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Role of hydroxyl concentrations in solvatochromic measures of solvent polarity of alcohols and alcohol–water mixtures—evidence that preferential solvation effects may be overestimated

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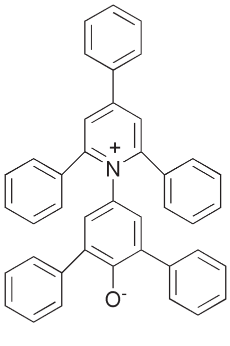
Received 27th May 2004, Accepted 22nd June 2004
First published as an Advance Article on the web 28th July 2004

For single solvents, primary alcohols and water, there is a good linear correlation ($r = 0.994$) between the solvent polarity index $E_T(30)$ and the molar concentration of OH groups (or $1000/V_m$, where V_m is the solvent molar volume). The corresponding correlations for alcohol–water mixtures are plots *vs.* the sum of molar concentrations of alcohol and water, alternatively expressed as plots of $E_T(30)$ *vs.* volume fraction. Our quantitative treatment is an extension of recent theoretical and experimental results. In contrast, previous studies of alcohol–water mixtures have relied on plots of $E_T(30)$ *vs.* mole fraction, and have overestimated the effect of preferential solvation of solvatochromic dyes by the more hydrophobic alcohols.

Introduction

$E_T(30)$ is a leading indicator of solvent polarity, and is calculated from the molar energy (in kcal mol^{-1}) of the longest wavelength electronic transition of the pyridinium-*N*-phenoxide betaine dye (**1**), and its derivatives;[1] it can be used as a probe for the polarity of pure solvents, and solvent mixtures, including solvents relevant to both organic and biochemical processes.[2]



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Of the many factors influencing values of $E_T(30)$,[1,3] recent work has highlighted several which are dominant for water and alcohols. The latest MO theoretical studies indicate that the large solvent-induced hypsochromic shift observed for protic solvents is due to both a dielectric effect and a hydrogen bonding effect.[4] Experimental data for concentrated aqueous solutions of amides, carbohydrates and polyethylene glycols (models for the cytoplasm, in which *in vivo* reactions occur) show a linear dependence on the molar water concentration of water; the results were explained by a dependence of solvent polarity on the proportion *by volume* of polar and apolar functionality.[2]

We have been investigating the extent to which molar concentrations of alcohol and water can account for rates and products of organic reactions in aqueous alcohol mixtures,[5] and this led us to study the factors influencing $E_T(30)$. We re-examined data for water and primary alcohols, spanning a range of $E_T(30)$ from 1-dodecanol (47.5 kcal mol^{-1}) to water (63.1 kcal mol^{-1}).[1] Although the number of solvents is relatively small, they span the upper half of the total *range* of $E_T(30)$ values,[1] and so major factors should be discernible.

We now show that recent experimental[2] and theoretical[4] work can be unified by correlating $E_T(30)$ of pure alcohol solvents with the molar concentration of ROH or water. The corresponding quantitative treatment for binary mixtures of alcohol and water is a plot of $E_T(30)$ *vs.* volume fraction. In contrast, many studies over more than a decade have related $E_T(30)$ to mole fraction, using various (but similar) theoretical models for preferential solvation (PS);[6–12] we will show that use of the mole fraction scale, and the neglect of other solvation effects, has led to overestimation of the role of PS, when one or more solvation shells differ significantly in mole ratio from the bulk solvent mixture.

Results and discussion

Factors influencing values of $E_T(30)$ for pure solvents

By considering a range of similar but pure solvents (*i.e.* alcohols in this case), we can obtain further insights into the factors influencing $E_T(30)$ in the absence of PS. Alcohols and phenols form a group of protic solvents (hydrogen bond donor (HBD), one of 3 main classes[1]) with $E_T(30)$ values ranging from 40.1 kcal mol^{-1} for 2,4-dimethylpentan-3-ol to 62.1[1b,c] (recently revised from 65.3[1a]) for 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP). Values for all other non hydrogen bond donor solvents (*i.e.* excluding amides and β-keto derivatives), vary from 30.7 (TMS) to 46.7 for acrylonitrile—*i.e.* they provide a smaller range of often lower values. It appears that OH groups are the dominant factor in determining values of $E_T(30)$ for alcohols, and $E_T(30)$ gives a good linear relationship *vs.* the molar concentration of OH groups for a series of monohydric alcohols ($[ROH] = 1000/V_m$, where V_m is the solvent molar volume; units are mol l^{-1}) for water and primary alcohols (Fig. 1).

The correlation line (Fig. 1), drawn through data points for very weakly acidic, primary alcohols ($pK_a > 15$),[13] may be regarded as a guide to 'normal' behaviour, deviations from which can be investigated further. Additional points for slightly more acidic alcohols, 2-chloroethanol ($pK_a = 14.3$)[13] and ethane-1,2-diol ($pK_a = 14.2$),[13] deviate slightly from the correlation. As might be expected,[1,14] larger deviations from Fig. 1 giving high values of $E_T(30)$ occur for stronger HBD solvents: *e.g.* CF_3CH_2OH, TFE ($pK_a = 12.4$,[13] $\alpha = 1.51$[15]) and HFIP ($pK_a = 9.3$,[16] $\alpha = 1.95$[15]), compared with MeOH ($pK_a = 15.5$,[13] $\alpha = 0.98$[15]). Alcohol OH groups could solvate **1** by donating hydrogen bonds and possibly also electron pairs. However, large deviations in the opposite direction occur for more sterically-hindered alcohols (*e.g.* *t*-BuOH, discussed later).

As water and primary alcohols are similar sterically, in that either a hydrogen atom or a methylene group is adjacent to an OH group, the number of solvent molecules in the primary solvation

DOI: 10.1039/b408052c

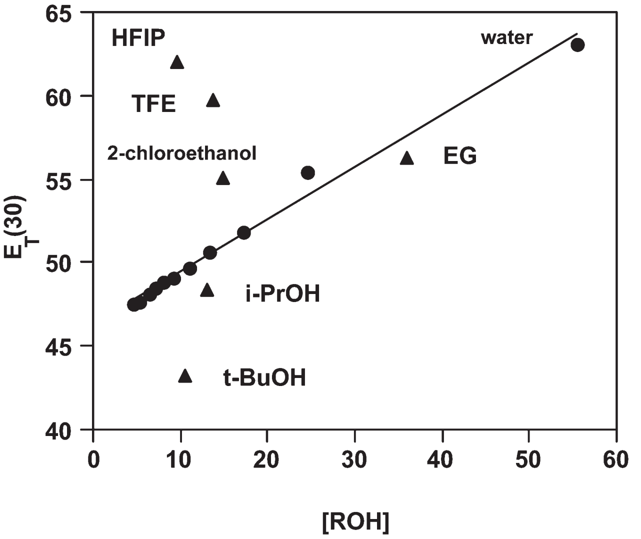

Fig. 1 Correlation of $E_T(30)$ in kcal mol^{-1} of pure solvents with molar concentrations of alcohols ($CH_3(CH_2)_{n-1}OH$) or water ($1000/V_m$, where V_m is the solvent molar volume = MW/density; units are mol l^{-1}) at 25 °C; the correlation line refers to data for water and ten primary alcohols (slope: 0.315 ± 0.014; intercept: 46.3 ± 0.3; $r = 0.994$); data for other labelled solvents were excluded from the correlation; data from refs. 1 and 13; data for *t*-BuOH at 30 °C, and for EG (ethane-1,2-diol) [ROH] = $2000/V_m$; other abbreviations: TFE is 2,2,2-trifluoroethanol and HFIP is 1,1,1,3,3,3-hexafluoropropan-2-ol.

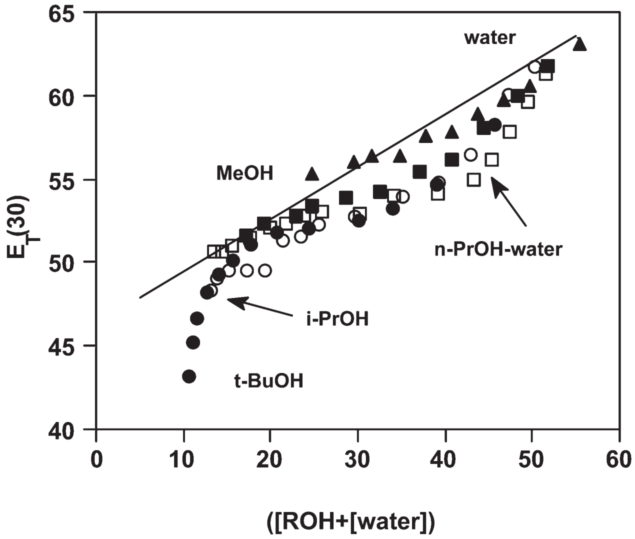

Fig. 2 Correlation of $E_T(30)$ in kcal mol^{-1} *vs.* ([ROH] + [water]) in mol dm^{-3} for mixtures of alcohols and water at 25 °C, including the correlation line from Fig. 1; all solvent codes are shown on the figure, except ■ referring to ethanol–water mixtures; $E_T(30)$ data from refs. 10 and 24.

shell around solutes such as **1** should be the same for all of these solvents. If only the first solvation shell were significant, a strong dependence on molar OH concentration would not be expected. Hence, an important implication of the correlation (Fig. 1) is that more distant solvent shells have a significant role, in contrast to simple one or two solvent exchange models, discussed later.[8–12] A contribution from more distant solvation shells is not surprising, considering the high dependence of solvatochromism on solvation—energy changes for $E_T(30)$ are double those for corresponding kinetic measures of solvent polarity (such as Y_{OTs}[14]).

The importance of molar concentrations of alcohol solvents has previously been emphasised,[1,5,17,18] particularly the concentration of the more polar solvent in binary mixtures (c_p);[17] $c_p = 1000/V_m$ for pure solvents; in this case, c has the same units (mol l^{-1}) as concentrations expressed more conventionally in square brackets (*e.g.* [ROH], see later), whereas c could have other units (*e.g.* mol (kg of solvent)$^{-1}$ or mol m^{-3}). A parameter (μ/V_m, where μ refers to the dipole moment) was introduced in a dipole–dipole model of solvent effects, which excluded hydrogen bonding solvents,[19] but μ/V_m was later applied successfully in multi-parameter correlations for the solvatochromic index Z (including alcohols solvents).[20]

Our extrapolation of the good linear relationship between ln c_p and $E_T(30)$ for the pure solvents, ethanol to 1-dodecanol (a range of 4.4 kcal mol^{-1}),[21] predicts less accurate values for methanol (error: *ca.* 2 kcal mol^{-1}, compared with 1.2 for Fig. 1) and water (error: *ca.* 6 kcal mol^{-1}, compared with 0.7 for Fig. 1), and two linear regions are required[21] in a ln c_p plot, if data for water and methanol are included (in contrast to Fig. 1).

Factors influencing $E_T(30)$ values for mixtures of monohydric alcohols and water

Following the above discussion of Fig. 1, we assume that the dominant factor is the total molar concentration of OH groups, $[ROH]_T$, with contributions from both water and alcohol: *i.e.* $[ROH]_T$ = ([ROH] + [water]).

To calculate $[ROH]_T$, we assume that the small volume changes on mixing alcohols and water can be neglected—densities[22,23] indicate that volumes are reduced by only a few % on mixing. Plots of $E_T(30)$ *vs.* ([ROH] + [water]) are shown in Fig. 2, onto which the correlation line for Fig. 1 has been superimposed for comparison. Results for methanol–water mixtures correlate well (*i.e.* behave close to 'normally'). Deviations from the line representing 'normal' behaviour increase as the alkyl chain length of the alcohols increase, possibly because of solvation effects beyond the first solvation shell.

It is tempting to explain the large deviation for pure *t*-BuOH (Figs. 1 and 2) by a steric effect on solvation, as suggested for hindered phenols;[1] if fewer OH groups solvated the solute, $E_T(30)$ would be lower. Consistent with the above explanations, similar deviations occur in a correlation of $E_T(30)$ with relative permittivities (ε_r) for pure solvents (plot not shown—it is similar to but less precise than Fig. 1).

Interestingly, addition of <10 v/v water to *t*-BuOH brings the data points close to the 'normal' correlation line; a possible explanation is that the more hydrophobic parts of **1** are solvated by *tert*-butyl groups rather than OH groups, and addition of water disrupts that interaction. Another possibility is that water disrupts the chain-like, hydrogen-bonded structures of pure alcohols.[24] Conversely, in the water-rich region, clusters of water molecules are disrupted by *t*-BuOH.[25]

The change in $[ROH]_T$ is proportional to the volume fraction (ϕ), as shown in eqn. 1 for a mixture of two liquids A and B with molar volumes V_A and V_B respectively.

$$([ROH] + [water])/1000 = [ROH]_T/1000 = (1/V_B) + \phi_A(V_B - V_A)/V_AV_B) \qquad (1)$$

Plots *vs.* volume fraction and mole fraction of alcohol are shown for EtOH–water (Fig. 3) and *n*-PrOH–water (Fig. 4); equivalent plots for volume fraction of water can be obtained for the other alcohols from Fig. 2, by drawing a straight line through the marked data points for MeOH, *i*-PrOH or *t*-BuOH and water. *Plots for all five binary aqueous alcohol mixtures vs.* ϕ *or* ([*ROH*] + [*water*]) (*Fig. 2*) *show smaller deviations from linearity than corresponding plots vs. mole fraction x.* The original paper on $E_T(30)$ shows quite a good correlation of $E_T(30)$ with vol% composition (100ϕ) for ethanol–water mixtures,[26a] and the first detailed study of $E_T(30)$ in binary solvents includes plots *vs.* vol% for aqueous MeOH, EtOH and *i*-PrOH.[26b]

Initial deviations from the line drawn through data points for the pure solvents are relatively small in plots of volume fraction (*e.g.* for addition of up to 30 vol% water to *n*-PrOH, Fig. 4); the one exception (out of ten possible combinations) is when water is added to *t*-BuOH–water, as discussed above.

Also, volume fractions (ϕ) correlate well with the relative permittivities (ε_r) of alcohol–water mixtures (Table 1). Although the experimental data for the mixed solvents are old,[27] they comprise a consistent and extensive data set; comparisons with modern data[13]

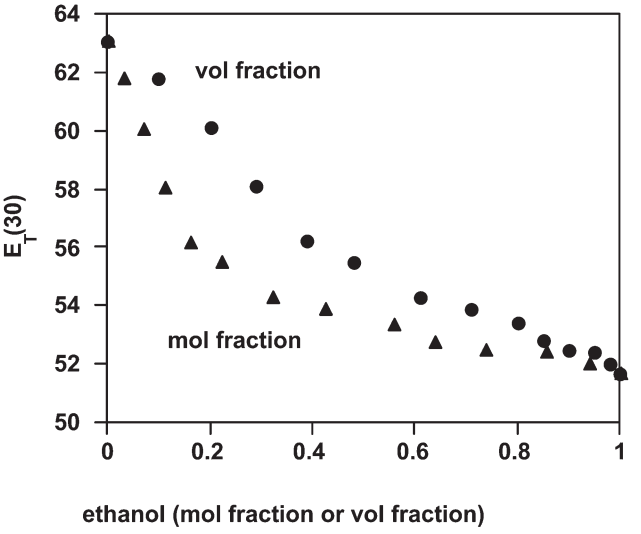

Fig. 3 Correlation of $E_T(30)$ in kcal mol^{-1} *vs.* volume fraction (●) or mole fraction (▲) of ethanol for binary aqueous mixtures at 25 °C—data from ref. 10.

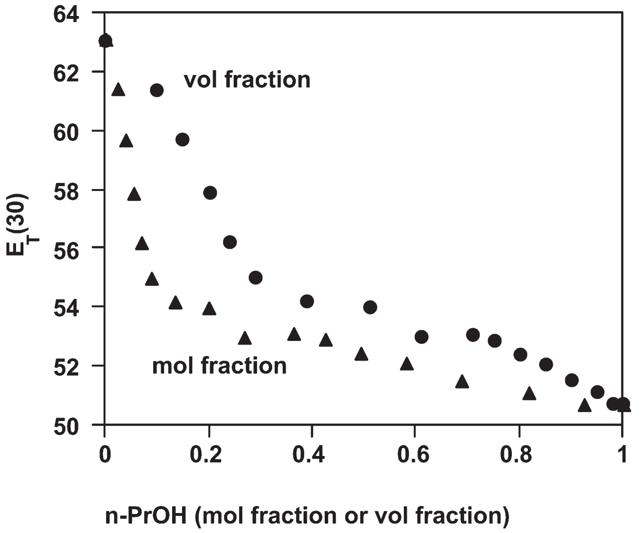

Fig. 4 Correlation of $E_T(30)$ in kcal mol^{-1} *vs.* volume fraction(●) or mole fraction (▲) of *n*-propanol for binary aqueous mixtures at 25 °C—data from ref. 10.

Table 1 Correlations of relative permittivities (ε_r) with volume fractions (ϕ) for mixtures of water and monohydric alcohols at 20 °C[a]

Alcohol	Slope	Intercept	r^b	n^c
Methanol	−48.5 ± 1.1	82.3 ± 0.7	0.998	11
Ethanol	−56.7 ± 0.6	81.7 ± 0.4	0.999	11
n-Propanol	−62.9 ± 1.6	80.3 ± 1.0	0.997	11
Isopropanol	−65.3 ± 1.5	80.6 ± 0.9	0.997	11
tert-Butanol[d]	−67.9 ± 1.9	72.3 ± 1.2	0.996	11
tert-Butanol[e]	−69.8 ± 1.9	78.6 ± 1.5	0.995	14
tert-Butanol[e,f]	−72.2 ± 1.7	79.5 ± 1.2	0.997	11

[a] Data from ref. 27 for wt.% alcohol–water, converted to volume fraction using solvent densities from ref. 13. [b] Correlation coefficient. [c] Number of solvents, including both pure solvents. [d] Data at 40 °C. [e] Data at 25 °C from ref 24. [f] Omitting 3 data points from $\phi = 0.98$ to 1.0, for which ε_r increases slightly from 11.74 to 12.4.

for pure solvents show errors of *ca.* 0.5, which would not greatly affect the correlations (Table 1). A modern data set[24] for *tert*-butanol–water mixtures also gives a satisfactory linear correlation with ϕ, despite the trend reversal which occurs between $\phi = 0.97$ and 1.00; in contrast, the non-linearity of plots *vs.* mole fraction was noted.[24] However, our empirical correlations with volume fraction (Table 1) are supported theoretically, because dielectric phenomena depend on polarisation *per unit volume*:[28] *e.g.* relative permittivities of composite materials are a function of volume fraction.[29]

In a detailed investigation of the effect of ε_r on solvatochromism, a plot of transition wavelength (λ) against ε_r showed a tendency for the transition energy to increase as ε_r increased (up to $\varepsilon_r = 100$);[4] an approximately linear relationship is obtained when $1/\lambda$ is plotted (proportional to transition to energy). *Consequently, plots of $E_T(30)$ vs. ϕ incorporate at least two of the possible solvent effects (ε_r and $[ROH]_T$) influencing $E_T(30)$ values in binary alcohol–water mixtures, even in the absence of PS.*

Our simple assumption about the dominance of $[ROH]_T$ is only a first approximation. A general, more precise, treatment (eqn. 2)[17,21] allows for two linear regions for pure primary alcohols (discussed above), and also accounts for the solvent dependence of a wide range of binary mixtures; there are two adjustable parameters: the slope E_D (dimensions are energy) and a concentration term c^*, above which it is suggested that interactions between the two solvent components become important for the polarity of the mixture. When $\ln c_p$ is plotted, two linear regions are observed for each binary mixture.[17]

$$E_T(30) = E_D \ln (c_p/c^* + 1) + E_T(30)^0 \qquad (2)$$

Eqn. 2 does fit the $E_T(30)$ data in Figs. 1 and 2 more precisely than our correlations, but an extra parameter is required. *Importantly, for both treatments, variations in molar concentration are the main solvent effect, and PS is not proposed.* Other possible solvent effects may be due to solvent–solvent interactions (eqn. 2), and/or effects due to outer solvation shells (noted above).

Our approach is (in one respect) only a minor refinement of the published c_p treatment,[17] because addition of a term for the contribution by the less polar component of the mixture only slightly reduces the curvature of plots. Similarly, the plots[2] employing [water] would only be slightly altered if a contribution from the cosolvent were included. However, because one solvent is replaced by another in the solvation shell, it does seem to be more reasonable to sum the contributions from both solvents—a main benefit is that the value of $E_T(30)$ when c_p or [water] is zero is then fully accounted for by the $E_T(30)$ value of the cosolvent.

Comments on alternative quantitative treatments of polarities of binary mixtures

For many aqueous mixtures, the dependence of $E_T(30)$ and related indices on solvent composition were initially considered as solvent effects, and were not associated with PS.[17,30] However, ideal behaviour requires a linear relationship between, for example, $E_T(30)$ and the solvent mole fraction (eqn. 3);[6,7,8a] x refers to mole fractions and subscripts A and B refer to the two solvents, so $E_T(30)_A$ is the value of $E_T(30)$ for the pure solvent A *etc.*

$$E_T(30)_{\text{mixture}} = x_A\, E_T(30)_A + x_B\, E_T(30)_B \qquad (3)$$

In 1986 it was suggested that deviations from eqn. 3 were 'indicative for preferential solvation effects'.[6] Independently soon afterwards, deviations from eqn. 3 were associated *solely* with PS (involving a change in composition of the solvation sphere compared with the bulk solvent);[7,8a] also, it was further speculated that, for aqueous alcohols (*e.g.* methanol, ethanol) and aqueous acetone, deviations from linearity of plots of log k for reactive solutes *vs.* mole fraction (*i.e.* non ideal behaviour) were due *solely* to PS of the solute by one of the two components of the solvent mixture.[7]

A contrary view is that deviations from linearity could be due to many possible solvent effects, and PS is only one such possibility; also mole fraction is not 'inherently superior'[31a] to other ways of representing composition (alternatives include wt% or volume fraction, ϕ). As argued above for alcohol–water mixtures, plots *vs.* ϕ (not x as in eqn. 3) are preferred, if separation of the role of PS is attempted.

However, more recent quantitative treatments of the solvent dependence of many binary mixtures (including aqueous alcohols), are based on the assumption that deviations from eqn. 3 are *solely* due to PS. As an example of one of the simpler interpretations, only one or two solvent molecules are considered to be exchanged over the whole range of compositions of a binary solvent mixture.[10] Equilibrium constants involving preferential solvation lead to equations for the dependence of $E_\mathrm{T}(30)$ on solvent composition in good agreement with experimental data,[8–12] and the quantitative expressions are very useful for correlations and interpolations. Whether[8–12] or not[17,30] PS is assumed, one or more adjustable parameters are required to fit data for each binary mixture of aqueous alcohols, and so a good mathematical fit does not prove the validity of the model used to derive it.

How realistic is the solvent exchange model for solvation? A substrate R is claimed[10] to be 'fully hydrated' by one or two water molecules (giving RW or RW_2), and similarly by one or two cosolvent molecules (giving RM or RM_2). The one-step model simply exchanges RW + bulk solvent with RM + bulk solvent, and the two step model similarly involves RW_2, RWM, and RM_2. Thus, it is an explicit assumption that values of $E_\mathrm{T}(30)$ depend on exchange by one or two solvent molecules. Although this might at first sight appear not too unreasonable, there is a highly questionable implicit assumption that no other solvent molecules affect values of $E_\mathrm{T}(30)$, over the whole range of compositions of each binary mixture.

Surprise at the simplification involving only one or two solvents exchanging within the solvation shell[10] has already been expressed incidentally, in a paper emphasising problems associated with analysing the electronic spectra of the mixtures of solvated complexes.[32] Within the confines of a crystal, in which the planar aromatic molecules stack closely together, two water molecules hydrogen bond to the phenolate anion; however, even in the crystal there are a total of 6 water molecules,[33] and many more would be expected to solvate such a large molecule as betaine (**1**) in free solution (see also discussion of Fig. 1).

An alternative, avoiding only one or two solvent molecule exchange,[10] is to assume that the number of molecules in the solvation shell is proportional to the number of molecules in the bulk solvent. For a binary solvent mixture, a preferential solvation parameter was then calculated from the ratio of the two proportionality constants.[9a] However, the assumption may not be valid over the whole range of solvent compositions, and two preferential solvation parameters were chosen for *n*-propanol–water and also for isopropanol–water mixtures;[9a] in contrast, data for these two solvent mixtures were correlated using only one exchange constant for each mixture.[10]

Deviations from linearity (Figs. 3 and 4) are greater for mol fraction (x) than vol fraction (ϕ), and ϕ fits well if only small amounts of cosolvent are added; if PS occurred, deviations would be expected in these regions. When larger amounts of cosolvent are present, the observed deviations could be due to solvation effects other than PS. It has recently been re-emphasised that 'PS characteristics are modified by solvent–solvent interactions'[34] (see also refs. 8*a* and 8*b*). Also, the solvation number of cations depends on the cosolvent,[31b,c] and it is accepted that eqn. 3 will fail, independently of PS, if the number of solvent molecules in the solvation shells change with solvent composition,[8c,31d] as is likely for *t*-BuOH–water mixtures.

The extent of PS, even judged solely by deviations from eqn. 3, depends greatly on the solvatochromic probe.[8a,35] Also, a wide variety of physical methods have been applied to aqueous binary mixtures in the absence of solute, and they reveal many complexities and subtleties; one of the most recent is studies of clusters of liquid droplets by mass spectrometry.[25] However, it has been pointed out that it is 'presently not decided whether clusterisation and PS are intrinsically interconnected'.[36] Early experimental studies of PS of **1** by ^{1}H and ^{13}C NMR[37] could be supplemented by studies of intermolecular nuclear Overhauser effects and theoretical studies by molecular dynamics.[38,39]

Conclusions

The relationship between $E_\mathrm{T}(30)$ and molar hydroxyl concentration (Fig. 1) highlights the major factor influencing the polarity of alcohols and water, and is consistent with a recent proposal[2] that solvent polarity is related to the volumes of solvating protic solvents. Molar concentrations of water (in binary mixtures[2]) or alcohol (in pure alcohol solvents—Fig. 1) have a dominant effect on $E_\mathrm{T}(30)$.

For alcohol–water mixtures, plots (Fig. 2) of $E_\mathrm{T}(30)$ *vs.* the total molar concentrations of water and alcohol (or volume fraction) allow for the concentration effect, and additional contributions from hydrogen bonding, and changes in relative permittivities (Table 1), proposed from recent theoretical work for pure solvents;[4] however, plots of volume fraction for alcohol–water mixtures are non-linear (*e.g.* Figs. 3 and 4), due to a wide variety of possible additional solvent–solvent and solvent–solute interactions, including preferential solvation (PS) of (**1**) by the more hydrophobic alcohol. Deviations from plots *vs.* mole fraction (eqn. 3, Figs. 3 and 4) overestimate PS, and good quantitative fits[8–12] may reflect (as one extreme of a range of possibilities) the use of an adequate number of fitting parameters rather than the validity of the PS model.

Experimental

Data were taken from the published literature, cited in footnotes to Table 1 and legends to Figs. 1–4. Linear regressions were performed using Microsoft Excel.

Acknowledgements

We are grateful to N. Asaad, O. El-Seoud, H. Langhals, J. O. Morley and C. Reichardt for very helpful comments and/or exchanges of information.

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