

Solvatochromic hydrogen bond donor acidity of aqueous binary solvent mixtures for reversed-phase liquid chromatography

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ABSTRACT

Solvatochromic hydrogen bond (HB) donor acidity (α_m) values for aqueous mixtures of methanol, ethanol, isopropanol, acetonitrile and tetrahydrofuran were measured by electronic absorption spectroscopy employing bis[α -(2-pyridyl)-benzylidene-3,4-dimethylaniline]bis(cyano)iron(II) as an indicator, and compared to available literature values. The HB donor acidity of all the aqueous organic mixtures increases in a nonlinear fashion as water is added to the organic solvent. For mixtures of acetonitrile and tetrahydrofuran, which are not acidic or are only slightly acidic, with water α_m increases rapidly as a small amount of water is first added, then shows a plateau region, and finally slowly rises to the acidity value of water. In contrast, the α_m for the mixtures of methanol, ethanol and isopropanol, which are quite acidic, increase slowly as the first small amount of water is added and then increase rapidly as the mixture approaches pure water. Literature values of α_m for water-methanol mixtures, which were determined from the $E_T(30)$ values of Reichardt's betaine dye, showed a minimum in the plot of α_m vs. volume fraction of organic component. It was also shown that the solvophobicity parameter (S_p) of methanol- and ethanol-water mixtures can be described by a combination of the dipolarity (π_m^*) and HB donor acidity (α_m) of the mixtures.

INTRODUCTION

Retention in reversed-phase liquid chromatography (RPLC) is determined by the difference in various types of interactions which a solute can undergo in the mobile and stationary phase. According to the solvophobic theory of Horváth *et al.*¹ the stationary phase is considered to be more or less passive. It is now known that the structure and composition of the stationary phase plays an active role in the separation process and has a major effect on selectivity^{2,3}. Since RPLC separations are often

performed by employing a fixed stationary phase and examining the effect of different mobile phases to obtain optimal separation conditions, understanding the various interactions of solutes with the mobile phase is important for elucidating the retention mechanism and hence the prediction of selectivity in RPLC. There have been many studies of the effect of the mobile phase on retention. Solubility parameter theory^{4,5}, the interaction index⁶, and statistical mechanics⁷ have been applied in attempts to better understand the mechanism of retention, but none of these approaches makes quantitative predictions of retention.

Recently the $E_T(30)$ scale of mobile phase polarity^{8–10} and linear solvation energy relationship (LSER) based on the Kamlet–Taft multiparameter scales^{11,12} were successfully used to study retention in RPLC. Johnson *et al.*⁸ have shown that plots of $\ln k'$ for a large number of solutes vs. the mobile phases' $E_T(30)$ solvatochromic parameters are very often more linear than are plots of $\ln k'$ vs. volume fraction of organic modifier. However, this approach only allows for the prediction of retention at different mobile compositions to be made, but provides no information about the relative strength of various interactions between a solute and the mobile phase, which are important in understanding the retention process. The $E_T(30)$ scale had been proposed as a single-parameter overall scale of solvent polarity, but Cheong and Carr¹³ recently pointed out that there can be no global single-parameter solvent polarity scale except when the solute and solvent are incapable of forming hydrogen bonds. In contrast, LSER approaches based on multiparameter scales^{11–13} seek to relate retention in a fixed mobile phase–stationary phase system to variations in the solute properties, or to variations in mobile phases' properties when the solute and stationary phase are fixed. The Kamlet–Taft multiparameter solvent scales are based on the differential evaluation of solvent dipolarity–polarizability (π^*), solvent HB donor acidity (α), and solvent hydrogen bond acceptor basicity (β)^{14–17}.

Kamlet and Taft and their co-workers have applied these measures of interaction strength based upon LSERs to about 600 processes¹⁸, including a large number of systems of immediate relevance to chromatography, such as Rohrschneider's gas–liquid partition coefficients¹⁹, Snyder's solvent strength scales for normal- and reversed-phase liquid chromatography^{20,21}, and retention in RPLC^{11,12,22}. In this work we will adopt the LSER formalism and report, in particular, the measurement of Kamlet–Taft hydrogen bond (HB) donor acidity (α_m) values for RPLC mobile phases.

THEORY

The α parameter can be obtained from several different methodologies such as ¹³C NMR, ¹⁹F NMR, electronic absorption spectroscopy and reaction rate measurements¹⁷, and is most conveniently obtained from measurements of the frequency of maximum absorption of carefully selected indicators. The LSER formalism¹⁷ indicates that when solute-to-solvent hydrogen bonding effects are excluded, as when solutes or indicators are non-protic and when only solvents with similar polarizability characteristic are considered, a spectroscopic property (XYZ , *e.g.*, the frequency of maximum absorption) of a solute in various solvents will be well correlated through an equation of the form:

$$XYZ = XYZ_0 + s\pi^* + a\alpha \quad (1)$$

where XYZ_0 is the intercept of the regression equation, s and a are regression coefficients for the solvatochromic parameters (π^* and α). Inclusion of the dipolarity–polarizability parameter (π^*) comes about naturally since any compound which is able to donate or accept hydrogen bonding will also undergo dipolar interactions. When the value of π^* is available for a given solvent, the α parameter can be estimated by the following equation:

$$\alpha = (XYZ - XYZ_0 - s\pi^*)/a \quad (2)$$

To minimize possible errors, due to self-association of strong HB donors or solvents and to errors in the π^* values, Kamlet *et al.*¹⁷ suggested that properties which meet the following criteria be chosen for formulating an α scale: (a) the properties should involve sufficiently strong HB acceptor that competitive solvent self-association should not materially influence the enhanced solvatochromic effects due to hydrogen bonding, (b) ratios of the a/s terms in eqn. 1 should not be too low (preferably > 1.0) so that uncertainties in the π^* values, which are necessarily less reliable for the HB donors than for the non-HB donor solvents, should not introduce unacceptable uncertainties in the α values.

To date there have been only a few studies on HB donor acidities of aqueous–organic mixtures^{8,23,24}. Krygowski *et al.*²³ and Johnson *et al.*⁸ reported measurement of $E_T(30)$ values, using Reichardt's betaine dye [4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide], for aqueous mixtures of a number of organic solvents including methanol, acetonitrile, tetrahydrofuran, isopropanol, etc. from 0% to 100% organic solvent. However, it has been shown that $E_T(30)$ values can be described by a combination of the Kamlet–Taft dipolarity parameter (π^*) and the related HB donor acidity scale (α) as follows¹⁷:

$$E_T(30) = 29.35 + 16.3\pi^* + 15.8\alpha \text{ (kcal/mol)} \quad (3)$$

$n = 19, r = 0.993, \text{S.D.} = 0.89, (a/s = 0.97)$

This equation holds for 19 solvents including aliphatic alcohols and other aliphatic HB donor solvents.

Recently, Cheong and Carr²⁴ reported measurement of Kamlet–Taft π_m^* values for a number of aqueous organic mixtures. The subscript m indicates that the values are for mixtures. They also estimated the α_m values of the same mixtures from Dorsey and Johnson's $E_T(30)$ values¹⁰ and their π_m^* values by assuming that eqns. 2 and 3 for pure solvents could be applied to a mixture. Even though there are a number of serious approximations and assumptions in using pure solvent regression results to interpolate data on mixed solvents, the trends in the α_m values with volume fraction of organic cosolvent (ϕ_0) were in good agreement with chemical intuition. For example, they observed a rapid rise in α_m for tetrahydrofuran and acetonitrile mixtures upon addition of a small amount of water, a plateau region, and a final rise to the value of α in water. However, a peculiar result was observed for the α_m values in water–methanol mixtures, *i.e.*, they observed a minimum in the plot of α_m vs. ϕ_0 . This is at variance with the chemical intuition. The HB acidity of the mixture is expected to increase as the more acidic solvent (water) is added. Cheong and Carr²⁴ suspected the existence of a specific solvation effect on Reichardt's betaine dye and concluded there must be an error in the α values of this mixture.

We believe it is likely that this unusual behavior of water–methanol mixture is due in part to the propagation of errors in the π_m^* values since the a/s ratio in eqn. 3 is not large and thus a small error in the π_m^* value might lead to a greater error in the estimated α_m value. In the present work errors of this kind were reduced by use of the wavenumber of the maximum absorption ($\bar{\nu}_{\max}$) of bis[α -(2-pyridyl) benzylidene-3,4-dimethylaniline]bis(cyano)iron(II) (abbreviated Fe complex)²⁵ in the aqueous–organic mixtures and by utilizing eqn. 2 and the following solvatochromic regression equation for the $\bar{\nu}_{\max}$ of this indicator in 13 pure solvents, where the ratio a/s is 1.59:

$$\begin{aligned} \bar{\nu}_{\max} &= 14.02 + 0.98\pi_m^* + 1.56\alpha \quad (4) \\ n &= 13, r = 0.999, \text{S.D.} = 0.04 \end{aligned}$$

The quality of the fit of $\bar{\nu}_{\max}$ for the pure solvents is also better than that with $E_T(30)$ and thus the use of this relationship will minimize errors in the estimated α_m values due to the propagation of errors in the π_m^* values.

EXPERIMENTAL

All solvents used in this work were HPLC grade and were used without further purification. The solvent mixtures were prepared by mixing a known volume of each liquid. The indicator, Fe complex, was prepared and recrystallized twice using a procedure given in the literature²⁵. Dilute solutions (typically 1 mM or less) were prepared in the solvent mixtures. The indicators for measurement of π_m^* for water–ethanol mixtures are 4-nitroanisole (1), 4-ethylnitrobenzene (4), N-methyl-2-nitroaniline (32), and 2-nitroanisole (45) were obtained commercially and recrystallized once before use. The number in parenthesis after each indicator refers to the Kamlet–Taft indicator designation¹⁷. All spectroscopic measurements were carried out by following the standard procedure²⁶ and repeated at least five times for each solution. A Hitachi Model 320 double-beam UV–VIS spectrophotometer was used to make measurements to ± 0.2 nm. In order to check for any concentration dependence, measurements were repeated at five different concentrations ranging from 0.05 to 1 mM and in all the cases standard deviations in the wavelength of maximum absorption was found to be less than 0.3 nm and did not vary with concentration. Consequently the solvent mixtures were examined at a single solute concentration chosen within the above range. The agreement between our measurements of $\bar{\nu}_{\max}$ of the Fe complex in 13 pure solvents and those in the literature²⁵ was within 0.1 kK except in water where the difference was about 0.3 kK. This led us to measure $\bar{\nu}_{\max}$ for water using two different spectrophotometers over a period of two months, and our value of 17.09 kK was not changed. Thus in the subsequent work on solvent mixtures we chose to use our value.

RESULTS AND DISCUSSION

The α_m values for aqueous mixtures of methanol, isopropanol, acetonitrile and tetrahydrofuran at various organic compositions were computed as follows from literature values²⁴ of π_m^* and our measured $\bar{\nu}_{\max}$ values for the Fe complex of the solvent mixtures:

$$\alpha_m = (\bar{\nu}_{\max} - 14.02 - 0.98\pi_m^*)/1.56 \quad (5)$$

^a kK = kiloKaysar, *i.e.*, 1000 wavenumbers.

TABLE I

THE VALUES OF α_m FOR WATER-ORGANIC COSOLVENT MIXTURESThe α_m values based on $E_T(30)$ are in parentheses.

φ_0	<i>Methanol</i>	<i>Isopropanol</i>	<i>Acetonitrile</i>	<i>Tetrahydrofuran</i>
0.1	1.20(1.01)	1.16(0.92)	1.16(1.01)	1.11(0.89)
0.2	1.17(0.93)	1.02(0.76)	1.08(0.94)	0.98(0.72)
0.3	1.15(0.92)	0.90(0.70)	1.01(0.90)	0.90(0.62)
0.4	1.10(0.88)	0.88(0.67)	0.95(0.90)	0.86(0.60)
0.5	1.07(0.86)	0.89(0.69)	0.90(0.89)	0.83(0.58)
0.6	1.04(0.87)	0.89(0.69)	0.90(0.88)	0.78(0.57)
0.7	1.02(0.91)	0.88(0.71)	0.88(0.89)	0.74(0.56)
0.8	1.02(0.96)	0.86(0.70)	0.82(0.85)	0.68(0.53)
0.9	1.02(1.00)	0.81(0.69)	0.71(0.81)	0.58(0.46)
1.0	1.02(1.09)	0.78(0.74)	0.32(0.33)	0.04(-0.09)

Based on eqn. 5 an error of ± 0.03 in π_m^* gives an error of ± 0.006 in α_m . Our values for α_m are given in Table I along with the values given by Cheong and Carr²⁴ in parentheses, and are plotted vs. φ_0 in Fig. 1.

As can be seen in Fig. 1, the α_m values obtained from the Fe complex are generally greater than those from the $E_T(30)$ values of betaine dye but the trends in the

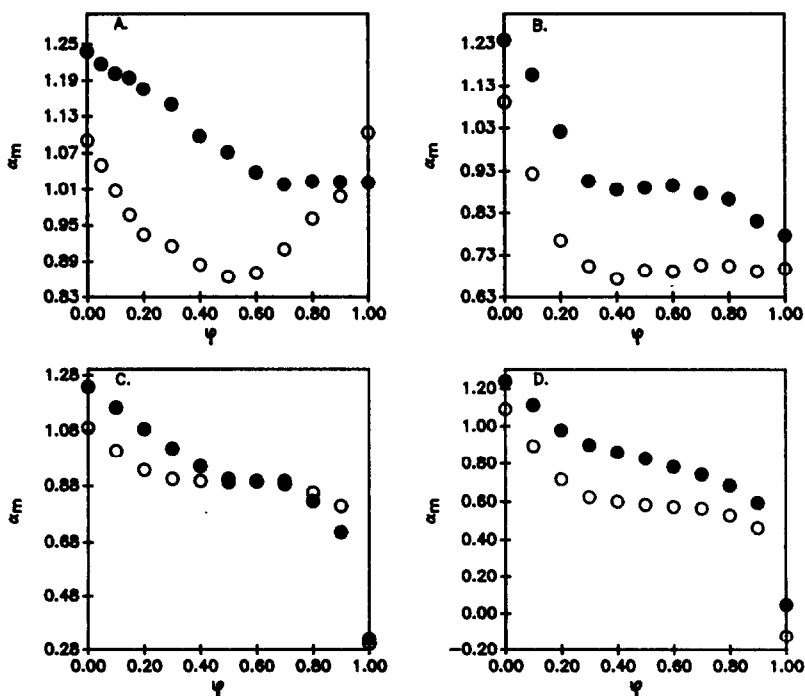


Fig. 1. Plots of α_m vs. volume fraction of organic cosolvents (φ_0). A, Methanol; B, isopropanol; C, acetonitrile; D, tetrahydrofuran. $\circ = E_T(30)$; $\bullet =$ this work.

changes of α_m values with ϕ_0 are very similar in all the mixtures except the methanol mixtures. Differences in α_m values determined by using two different indicators are entirely possible, particularly in solvent mixtures. Although the two indicators sense via their solvatochromic shifts the same intermolecular interactions exerted by the solvent, the sensitivity of the two indicators to the effects can be different. It should, however, be noted that there is no distinct minimum in the plot for methanol mixtures when the α_m values are obtained with the Fe complex, while the same plot for α_m values obtained via the $E_T(30)$ values has a distinct minimum. Since both the betaine dye and the Fe complex are sensitive to their environment as a consequence of a large change in dipole moment upon excitation and are also very strongly dependent on the HB donor acidity of the solvent, as indicated by the s and a coefficients in both eqns. 3 and 4 for the pure solvents, variations in the E_T values (kcal) with ϕ_0 for the mixtures are expected to be very similar for the two indicators. Fig. 2 shows plots of the E_T values for the Fe complex *vs.* those for Reichardt's betaine dye [$E_T(30)$]. All the plots show good linear relationships except the methanol mixtures, where a convex curve is evident. Non-linearity in the plot for the methanol mixtures is an indication that the cybotactic region about the two indicators have different compositions than the bulk mixtures, resulting in different effects on solvatochromic shifts of the two indicators.

In order to see if the behavior of betaine is unique to water-methanol mixtures, we measured α_m for water-ethanol mixtures with the Fe complex. We also measured the π_m^* values for ethanol-water mixtures with four indicators and determined two sets

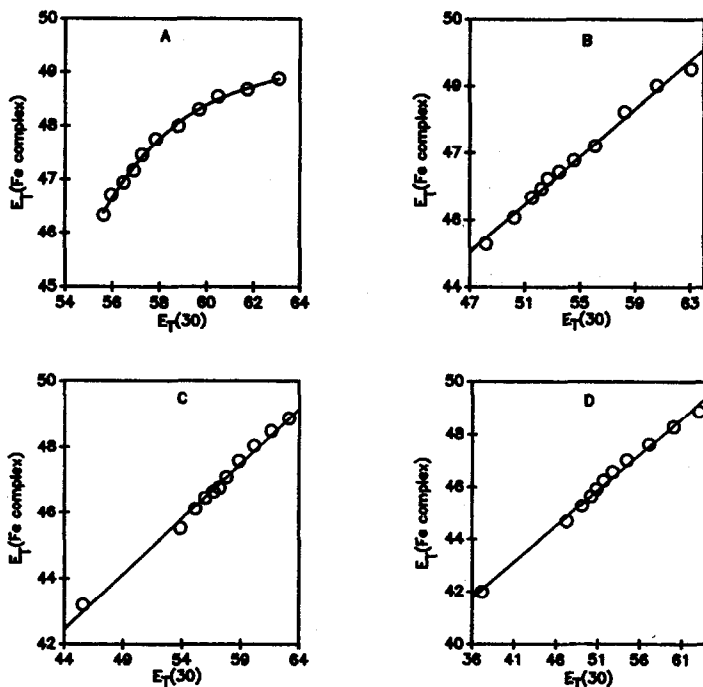


Fig. 2. Plots of E_T (kcal) for the Fe complex *vs.* $E_T(30)$ for the betaine. A, Methanol; B, isopropanol; C, acetonitrile; D, tetrahydrofuran.

TABLE II

THE VALUES OF π_m^* AND α_m FOR ETHANOL-WATER MIXTURES

φ_0	π_m^{*a}	α_m^b	α_m^c
0.0	1.16(0.17)	1.24	1.10
0.1	1.18(0.14)	1.17	0.99
0.2	1.18(0.14)	1.11	0.87
0.3	1.17(0.14)	1.05	0.75
0.4	1.08(0.12)	0.98	0.74
0.5	1.01(0.11)	0.94	0.73
0.6	0.94(0.10)	0.91	0.75
0.7	0.87(0.09)	0.90	0.76
0.8	0.79(0.09)	0.90	0.80
0.9	0.67(0.04)	0.91	0.86
1.0	0.54(0.06)	0.89	0.91

^a The π_m^* values are the average based on four indicators. The figures in parentheses indicates standard deviation.

^b The α_m values calculated from \bar{v}_{\max} values of the Fe complex using the corresponding solvatochromic equation.

^c The α_m values calculated similarly from $E_T(30)$ values from literature²⁷.

of α_m values based on literature data²⁷ for $E_T(30)$ and our measurements of \bar{v}_{\max} for the Fe complex. The values are given in Table II and plotted vs. φ_0 in Fig. 3. There is a minimum in the plot of α_m values based on $E_T(30)$ while there is no minimum based on the Fe complex. We also note that the differences between the two sets of α_m values are smaller than those for the methanol mixtures.

Cheong and Carr²⁴ stated that within the framework of the solvatochromic LSER model of retention in RPLC the mobile phase HB acidity must increase as water is added and thus there should be no minimum in the plot of α_m vs. φ_0 . Our results are in agreement with their conclusion and thus we believe that our α_m values are more reliable than those based on $E_T(30)$. The values of α_m calculated from \bar{v}_{\max} of the Fe

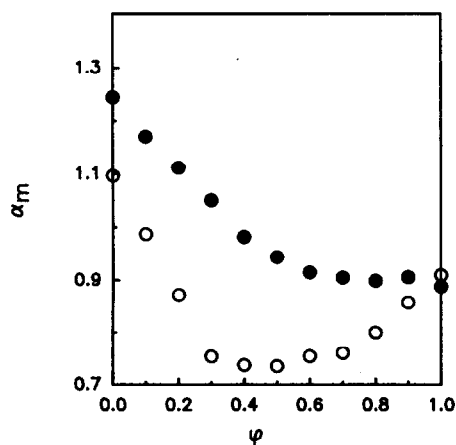


Fig. 3. Plots of α_m vs. volume fraction of ethanol. ○ = $E_T(30)$; ● = this work.

complex are 1.24, 1.02, 0.91, 0.78, 0.32 and 0.04 for water, methanol, ethanol, isopropanol, acetonitrile and tetrahydrofuran, respectively. These should be compared to the literature values²⁸ of 1.17, 0.93, 0.83, 0.76, 0.19 and 0.00. Recent work of Taft²⁹ indicates that α values determined by different methods have a variability of ± 0.10 units. Our values of α for these pure liquids are well within this range. In view of the fact that RPLC separation is more often applied to uncharged compounds, the HB donor acidity values measured via the uncharged Fe complex are expected to represent the HB acidity toward the solutes in the RPLC mobile phases in a more realistic fashion and to be more useful than those via a charged betaine.

The solvophobic strength of the mobile phases in RPLC has been of great interest to liquid chromatographers¹. Recently, Abraham *et al.*³⁰ proposed a new measure of a solvent's solvophobic effect (S_p) for pure liquids and for aqueous mixtures based on the Gibbs free energies of transfer of inert solutes from water to the second liquid. Following Horváth's interpretation of hydrophobic interactions that they originate in the net repulsion between water and the non-polar stationary phase and the non-polar moiety of the solute, we expect that the S_p should be well correlated with the dipolarity (π_m^*) and HB acidity (α_m) and basicity (β_m) of the mobile phases. Thus we regressed S_p values for the methanol and ethanol mixtures against π_m^* , α_m and β_m . The β_m values for the mixtures are from Krygowski *et al.*²³. The values of S_p for other aqueous-organic mixtures of interest to RPLC are not available. Based on previous experience, we have found that it is important to build up the regression in a stepwise fashion in order to avoid addition of unnecessary parameters. For S_p values at nine different volume fractions of organic cosolvent we obtain:

For methanol mixtures,

$$S_p = -0.77(\pm 0.17) + 1.43(\pm 0.17)\pi_m^* \quad (6)$$

$$r = 0.941, \text{ S.D.} = 0.10$$

For ethanol mixtures,

$$S_p = -0.88(\pm 0.18) + 1.40(\pm 0.18)\pi_m^* \quad (7)$$

$$r = 0.947, \text{ S.D.} = 0.09$$

RPLC mobile phases contain water, and water is very strong HB donor (see Table II). Thus the HB acidity parameter for the mobile phases was included in the regression equation:

For methanol mixtures,

$$S_p = -1.44(\pm 0.08) + 1.22(\pm 0.06)\pi_m^* + 0.81(\pm 0.12)\alpha_m \quad (8)$$

$$r = 0.998, \text{ S.D.} = 0.02$$

For ethanol mixtures,

$$S_p = -1.72(\pm 0.07) + 0.67(\pm 0.06)\pi_m^* + 1.58(\pm 0.12)\alpha_m \quad (9)$$

$$r = 0.998, \text{ S.D.} = 0.02$$

Incorporation of HB acidity obviously improves the quality of the fit very consider-

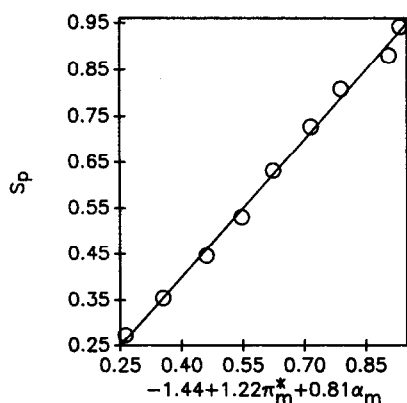


Fig. 4. Plot of experimental S_p vs. calculated S_p for water-methanol mixtures. Results calculated from eqn. 8.

ably. The Ehrenson test³¹ indicates that the α_m parameter is significant at the 99.9% confidence level. Since methanol and ethanol are much more basic in HB interactions than water, it seems necessary to include the HB basicity of the mixtures in the regression equation. The three-parameter equations so obtained are:

For methanol mixtures,

$$S_p = -1.42(\pm 0.47) + 1.21(\pm 0.08)\pi_m^* + 0.79(\pm 0.32)\alpha_m - 0.01(\pm 0.26)\beta_m \quad (10)$$

$$r = 0.998, \text{ S.D.} = 0.02$$

For ethanol mixtures,

$$S_p = -1.68(\pm 0.26) + 0.67(\pm 0.06)\pi_m^* + 1.55(\pm 0.19)\alpha_m - 0.02(\pm 0.14)\beta_m \quad (11)$$

$$r = 0.999, \text{ S.D.} = 0.02$$

We find there is no improvement in the goodness of either fit and the b coefficients are very small (statistically zero). The Ehrenson test also shows that the β_m parameter is not significant. The quality of the fit for methanol mixtures based on eqn. 8 is demonstrated in Fig. 4 as an example. Based on the above regression results one can say that the solvophobic property of methanol and ethanol mixtures with water is a combination of the dipolarity and HB acidity of the mobile phases themselves. As described previously¹⁸, transfer from one solvent to another should involve the difference in two cavity terms. Since no cavity formation parameter, such as Hildebrand solubility parameter (δ_H), was included in our model of S_p we believe that it is incomplete. Nonetheless rather good correlations were obtained most likely because δ_H covaries with π^* and α . Retention in RPLC involves transfer of the solute between the mobile and stationary phases. Thus, when regressions of retention in RPLC vs. mobile phase parameters include S_p , a parameter representing the cavity formation term should also be included. Work is in progress to correlate RPLC retention with the solvatochromic mobile phase properties.

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