane as mobile phase and several non-protic solutes. Here it is possible to measure differences in $\alpha' \varepsilon_{AB}$ ($\Delta\alpha' \varepsilon_{AB}$) by means of eqn. 1. These experimental $\Delta\alpha' \varepsilon_{AB}$ values are averaged and tabulated in Table IV for various solutes from the study of ref. 22. As required by eqn. 1, values of $\Delta\alpha' \varepsilon_{AB}$ for a given pair of mobile phases (*e.g.*, 7.2 and 9.0%, w/v, ethyl acetate) are approximately constant for different solutes (*e.g.*, standard deviation ±0.0009 for the example 9.0:7.2).

It is also possible to calculate $\alpha' \varepsilon_{AB}$ taking localization into account for each mobile phase of Table IV from the data of Table I, assuming some value of α'. The surface of silica is believed to be essentially homogeneous or of uniform energy toward the adsorption of polar solutes[14]. Therefore, the value of α' used in the calculations of Table IV should be the same as assumed in deriving the data of Table I for this adsorbent/B-solvent combination, namely $\alpha' = 0.57$. Resulting values of ε_{AB} (eqns. 2 and 9) are given in Table IV. Finally, differences in $\alpha' \varepsilon_{AB}$ between the mobile phases of Table IV were calculated. The resulting agreement between the latter calcu-

TABLE IV

COMPARISON OF SOLVENT-STRENGTH VALUES PREDICTED BY EQNS. 2 AND 9 *VS.* EXPERIMENTAL VALUES FROM REF. 22 AND EQN. 1

Water-free silica, ethyl acetate–heptane mobile phase.

Solute	A_S*	$\Delta\alpha'\varepsilon_{AB}$**		
		9.0/7.2	*10.8/7.2*	*12.6/7.2*
Benzyl acetate	15.0	0.0072	0.0101	0.0140
Methyl acetate	12.1	0.0054	0.0101	0.0135
Acetophenone	15.2	0.0064	0.0098	0.0136
Methylethyl ketone	11.8	0.0074	0.0130	0.0178
Acetone	11.4	0.0075	0.0131	0.0185
Expt. avg. (SD)		0.0068 ±0.0009	0.0112 +0.0016	0.0155 ±0.0025
Eqn. 2, 9		0.0056***	0.0102***	0.0141***

* Calculated from Table 8-4 in ref. 7.

** Difference in $\alpha'\varepsilon_{AB}$ values *versus* 7.2% (w/v) ethyl acetate–heptane; *e.g.*, 9.0/7.2 refers to $\alpha'\varepsilon_{AB}$ value for 9.0% (w/v) ethyl acetate in heptane minus value for 7.2% (w/v).

*** Calculated values; $n_b = 5.2$, $\varepsilon'_B = 0.94$, ε''_B. $= 0.48$, $\alpha' = 0.57$ (see Table I and text); ε_{AB} values are: 0.2792 (7.2); 0.2891 (9.0); 0.2971 (10.8); 0.3040 (12.6).

lated values of $\Delta\alpha'$ ε_{AB} and the experimental values of ref. 22 is quite good (S.D. = 0.0013). The overall agreement of eqns. 1, 2 and 9 with the data of ref. 22 constitutes a further verification of the present approach for estimating solvent strength in LSC.

Finally, data have been reported recently by McCann *et al.*[23] for several solutes using silica as adsorbent and diethyl ether–carbon tetrachloride as mobile phase. In two cases (nitromethane and nitroethane as solutes) the systems studied are free of solvent–solute hydrogen bonding effects, and we can compare values of ε^0 calculated from eqns. 2 and 9 with experimental values. Table V summarizes this comparison. In this case it was necessary to determine the best values of the corrected retention volume (V_R) for the two solutes, using eqn. 1 and calculated values of ε^0 (as summarized in Table V). The experimental values of ε^0 are seen to agree closely with each other for the same mobile phase and the two solutes. Average experimental values of ε^0 for the two solutes in turn agree with calculated ε^0 values within ±0.023 (1 S.D.), which is comparable to the agreement found for the mobile phases of Table I (±0.017).

Deviations from eqns. 2 and 9

In the course of comparing calculated and observed values of ε_{AB}, a few discrepancies in the data of refs. 16–20 were observed. However, we believe these are due either to experimental error, or to differences in the adsorbents used by one of us (L.R.S.) at various times between 1957 and 1971. Specific data that were excluded from the final correlations of Table I include the following: (1) the value for 10% (v/v) acetone in pentane and alumina; the S.D. for inclusion of this mobile phase is six-fold greater than for the remaining five mobile phases containing acetone; (2) all data[17,18] for nitromethane (alumina) as B-solvent; these four mobile phase compositions gave ε_B values that could not be rationalized among the different mobile phases; (3) data

TABLE V

COMPARISON OF SOLVENT STRENGTH VALUES PREDICTED BY EQNS. 2 AND 9 *VS.* EXPERIMENTAL VALUES FROM REF. 23

Water-free silica, diethyl ether–carbon tetrachloride mobile phase.

Diethyl ether (%, v/v)	*log V_R**		ε^0		
	Nitromethane	*Nitroethane*	*calc.***	*expt.****	*expt.* §
2.5	0.65	0.40	0.119	0.161	0.165
5	0.57	0.31	0.163	0.174	0.178
10	0.38	0.16	0.202	0.204	0.201
20	0.26	0.01	0.235	0.223	0.224
40	0.06	−0.18	0.262	0.255	0.253
70	−0.13	−0.39	0.291	0.285	0.285
100	−0.29	−0.52	0.340	0.310	0.305

* Calculated from Fig. 2 of ref. 23.

** Calculated from eqns. 2 and 9; assumes $\alpha' = 0.57$, A_s equals 11.1 for nitromethane, 11.5 for nitroethane (values from Table 8-4 of ref. 7); log V_R for $\varepsilon^0 = 0$ was 1.67 (nitromethane) and 1.48 (nitroethane).

*** Experimental value for nitromethane.

§ Experimental value for nitroethane.

for 2 and 5% (v/v) pyridine in pentane (alumina)[18] gave ε_{AB} values about 0.15 units lower than corresponding mobile phases reported in ref. 17. We can see no commonality in these seven excluded data points to suggest some new effect not considered in the present model.

Alcohols as solvents

Except for diethylamine, no B-solvent in Table I is capable of self-hydrogen-bonding. Actually, the extent of hydrogen bonding in pure diethylamine is small, as judged from its solubility parameter[24]. A previous paper[14] has classified LSC solvents into three groups according to relative polarity. These groups, with added comment and further sub-division of class-P solvents are as follows:

(1) Class N: less polar solvents that show no tendency to localization at low values of N_B; strictly speaking, solvents whose molecules possess no functional group with $Q_k^0 \geqslant 1.0$.

(2) Class P: more polar solvents that cannot self-hydrogen bond; *i.e.*, solvents that can localize at low N_B values, but exclusive of alcohols, phenols, carboxylic acids, etc. For practical purposes, primary and secondary amines may be included in this group. *Sub-class P-a*: Solvents of class P in which there is only one polar functional group in the molecule, and where that group has only one hetero-atom (*e.g.*, alkyl ethers, ketones, nitriles, halides). *Sub-class P-b.* Solvents of class P in which the molecule is aromatic (*e.g.*, pyridine), multi-functional (*e.g.*, dioxane) or in which the polar functional group contains more than one hetero-atom (*e.g.*, nitromethane, ethyl acetate).

(3) Class AB: amphoteric molecules which can self-hydrogen bond and which are quite polar; *e.g.*, alcohols, phenols, carboxylic acids.

The above solvent classification scheme helps us to understand how different

B-solvents will behave in terms of the dependence of ε_{AB} on N_B. However, we have so far not discussed the case of class AB solvents such as the alcohols, carboxylic acids, phenols, etc. In ref. 14 it was pointed out that the latter solvents probably do not fit the basic LSC retention model developed in this paper, and therefore, eqns. 2 and 9 are probably not useful for predicting solvent strengths of alcohol-containing binary solvent mobile phases. This is indeed the case, as illustrated in Fig. 2. Here, data from ref. 17 for isopropanol–pentane binaries with alumina as adsorbent are plotted as $\%_{\text{olc}}$ *vs.* θ_B. Clearly, these data do not follow the $\%_{\text{olc}} - \theta_B$ curve defined by other class P solvents. Whether other class AB B-solvents behave similarly is not known, nor is the behavior yet defined of alcohol B-solvents with silica as adsorbent.

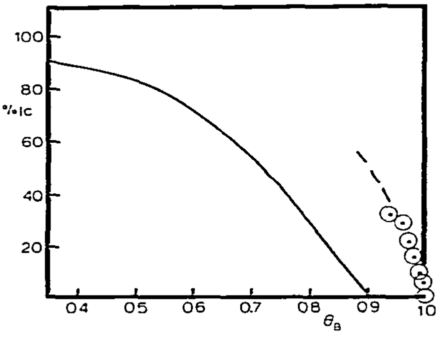

Fig. 2. Anomalous behavior of alcohols as B-solvent. Data for isopropanol–pentane mobile phases and alumina as adsorbent[17]. O, Experimental points; ——, $\%_{\text{olc}}$ *vs.* θ_B curve from Fig. 1.

The relationship of ε'_B to ε''_B

The adsorption energies of localized and delocalized solvent molecules have been addressed in detail in ref. 17. For the case of a monofunctional, aliphatic solvent molecule (only one hetero-atom), the adsorption energy Q_k^0 for the polar solvent group k will vary with whether k is localized or not. For the localized solvent, we can write[7,17]:

$$Q_k^0 = \varepsilon'_B n_b \tag{12}$$

When k is delocalized, its adsorption energy decreases by the factor $(1 - \text{f}(Q_k^0))$, where $\text{f}(Q_k^0)$ is a localization function defined in Fig. 17 of ref. 17. The function $\text{f}(Q_k^0)$ has been shown to define the adsorption energy of a broad range of polar solute and solvent molecules on different adsorbents[7]. Consequently, from eqn. 12, we should be able to relate ε'_B and ε''_B for monofunctional solvents as

$$\varepsilon''_B = \varepsilon'_B \, (1 - \text{f}(Q_k^0)) \tag{13}$$

Eqn. 13 states that the adsorption energy of the delocalized solvent (as measured by ε''_B), is equal to $(1 - \text{f}(Q_k^0))$ times the adsorption energy of the localized solvent (as measured by ε'_B).

According to eqn. 13, the ratio $\varepsilon'_B/\varepsilon''_B$ should be equal to $[1 - \text{f}(Q_k^0)]$, for monofunctional B-solvents. This relationship is tested in Table VI and in Fig. 3a.

Values of $\varepsilon''_B/\varepsilon'_B$ for monofunctional solvents from Table I are listed in Table VI (first eight values) along with the function $\varepsilon'_B\ n_b = Q_k^0$. In Fig. 3a this experimentally determined solvent ratio is plotted *vs.* Q_k^0, and the expected relationship —equal to $[1 - f(Q_k^0)]$— is superimposed as the solid curve. The agreement of data with theory is reasonable.

TABLE VI

SOLVENT DELOCALIZATION AS A FUNCTION OF THE LOCALIZATION FUNCTION $f(Q_k^0)$

Data for systems of Table I.

B-solvent	*Adsorbent*	$\varepsilon''_B/\varepsilon'_B$	$\varepsilon'_B\ n_b$
Isopropyl ether*	Alumina	0.90	1.58
Diethyl ether*	Alumina	0.76	2.25
	Silica	0.55	3.51
Ethyl sulfide*	Alumina	0.91	2.15
Methyl *tert.*-butyl ether**	Silica	0.67	2.61
Tetrahydrofuran	Alumina	0.67	3.80
Acetonitrile*	Alumina	0.42	4.06
Acetone*	Alumina	0.57	4.24
Diethyl amine*	Alumina	0.39	7.2
Ethyl acetate***	Alumina	0.78	4.00
	Silica	0.51	4.89
Dioxane***	Alumina	0.77	4.74
Pyridine***	Alumina	0.74	5.5

* Class P-a solvent.
** Data of ref. 15.
*** Class P-b solvent.

For the case of multi-functional B-solvents (all the remaining solvents in Table I), the value of Q_k^0 can be approximated as half that of the quantity $\varepsilon'_B\ n_b$ (assumes two functional groups in the molecule). In Fig. 3b we plot solvents 1–8 of Table I and the remaining four solvents of Table V *vs.* $Q_k^0 = (1/2)\ \varepsilon'_B\ n_b$, and again superimpose the theoretical function $[1 - f(Q_k^0)]$ as a solid curve; reasonable agreement between experimental data points and theory is again observed*.

The utility of the approximate relationships in Fig. 3 is that values of ε'_B and ε''_B can be estimated when only a single ε_{AB} value (and value of N_B) is available for a given B-solvent. Thus, the values of ε'_B and ε''_B determined must simultaneously satisfy eqn. 9 and Fig. 2, and the actual determination of ε'_B and ε''_B can be done by trial-and-error. Several B-solvents in Table I (*e.g.*, triethylamine, 1,2-dichloroethane) show estimated values of ε'_B and ε''_B determined in this fashion. However, these values must be considered only approximate in view of the scatter of the plots of Fig. 3.

Approximate solvent strength relationships and "best" values of ε''_B

Solvent strength values ε_{AB} were originally estimated from eqn. 2, assuming

---

* Except for the solid data point of Table V (ethyl acetate). This solvent is the only example in Table V of a localizing multi-hetero-atom monofunctional molecule. Such solvents may behave like class P-a solvents on silica (*vs.* alumina), for some as yet undefined reason.

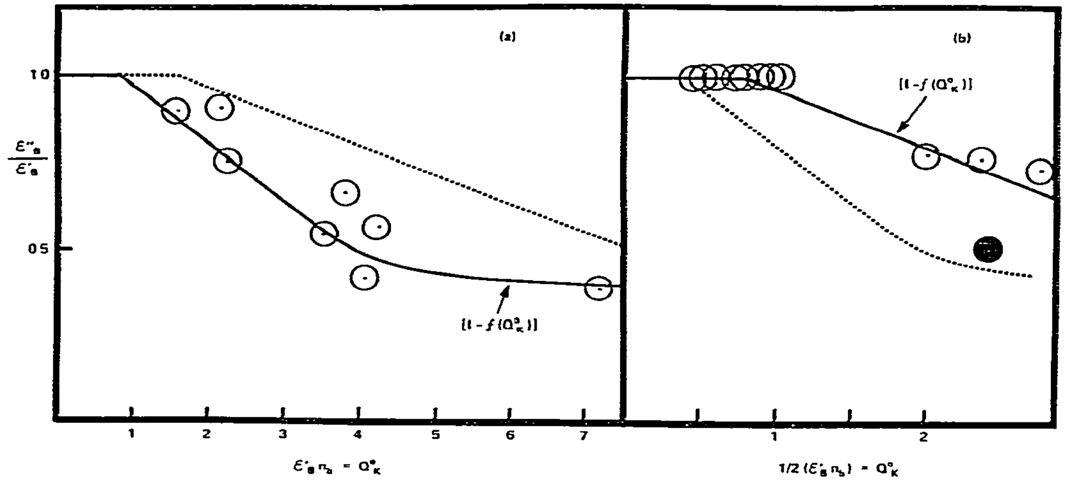

Fig. 3. Dependence of ε'_B on ε''_B. (a) Monofunctional solvents (class P-a) of Table I; (b) polyfunctional solvents (class P-b) of Table I. ——, $[1 - f(Q^0_k)]$ *vs.* Q^0_k; – – –, expected relationship for other solvent type: $[1 - f(Q^0_k)]$ *vs.* $1/2\,[\varepsilon'_B n_b]$ in Fig. 2a, for class P-b solvents, and *vice versa* in Fig. 3b; O, experimental values.

that $\varepsilon'_B = \varepsilon''_B$. As noted in earlier sections, except for more polar solvents, this approach gives generally reliable estimates of ε_{AB}. This fact is demonstrated in Table VII, where the error in this approach (*vs.* the use of separate ε'_B and ε''_B values) is shown for several class P solvents from Table I. Table VII also shows when the more precise (but more complex) scheme described in Appendix II must be used, *i.e.* class P-a solvents with large values of n_b and/or ε''_B, smaller values of N_B, and more often for silica than for alumina.

TABLE VII

ERROR IN THE USE OF EQN. 2 WITH A CONSTANT VALUE OF ε_B

Assumes $\varepsilon'_B = \varepsilon''_B$.

B-solvent	*Adsorbent*	*Error in ε_{AB}**				
		B (%, v/v) = 1	*2*	*5*	*10*	*25*
Isopropyl ether	Alumina	0.00	0.00	0.01	0.01	0.01
Diethyl ether	Alumina	0.02	0.03	0.05	0.05	0.03
	Silica	0.09	0.12	0.13	0.11	0.05
Tetrahydrofuran	Alumina	0.10	0.09	0.06	0.03	0.00
Acetonitrile	Alumina	0.23	0.23	0.19	0.13	0.04
Acetone	Alumina	0.15	0.13	0.09	0.04	0.01
Diethylamine	Alumina	0.22	0.18	0.11	0.05	0.01
Ethyl acetate	Alumina	0.07	0.06	0.02	0.01	0.00
	Silica	0.14	0.14	0.11	0.07	0.02
Dioxane	Alumina	0.05	0.02	0.00	0.00	0.00
Pyridine	Alumina	0.03	0.01	0.00	0.00	0.00

* Value of ε_{AB} from eqn. 2 using $\varepsilon_B = \varepsilon''_B$, minus ε_{AB} value calculated as in Appendix II.

The ε_B'' values derived from the data in Table I can be compared with previous values of ε^0 for these various solvents[7]. With few exceptions, these new values for alumina agree with the values of ref. 7 within 0.01–0.02 units. In some cases the previous values are based on a larger number of k' values (eqn. 1), and are therefore more reliable. However, previously published values for dioxane (0.56) and diethylamine (0.63) should be replaced by the values in Table I.

Similar comparisons of ε^0 values from ref. 7 with ε_B'' values from Table I for silica as adsorbent show somewhat greater discrepancies for class P solvents, a consequence of too few data for reliable estimates of ε^0 in ref. 7. Forthcoming work[5] will review and extend the data of Table I for silica.

The experimental ε_B'' values of Table I for several solvents can be compared with ε^0 values estimated by eqn. 10 and reported previously in ref. 7:

Solvent (alumina)	*ε^0 (ref. 7)*	*ε_B''*	*Average*
Bromoethane*	0.37	0.34	0.36
Chlorobenzene*	0.27	0.31	0.29
1,2-Dichloroethane*	0.49	0.44	0.47
Triethylamine*	0.48	0.36	(0.42)
Tetrahydrofuran	0.45	0.51	0.48

The agreement is reasonable, considering that solvents marked with an (*) have ε_B'' values in Table I that are based on a single binary composition ($n = 1$). Values from Table I for these solvents are approximate, because of the scatter around the curves in Fig. 3. The average values shown above should be used until further experimental data are available.

CONCLUSION

Except for mobile phases that contain an alcohol, it is now possible to calculate the solvent strength in LSC of any solvent-binary with greater accuracy than previously, and without empirical approximations such as the assumption of fictitious solvent molecular-area values (n_b). The procedure described here appears to be accurate to better than 0.02 units (1 S.D.) in ε^0, as illustrated with data from 108 different mobile phases for alumina or silica as adsorbent. This precision in calculated ε_{AB} values is more than adequate for determining LSC mobile phase compositions that must have the same solvent strength, for purposes of solvent–selectivity optimization.

It will be shown in a following paper[15], where the present treatment is extended to the case of ternary or more complex mobile phases, that the present approach to understanding solvent strength in LSC is required to calculate accurate ε^0 values for such mixtures. The present treatment also further confirms the reliability of the Snyder–Soczewinski model of retention in LSC[8] and the importance of localization effects in understanding retention in LSC for polar (class P) solvents and/or solutes.

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APPENDIX I

Determination of values of ε'_B and ε''_B from experimental ε_{AB} values

At least two values of ε_{AB} are required for different values of N_B. Take as an example data for tetrahydrofuran (THF) and alumina from ref. 17: $\varepsilon_{AB} = 0.198$ for 2% (v/v) THF and 0.242 for 5% (v/v) THF. From ref. 7 $n_b = 5.0$ for THF, and $\alpha' = 0.63$ for alumina[17]. The mole fractions can be calculated as: $N_B = 0.0281$ (2%, v/v) and 0.0693 (5%, v/v). Inserting these values into eqn. 2, it can be determined by successive approximation or solving for ε_B that the values of ε_B are: 0.65 (2%, v/v) and 0.59 (5%, v/v). The latter values then allow the determination of θ_B from eqns. 4b and 5b: 0.76 (2%, v/v) and 0.84 (5%, v/v), which in turn define values of $\%_{olc}$ (Table III): 0.55 (2%, v/v) and 0.31 (5%, v/v). Eqn. 9 can be rearranged:

$$\%_{olc}\ \varepsilon'_B + (1 - \%_{olc})\ \varepsilon''_B - \varepsilon_B = 0. \tag{i-1}$$

Substituting values of ε_B and $\%_{olc}$ into i-1 for 2 and 5% (v/v) THF gives two equations and two unknowns. Solving for ε'_B abd ε''_B gives: $\varepsilon'_B = 0.761$, $\varepsilon''_B = 0.514$.

Note that if $n = 2$ in Table V, this determines the resulting values of ε'_B and ε''_B, and the values of ε_{AB} then calculated from eqns. 2 and 9 *must* fit the experimental values exactly. For this reason, S.D. values in Table V are not reported unless n equals 3 or greater.

The precision of calculated ε'_B and ε''_B values based on the above approach is directly related to the precision of experimental ε_{AB} values used for this calculation, and to the difference in $\%_{olc}$ values. When the two mobile phases used to determine ε'_B and ε''_B have $\%_{olc}$ values that differ by less than 0.3, and ε_{AB} values are not precise within 0.003–0.005 units, significant error in resulting values of ε'_B and ε''_B may be found. The precision of this calculation can be increased substantially by using more than two values of ε_{AB} (and derived values of ε'_B and ε''_B), and fitting eqn. i-1 to the data by least-squares techniques. Alternatively, the above approach for two mobile phase ε_{AB} values can be applied to successive solvent pairs, and the derived values can be averaged.

APPENDIX II

Calculation of ε_{AB} for binary-solvent mobile phases, when the B-solvent can localize

First, it is assumed that values of ε'_B and ε''_B are known for the B-solvent, and that $\%_{olc}$ from eqn. 9 is given by eqn. 10. On the basis of data so far considered, this appears to be generally the case. A specific example will be used here to illustrate the general approach. Details of a computer program for this procedure are available (JLG).

Assume that a solvent strength value is desired for a 0.5% acetonitrile in pentane mobile phase with alumina (25% humidity, or 4% water) as adsorbent. The following values can be obtained: $\varepsilon_A = 0.00$, $\varepsilon'_B = 1.31$, and $\varepsilon''_B = 0.55$; $n_b = 3.1$ and $\alpha' = 0.63$ (data of ref. 7 and/or Table I). The approach is to first estimate $\%_{\text{olc}}$, then calculate ε_B from eqn. 9, which can be rearranged to:

$$\varepsilon_B = \%_{\text{olc}}\ (\varepsilon'_B - \varepsilon''_B) + \varepsilon''_B \tag{ii-1}$$

This value of ε_B is then used in eqn. 5b to calculate K, which can be used in eqn. 4b to calculate θ_B. The value of $\%_{\text{olc}}$ corresponding to the latter value of θ_B is then determined by eqn. 10. If the latter value of $\%_{\text{olc}}$ differs from the initially assumed value, the two values are averaged and the calculation of θ_B and $\%_{\text{olc}}$ is repeated. Again, the last two values of $\%_{\text{olc}}$ are averaged (if different) and the procedure continued until the calculated value of $\%_{\text{olc}}$ equals the initially assumed value. Continuing with the illustrative calculation, a first estimate of $\%_{\text{olc}} = 0.50$ is used, which from eqn. ii-1 gives $\varepsilon_B = 0.930$. From eqn. 5b, $K = 10^{0.63 \cdot 3.1 \cdot 0.930} = 65.5$. The value of N_B corresponding to 0.5% (v/v) acetonitrile in pentane is 0.0109, so that $N_A = 0.9891$. Eqn. 4b then gives $\theta_B = 0.419$. From eqn. 10, this corresponds to $\%_{\text{olc}} = 0.955$. If this value of $\%_{\text{olc}}$ is assumed for the second-approximation calculation of θ_B, a very slow convergence to the correct θ_B value is obtained. Better convergence is obtained by averaging the two $\%_{\text{olc}}$ values: $\%_{\text{olc}} = (0.5 + 0.955)/2 = 0.728$. Using the latter value, and repeating the calculation of θ_B, we obtain in the second approximation $\theta_B = 0.608$, and $\%_{\text{olc}} = 0.850$. Averaging the latter two values of $\%_{\text{olc}}$ again, $\%_{\text{olc}} = 0.789$. This value (third approximation) gives $\theta_B = 0.660$ and $\%_{\text{olc}} = 0.778$. A final value of $\%_{\text{olc}} = 0.784$ can be assumed. This value in turn (eqn. i-1) yields $\varepsilon_B = 1.146$, and eqn. 2 then gives $\varepsilon_{AB} = 0.235$.

For a new mobile phase/adsorbent system for which values of ε'_B and ε''_B are not known, it is necessary to determine experimentally (using eqn. 1) the solvent strength values ε_{AB} for at least two mobile phase compositions. From eqn. 2, corresponding values of ε_B can be determined for each mobile phase composition, which allows calculation of θ_B for each mobile phase (eqns. 4b and 5b). The analysis described in the main text then allows the determination of ε_B *vs.* θ_B.

GLOSSARY

A, B	Refers to non-polar solvent A and polar solvent B
A_s	Molecular area of solute molecule
$f(Q_k^0)$	Solvent–solute localization function, defined in ref. 7 with values from Table VII of ref. 17
k'	Solute capacity factor (see ref. 1)
k_1, k_2, k_A, k_B, k_{AB}	k' values for a solute with mobile phases 1, 2, pure A, pure B and the binary A–B, respectively
K	Equilibrium constant for competitive adsorption of solvents A and B; eqn. 4
n_b	Molecular area of a solvent molecule B (see ref. 7)
N_A, N_B	Mole fractions of A and B in the mobile phase
Q_k^0	Dimensionless adsorption energy of a polar functional group k in a molecule of B-solvent; see ref. 7
α	Separation factor; see ref. 1

α'	Adsorbent activity function; referred to as α in ref 7
ΔE	Dimensionless energy of adsorption of solvent B from mixture A–B; equal to log K
$\Delta\alpha'$ ε_{AB}	Difference in solvent strengths (equal to log k_1/k_2) for two solvents 1 and 2
ε^0	Solvent strength parameter in LSC; see ref. 7
ε_1, ε_2, ε_A, ε_B, ε_{AB}	Values of ε^0 for solvents 1, 2, pure A, pure B or mixture A–B
ε'_B	Value of ε_B as $N_B \rightarrow 0$; for localized solvent B
ε''_B	Value of ε_B as $N_B \rightarrow 1$; for delocalized solvent B
θ_A, θ_B	Mole fractions of A and B in the adsorbed (monolayer) phase

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