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Correlation of the eluting strengths of solvents in adsorption chromatography with solvatochromic parameters

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ABSTRACT

The Snyder measure of solvent eluting strength (ε^0) in adsorption chromatography correlates well with the molecular dipolarity/polarizability (π^*), hydrogen bond acidity (α), and hydrogen bond basicity (β) solvatochromic parameters. In addition, the δ correction term to π^* is a minor influence but statistically significant. There is also a good correlation with a combination of the donor number and acceptor number parameters. These correlations indicate that both acidic and basic sites on the alumina interact with the eluting solvent.

INTRODUCTION

The ε^0 scale of Snyder has been used for many years as a measure of solvent eluting strength in adsorption chromatography [1–3]. By the use of solvatochromic parameters in other areas of chromatography, it has been possible to find correlations which permit the estimation of retention times under a given set of conditions. In addition, often information is gained about the process not otherwise available such as the relative importance of dispersion and hydrogen bonding interactions in gas chromatography [4–13]. Krygowski *et al.* [14] reported a good correlation of ε^0 for alumina with the $E_T(30)$ parameter and a modified β (hydrogen bond basicity) parameter for 28 solvents. However, as pointed out by Park and Carr [15], the $E_T(30)$ parameter is a composite parameter of the Kamlet–Taft parameters π^* (molecular dipolarity/polarizability) and α (hydrogen bond acidity), so it is not truly a measure of a single specific solvent characteristic which complicates chemical interpretation of the results. Park and Carr [15] thoroughly studied the correlation of ε^0 values for 23 solvents with both alumina and silica as solid phases. It was indicated that for alumina, ε^0 depends on the π^* parameter, the α hydrogen bond donor (HBD), and the β hydrogen bond acceptor (HBA) parameters of Kamlet and co-workers [11–13]. In addition, there was a slight dependence on the δ polarizability correction term. However, the ratio of solvents to parameters used was not as high as desirable for firm statistical reliability [16]. Therefore, this study was initiated with the object of including as many solvents as possible in the correlation using the most recent measurements of solvent parameters as well

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as a very recently published methodology of reliably estimating values of solvatochromic parameters if values for closely related solvents are available [17]. It was possible to collect values for 37 solvents which greatly increases the confidence of the results as compared to the results of Park and Carr for 23 solvents [15]. Another advantage of this study is that solvents with a wider range of ε^0 and π^* were included which should also improve the statistical reliability of the results.

RESULTS

The P' solvent parameter of Snyder [18] ranks the relative eluting strength of solvents in bonded-phase partition chromatography. Although applied in completely different chromatographic modes, the relative order of the ε^0 and P' scales is similar enough to suggest a relationship.

However, when the ε^0 parameter is regressed against the P' parameter to test for a possible relationship, the result is $\varepsilon^0 = (0.127 \pm 0.012)P'$; $r = 0.877$, $s = 0.07$, $n = 34$. This indicates some correlation of the two scales but not an identity by any means.

Next the data for ε^0 were fitted to the general linear solvation energy relationship (LSER) equation of Kamlet and co-workers [11–13], $XYZ = XYZ_0 + s(\pi^* + d\delta) + a\alpha + b\beta$, where π^* is a measure of the solvent polarity/polarizability, α is a measure of the HBD strength of the solvent, and β is a measure of the HBA strength of the solvent. The δ is an index parameter which is 1.0 for aromatic solvents, 0.5 for polychlorinated aliphatic solvents, and 0.0 for other aliphatic solvents. The δ term attempts to correct for situations where the effects of solvent polarizability are different from the effects on the π^* probe. Multiple linear regression for those solvents for which data were available or the solvatochromic parameters could be reliably estimated gave $\varepsilon^0 = (0.563 \pm 0.040)(\pi^* - 0.16\delta) + (0.272 \pm 0.056)\alpha + (0.394 \pm 0.049)\beta$; $R = 0.970$, $s = 0.07$, $n = 37$ (see Fig. 1). The constant term was not significantly different from zero at the 90% confidence level. In addition, since many correlations have been observed where the molar volume, V, is significant [19–22], the dependence of ε^0 on V was tested and found to be statistically not significant.

It is observed that there is an approximately equal dependence of ε^0 on π^* and α. This explains the success of Krygowski *et al.* [14] in correlating ε^0 with the $E_T(30)$ parameter of Dimroth and Reichardt [23] and β since $E_T(30)$ has a similar dependence on π^* and α [11]. Furthermore, the β HBA parameter is known to be highly correlated with the donor number, DN, of Gutmann [11–13,24] and the acceptor number [25], AN, of Gutmann is known to also be correlated with a linear combination of π^* and α [11–13]. The AN and DN are still used by many workers, especially in Europe. In order to compare the effectiveness of the Kamlet–Taft and the Gutmann set of parameters, we carried out a correlation of ε^0 with a linear combination of DN

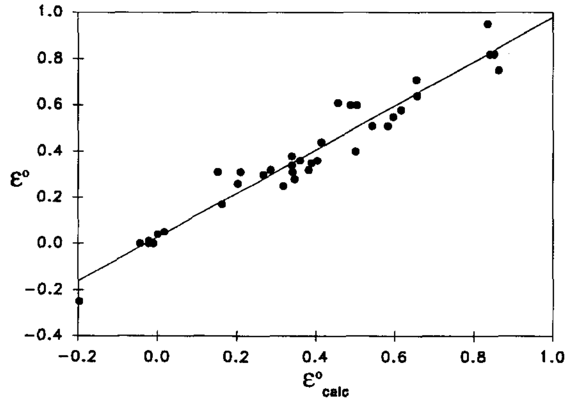

Fig. 1. Correlation of ε^0 with $0.563(\pi^* - 0.16\delta) + 0.272\alpha + 0.394\beta$.

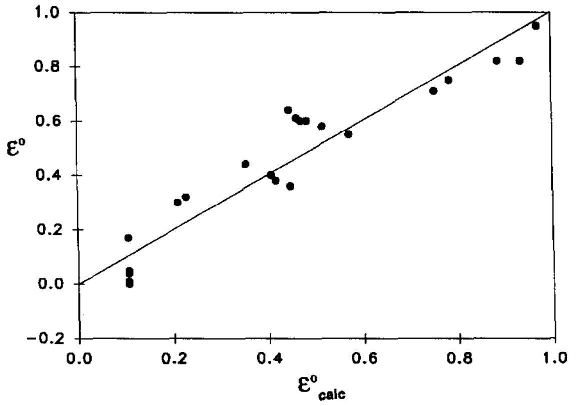

Fig. 2. Correlation of ε^0 with 0.0148AN + 0.0132DN + 0.11.

TABLE I

ε^0 VALUES AND SOLVATOCHROMIC PARAMETERS

ε^0 Values are from refs. 1, 2 and 15. π^*, α and β values are from refs. 12 and 30.

Compound	ε^0	π^*	α	β	δ	$\varepsilon^0_{\text{calc}}$
(1) Pentane	0.00	−0.08	0.00	0.00	0.0	−0.05
(2) Hexane	0.00	−0.04	0.00	0.00	0.0	−0.02
(3) Heptane	0.00	−0.02	0.00	0.00	0.0	−0.01
(4) Isooctane	0.01	−0.04	0.00	0.00	0.0	−0.02
(5) Cyclohexane	0.04	0.00	0.00	0.00	0.0	0.00
(6) Cyclopentane	0.05	0.03	0.00	0.00	0.0	0.02
(7) Carbon tetrachloride	0.17	0.29	0.00	0.00	0.5	0.16
(8) Toluene	0.30	0.55	0.00	0.11	1.0	0.27
(9) 1-Chloropropane	0.31	0.37	0.00	0.00	0.0	0.21
(10) Chlorobenzene	0.31	0.71	0.00	0.07	1.0	0.34
(11) Benzene	0.32	0.59	0.00	0.10	1.0	0.28
(12) Bromoethane	0.34	0.60	0.00	0.00	0.0	0.34
(13) Triethylamine	0.36	0.14	0.00	0.71	0.0	0.36
(14) Diethyl ether	0.38	0.27	0.00	0.47	0.0	0.34
(15) Chloroform	0.36	0.58	0.44	0.00	0.5	0.40
(16) Methylene chloride	0.40	0.82	0.30	0.00	0.5	0.50
(17) 1,2-Dichloroethane	0.44	0.81	0.00	0.00	0.5	0.41
(18) Tetrahydrofuran	0.51	0.58	0.00	0.55	0.0	0.54
(19) Acetonitrile	0.55	0.75	0.19	0.31	0.0	0.60
(20) 2-Butanone	0.51	0.67	0.06	0.48	0.0	0.58
(21) *p*-Xylene	0.26	0.43	0.00	0.12[a]	1.0	0.20
(22) Fluoroalkanes	−0.25	−0.35	0.00	0.00	0.0	−0.20
(23) Acetone	0.58	0.72	0.08	0.48	0.0	0.61
(24) Ethyl acetate	0.60	0.55	0.00	0.45	0.0	0.49
(25) Methyl acetate	0.60	0.60	0.00	0.42	0.0	0.50
(26) Nitromethane	0.64	0.85	0.22	0.30[a]	0.0	0.66
(27) Pyridine	0.71	0.87	0.00	0.64	1.0	0.65
(28) Dimethyl sulfoxide	0.75	1.00	0.00	0.76	0.0	0.86
(29) 2-Propanol	0.82	0.48	0.76	0.95	0.0	0.85
(30) 1-Propanol	0.82	0.52	0.78	0.85[a]	0.0	0.84
(31) Methanol	0.95	0.60	0.93	0.62	0.0	0.84
(32) Diisopropyl ether	0.28	0.27	0.00	0.49	0.0	0.35
(33) 2-Chloropropane	0.31	0.27	0.00	0.00	0.0	0.15
(34) Di-*n*-butyl ether	0.25	0.24	0.00	0.46	0.0	0.32
(35) Bromobenzene	0.32	0.79	0.00	0.06	1.0	0.38
(36) Iodobenzene	0.35	0.81	0.00	0.05	1.0	0.39
(37) Dioxane	0.61	0.55	0.00	0.37	0.0	0.46

[a] Estimated.

and AN. Correlations of solvent effects with a combination of the AN and DN have been done occasionally [25–27] although the usual practice is to do a correlation with only one of these parameters at a time. Multiple linear regression gave: $\varepsilon^0 = 0.11 \pm 0.03 + (0.0148 \pm 0.0019)\text{AN} + (0.0132 \pm 0.0021)\text{DN}$; $r = 0.949$, $s = 0.10$, $n = 24$ (see Fig. 2). All the ε^0 values and solvent parameters used in this study are given in Tables I and II.

DISCUSSION

The results of multiple linear regression using the LSER equation indicate that ε^0 has a substantial dependence on the π^* polarity/polarizability parameter as well as the α HBD and the β HBA parameters. There is a very small but statistically significant dependence on the δ polarizability index parameter. Because of the nature of the probe used

TABLE II

ε^0 VALUES AND ACCEPTOR AND DONOR NUMBERS

ε^0 Values are from refs. 1, 2 and 15. AN and DN values are from refs. 24 and 25.

Compound	ε^0	AN	DN	$\varepsilon^0_{\text{calc}}$
(1) Pentane	0.00	0.0[a]	0.0[a]	0.11
(2) Hexane	0.00	0.0[a]	0.0[a]	0.11
(3) Heptane	0.00	0.0[a]	0.0[a]	0.11
(4) Isooctane	0.01	0.0[a]	0.0[a]	0.11
(5) Cyclohexane	0.04	0.0[a]	0.0[a]	0.11
(6) Cyclopentane	0.05	0.0[a]	0.0[a]	0.11
(7) Carbon tetrachloride	0.17	0.0	0.0[a]	0.11
(8) Toluene	0.30	7.0[a]	0.0[a]	0.21
(9) Benzene	0.32	8.2	0.0	0.23
(10) Chloroform	0.36	23.1	0.0[a]	0.45
(11) Ether	0.38	3.9	19.2	0.42
(12) Methylene chloride	0.40	20.4	0.0[a]	0.41
(13) 1,2-Dichloroethane	0.44	16.7	0.1	0.35
(14) Acetone	0.58	12.5	17.0	0.52
(15) Ethyl acetate	0.60	9.3	17.1	0.47
(16) Methyl acetate	0.60	10.7	16.5	0.48
(17) Dioxane	0.61	10.8	14.8	0.46
(18) Nitromethane	0.64	20.5	2.7	0.45
(19) Pyridine	0.71	14.2	33.1	0.75
(20) Dimethyl sulfoxide	0.75	19.3	29.8	0.79
(21) 2-Propanol	0.82	33.6	21.5[a]	0.89
(22) 1-Propanol	0.82	37.3	21.0[a]	0.94
(23) Methanol	0.95	41.5	19.0	0.97
(24) Acetonitrile	0.55	18.9	14.1	0.57

[a] Estimated.

to measure π^* and the way the index parameter is defined, d, the coefficient of δ in the LSER equation, is never positive. Values of the coefficient of δ are always found to be in the range 0.00 to -0.40. A value of the coefficient between -0.3 and -0.4 indicates the absence of any dispersion interaction. The value of -0.16, obtained in the correlation in this study, indicates a moderate polarizability or dispersion interaction of the solvent with the alumina [28].

The results in this study turned out to be drastically different from the situation in bonded-phase chromatography where only polarity interactions are significant in determining the solvent eluting strength [9]. The substantial coefficients of π^*, α and β in the correlation of ε^0 parameter with the solvatochromic parameters indicate that polarity/polarizability, HBD, and HBA are each of importance in the adsorption of the solvent to alumina and thus its strength as an eluting solvent in adsorption chromatography. Both acidic and basic sites on the alumina must be interacting with the solvent molecule which is consistent with the behavior of activated alumina as a catalyst [29]. In contrast, adsorption on activated carbon depends on π^*, β, and the molar volume of the solvent but not on the α HBD parameter indicating that activated carbon has acidic sites but no basic sites of importance [20]. The study of Park and Carr [15] showed that adsorption on silica was similar to adsorption on alumina except that basic sites on the silica are not significant.

It was interesting that the multiple linear correlations of ε^0 with the pair of parameters AN and DN was virtually as good as the multiple linear correlation with π^*, α and β. Ordinarily, a correlation using a smaller number of parameters is much preferred, but in this case, since AN has been shown to be a composite parameter depending on both π^* and α, it is considered that the correlation with π^*, α

and β gives clearer chemical information than the correlation with AN and DN or the correlation with $E_T(30)$ and β carried out by Krygowski *et al.* [14] and Park and Carr [15].

In general, the results of this study with the larger number of solvents fully confirm the earlier work of Park and Carr [15]. The coefficients of π^*, δ, α and β are the same as those obtained by Park and Carr [15] at the 90% level of confidence. A minor difference is that the constant term XYZ_0 was not statistically different from zero in this study whereas with the smaller data set of Park and Carr [15] it was small yet statistically different from zero.

It was not realistic to assume beforehand, as Krygowski *et al.* [14] did, that polarity, HBD, and HBA ability of the solvent would each be significant in adsorption chromatography. It is unusual for as many terms of the LSER equation to be statistically different from zero as was the case in this study [11–13].

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