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Understanding solvation*

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Abstract: The effects of solvents on different chemical phenomena, including reactivity, spectroscopic data, and swelling of biopolymers can be rationalized by use of solvatochromic probes, substances whose UV–vis spectra, absorption, or emission are sensitive to the properties of the medium. Thermo-solvatochromism refers to the effect of temperature on solvatochromism. The study of both phenomena sheds light on the relative importance of the factors that contribute to solvation, namely, properties of the probe, those of the solvent (acidity, basicity, dipolarity/polarizability, and lipophilicity), and the temperature. Solvation in binary solvent mixtures is complex because of “preferential solvation” of the probe by some component of the mixture. A recently introduced solvent exchange model is based on the presence in the binary solvent mixture of the organic component (molecular solvent or ionic liquid), S, water, W, and a 1:1 hydrogen-bonded species (S-W). Solvation by the latter is more efficient than by its precursor solvents, due to probe-solvent hydrogen-bonding and hydrophobic interactions; dimethyl sulfoxide (DMSO)-W is an exception. Solvatochromic data are employed in order to explain apparently disconnected phenomena, namely, medium effect on the pH-independent hydrolysis of esters, ¹H NMR data of water-ionic liquid (IL) mixtures, and the swelling of cellulose.

Keywords: solvation, mechanism of; solvatochromism; thermo-solvatochromism; reactivity, effects of solvents; spectroscopy; effects of media.

INTRODUCTION

Why is understanding solvation important? An obvious answer to this question is that most chemical reactions and all biochemical reactions in the human body occur in solution. An additional reason is that it is possible to explain several apparently disconnected phenomena by using a common approach, based on understanding the interactions between the species of interest (reactant, activated complex, polymer, etc.) and the solvent. For mixtures, we consider the interactions solvent–solvent, as well as those between the species of interest and each solvent. The following representative examples drive the point home:

- i. Consider simple chemical reactions in a binary solvent mixture, where water is a reactant, e.g., pH-independent acyl transfer [1], and reversible hydration of carbonyl compounds [2]. The kinetic order with respect to water (n) can be calculated from the equation $\log(k_{\text{obs}}) = \text{constant} + n \log[W]$, where k_{obs} is the observed rate constant, W, refers to water, and [W] refers to its molarity in the binary mixture. However, attempts to calculate a single value for (n) may fail because

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the plots may not be linear, as shown by Fig. 1 for the pH-independent hydrolysis of 4-nitrophenyl chloroformate in mixtures of water and acetonitrile [1b]. The plot shown can be divided into three water concentration ranges, with slopes of 2, 1.3, and 2.3, respectively. Explaining this result on the basis of a transition state with a variable number of water molecules is tenuous because the value of (n) does not change systematically, i.e., it does not increase as a function of increasing [water]. In fact, a proton-inventory study of the reaction shown in Fig. 1 has indicated that (n) = 2, independent of water concentration [1b].

- ii. The ^1H NMR spectra of mixtures of water and an ionic liquid (IL), 1-allyl-3-butylimidazolium chloride were recorded as a function of increasing χ_{L2O} , where χ refers to mole fraction, (L) is (H) or (D), and $\Delta\delta = \delta(\chi_{\text{L2O}=0.1058}) - \delta(\chi_{\text{L2O}=0.9912})$, ppm. As shown in Fig. 2, the dependence of ($\Delta\delta_{\text{obs}}$) on (χ_{L2O}) is monotonic for the hydrogens of the imidazolium ring (of which H2 is an example), but shows abrupt changes at a certain (χ_{L2O}) range for HOD and the hydrogens of the side chains (plots not shown) [3]. These NMR results show the complexity of the interactions between the components of the binary mixture. For example, this behavior is not due *solely* to W-IL hydrogen bonding because the equivalent plots for aliphatic alcohols show systematic changes of ($\Delta\delta_{\text{obs}}$) as a function of increasing χ_{L2O} [4].
- iii. Cellulose swelling is an important initial step for many applications, e.g., its dissolution in appropriate solvents, including ILs, extrusion from solution and regeneration in form of fibers, films, or slabs, or functionalization [5]. A treatment of cellulose that is employed in order to increase swelling is the so-called “mercerization”. The fiber, slack or stretched, is treated with an alkali solution, usually NaOH. Swelling by protic solvents, e.g., water and aliphatic alcohols is inter-crystalline, i.e., occurs mainly within the amorphous region of the fiber [6]. Figure 3 shows the dependence of the swelling of cotton cellulose on the number of carbon atoms of n-chain aliphatic alcohols, from methanol to 1-octanol. The swelling is expressed as (n ; solvent), the number of moles of solvent absorbed per anhydroglucose unit of cellulose; the Y-axis is given as a ratio between the swelling by water (most efficient) and that by alcohols [7]. This example is interesting because of the large difference between the responses of native and mercerized fibers to a systematic variation of a solvent property, namely, its molar volume.

The above-shown examples have the following in common: They are manifestations of the effects of pure solvents, or binary solvent mixtures on different phenomena, namely, reactivity, Fig. 1, a spectroscopic property, Fig. 2, or a “physical” process in a polymer, Fig. 3. A corollary to the statement that solvent effects have a common ground is that it should be possible to rationalize them by employing a common approach; this is the aim of the remaining part of this account.

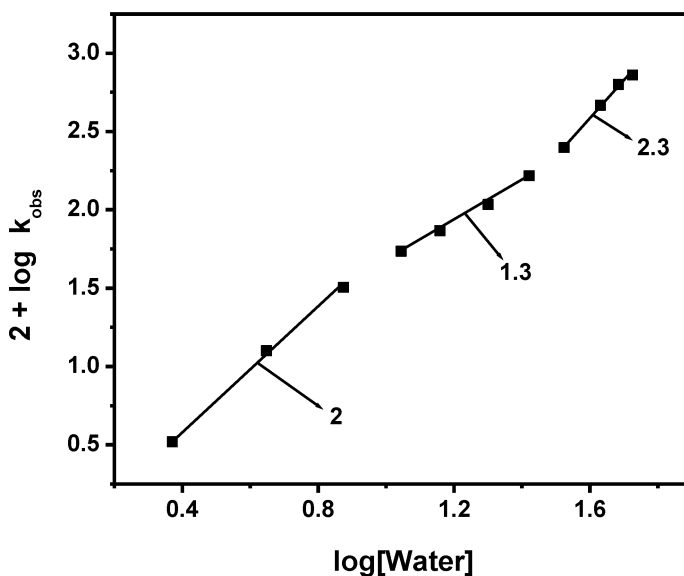


Fig. 1 Dependence of $\log(k_{\text{obs}})$ on $\log[\text{water}]$ for the pH-independent hydrolysis: $4\text{-O}_2\text{NC}_6\text{H}_4\text{OCOCl} + \text{H}_2\text{O} \rightarrow 4\text{-O}_2\text{NC}_6\text{H}_4\text{OH} + \text{HCl} + \text{CO}_2$. Data recalculated from ref. [1b].

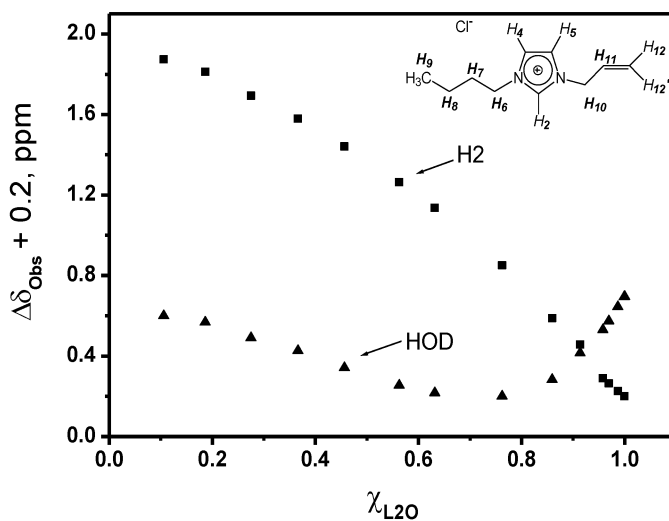


Fig. 2 Dependence of $(\Delta\delta_{\text{obs}})$ on $\chi_{\text{L}_2\text{O}}$ for solutions of 1-allyl-3-butylimidazolium chloride in L_2O , at 25 °C. The plots shown are for H2 of the imidazolium ring (■) and HOD (▲). The numbering of hydrogens of the IL is shown in the insert. Data taken from ref. [3b].

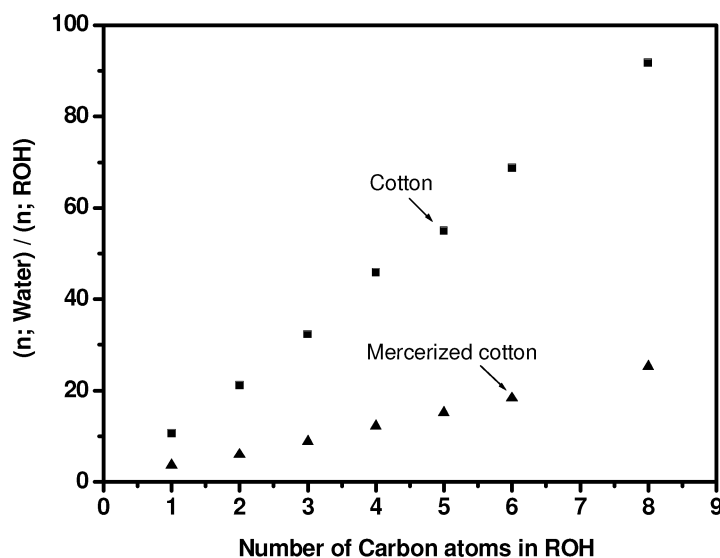


Fig. 3 Dependence of the ratio $(n; \text{Water})/(n; \text{ROH})$ on the number of carbon atoms of normal-chain alcohols. The plots are for native (■) and mercerized cotton cellulose (▲), respectively. Data recalculated from ref. [7].

UNDERSTANDING SOLVATION IN PURE SOLVENTS

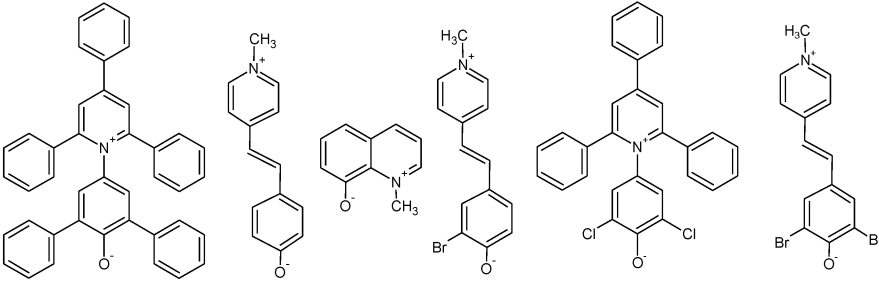
Solute–solvent interactions include, inter alia, hydrogen-bonding, ion–dipole, dipole–dipole, dipole-induced dipole, solvophobic, and dispersion or London interactions. It comes as no surprise, therefore, that the effects of solvents on chemical phenomena cannot be rationalized by a single, macroscopic solvent property (e.g., its relative permittivity) or one of the Kirkwood dielectric functions [8]. It also follows that these effects are best treated as the sum of several solvent properties as given, e.g., by the Taft–Kamlet–Abboud (TKA) equation [9]:

$$\text{SDP} = \text{constant} + a \alpha_S + b \beta_S + s (\pi^*_S + d\delta) + h (\delta^2_{\text{H}})_S \quad (1)$$

Where the solvent-dependent phenomenon (SDP), such as rate constant, equilibrium constant, spectroscopic shift, is modeled as a linear combination of two hydrogen-bonding terms, in which the solvent is the hydrogen bond donor ($a \alpha_S$), or the hydrogen bond acceptor ($b \beta_S$), a dipolarity/polarizability term [$s (\pi^*_S + d\delta)$], and a cavity term [$h (\delta^2_{\text{H}})_S$], related to Hildebrand solubility parameter. In eq. 1, dd is a correction term for π^*_S , its value = 0, 0.5, or 1 for aliphatic; chlorinated aliphatic, and aromatic solvents, respectively. The parameters α_S , β_S , and π^*_S , are known as solvatochromic parameters because they are determined by using solvatochromic probes (vide infra; hereafter designated as “probes”); the subscript (S, for solvent) is employed so that they are not confused with other known quantities, e.g., α and β of Brønsted equation. SDP can be rationalized, therefore, once the contributing terms of eq. 1 are known.

The fact that the UV–vis spectra, absorption or emission, of some compounds are particularly sensitive to the medium (solvent, solvent mixtures, etc.) has been exploited in order to calculate α_S , β_S , and π^*_S of eq. 1 [8]. Figure 4 shows the structures of some of these probes, along with their acronyms, pK_a in water, and $\log P$ [10].

The acronyms employed are related either to the discoverer (Reichardt betaine, RB; Wolfbeiss betaine, WB), or to a generic chemical name (quinoline betaine, QB; methylpyridinium merocyanine dibromide, MePMB₂). $\log P$ is extensively employed as a measure of lipophilicity or hydrophobic character; it refers to the partition coefficient of a substance between (mutually saturated) 1-octanol and water: $\log P = \log ([\text{substance}]_{1\text{-octanol}}/[\text{substance}]_{\text{water}})$ [11]. Intramolecular charge transfer (CT) oc-



	RB	MePM	QB	MePMBr	WB	MePMBr ₂
pK_a in water:	8.65	8.37	6.80	6.89	4.78	5.22
$\log P$	very large	-1.94	-0.63	-1.0	1.79	-0.16

Fig. 4 Molecular structures of selected solvatochromic probes, along with their pK_a values in water and $\log P$.

curs in these probes, from the phenolate oxygen to the heterocyclic nitrogen; the corresponding CT band is sensitive to the solvent, i.e., is solvatochromic [8]. An illustrative example is that of MePMBr₂, where at 25 °C $\Delta\lambda_{\max} = 625.8$ (dioxane) – 438.2 (water) = 187.6 nm [10]; this probe is red, yellow, pink, and blue in ethanol, water, acetone, and CH₂Cl₂, respectively. The transition energy of this CT is given by

$$E_T(\text{probe}), \text{kcal/mol} = 28591.5/\lambda_{\max}(\text{nm}) \quad (2)$$

$E_T(\text{probe})$ is an empirical solvent polarity scale; for the probes depicted in Fig. 4, these scales are referred to as $E_T(30)$; $E_T(\text{MePM})$; $E_T(\text{QB})$; $E_T(\text{MePMBr})$; $E_T(33)$; and $E_T(\text{MeQMBR}_2)$, respectively. The effect of solvents on $E_T(\text{probe})$ is an example of SDP, for which eq. 1 applies, after dropping the cavity term, because the Frank–Condon principle is obeyed during the transition ground state \rightarrow excited state, i.e.:

$$E_T(\text{probe}) = \text{constant} + a \alpha_S + b \beta_S + s(\pi^*_S + d\delta) \quad (3)$$

Equation 3 can be divided into contributions from solvent “acidity”, α_S ; “basicity”, β_S ; and dipolarity/polarizability, π^*_S , by use of RB and pairs of homomorphic probes (molecules that have the same, or closely related geometry), e.g., 4-nitroaniline and *N,N*-diethyl-4-nitroaniline; 4-nitrophenol, and 4-nitroanisole, etc. Values of λ_{\max} of the CT bands of these probes in the appropriate solvents are determined; after the latter are converted into frequencies, ν , they are manipulated mathematically in order to calculate the solvatochromic parameter of interest. For example, π^*_S can be calculated by relating the values of (ν) in the solvent to those in cyclohexane and dimethyl sulfoxide (DMSO), respectively. The same approach and indicators are employed for the determination of acidity, basicity, and dipolarity/polarizability of binary solvent mixtures. Compilations of these solvatochromic parameters can be found elsewhere [8,9]. Catalán and coworkers have introduced a set of solvatochromic parameters; each relies on the use of a single homomorphic pair, instead of several solvatochromic probes, as in the TKA approach [12]. Our recent study on the solvatochromic behavior of the probes shown in Fig. 4 has indicated that the use of Catalán’s parameters offers no advantage over those of TKA, and leads to unexplained decrease in susceptibility toward solvent dipolarity/polarizability [10]. It would be interesting to compare the correlations of a large number of SDP with both sets of solvatochromic parameters.

INFORMATION FROM SOLVATOCHROMIC DATA

Equation 3 can be employed to determine the relative contribution (or importance) of solvent properties to a particular SDP. As an example of the latter, consider the probes shown in Fig. 4. Their exci-

tation from a predominantly zwitterionic structure to a predominantly diradical structure leads to a large change in the dipole moment, hence in the polarity of the molecule. Therefore, the effects of solvents on $E_T(\text{probe})$ can be employed as a simple, and extremely convenient, model for the same effects on other SDP, in particular reactions where there is a large difference in polarity between the ground and excited state. An analysis of the spectroscopic data of 21 probes has indicated that solvation depends on their molecular structures. For examples, the solvation of RB, WB, and QB is adequately described by a two-term version (α_S and π^*_S) of eq. 3; solvent acidity is statistically more important than its dipolarity/polarizability. On the other hand, the solvation of the homologous series of probes RPMBr_2 , where R was increased from methyl to 1-octyl is sensitive to α_S and π^*_S , and $\log P$, again with predominance of solvent acidity. This sensitivity to solvent lipophilicity has led to the introduction of a new version of eq. 3 with $\log P_S$ substituting β_S . Probes that carry a relatively acidic hydrogen, e.g., 4-nitrophenol, 4-nitro-*N*-methylaniline, and 3-methyl-4-nitroaniline are biased toward solvent basicity [13].

Additional information can be obtained by correlating the regression coefficients of the TKA equation with the physicochemical properties of the probes, in particular their $\text{p}K_a$ in water, because of the importance to solvation of hydrogen-bonding to the phenolate oxygen of the probe [14]. This approach has been recently applied to the probes of Fig. 4. The regression coefficients (a) for each pair of probes of similar $\text{p}K_a$, QB, MePMB, and WB, MePMB $_2$ were found to be similar. The exception is the pair RB and MePM; the former is less susceptible to solvent acidity, because of the severe crowding around its phenolate oxygen. Although they belong to different chemical classes, a linear correlation has been found between their dipole moments and the regression coefficients (s) of solvent dipolarity/polarizability. Excellent correlations were found for the structurally related probes, MePM, MePMB, and MePMB $_2$, as shown by the following equations, where (r) is the correlation coefficient [10]:

$$\text{p}K_a \text{ in water} = 8.401 - 1.575 (\text{number of Br atoms}) \quad r = 0.99758 \quad (4)$$

$$\Delta G_{\text{solvation, Water}} = -13.898 - 0.705 (\text{number of Br atoms}) \quad r = 0.9999 \quad (5)$$

$$(a) = 0.933 - 0.06 (\text{number of Br atoms}) \quad r = 0.9954 \quad (6)$$

$$(s) = 0.568 + 0.055 (\text{number of Br atoms}) \quad r = 0.9673 \quad (7)$$

$$\text{ratio of } (a/s) = 0.9788 + 0.6819 e^{-(\text{number of Br atoms}/1.8418)}, \quad r^2 = 1 \quad (8)$$

Equation 4 shows that the introduction of (electron-withdrawing) bromine atoms leads to a systematic decrease of the $\text{p}K_a$ of the probe in water, by 1.575 $\text{p}K_a$ units/Br atom. The excellent correlation coefficient of eq. 5 is satisfying because the free energy of solvation in water was theoretically calculated by use of the equation: $\Delta G_{\text{solvation}} = \Delta G_{\text{electrostatic}} + \Delta G_{\text{dispersion-repulsion}} + \Delta G_{\text{cavity}}$. Equations 6 and 7 show that the introduction of the bromine atoms has decreased the susceptibility of the probe toward solvent acidity, and increased it toward solvent dipolarity/polarizability. The result of the opposing effects of the bromine atoms on the $\text{p}K_a$ (a decrease) and dipole moment (an increase) is that the ratio of (a/s) decreases smoothly by a first-order exponential decay, as shown by eq. 8. This type of analysis should lead to a much clearer understanding of the dependence of solvation on the physicochemical properties of the species of interest and the properties of solvents. Additional information that can be obtained from the use of probes is deduced from the study of thermo-solvatochromism, i.e., effects of temperature on solvatochromism; this is discussed below.

SOLVATION IN BINARY SOLVENT MIXTURES

Binary mixtures of liquids are very practical solvents because the properties of the medium, in particular its solvation power, can be "fine tuned" by changing its composition. The following discussion is concerned with binary mixtures of water with an organic solvent, or an IL. Much less work has been

carried out on solvation by ternary mixtures, the results also indicate preferential solvation of the probe [15], *vide infra*. Solvation by binary solvent mixtures is complex because the dependence of medium properties, e.g., density, polarity, surface tension, viscosity, etc., on its composition is rarely ideal; Fig. 5 is an example.

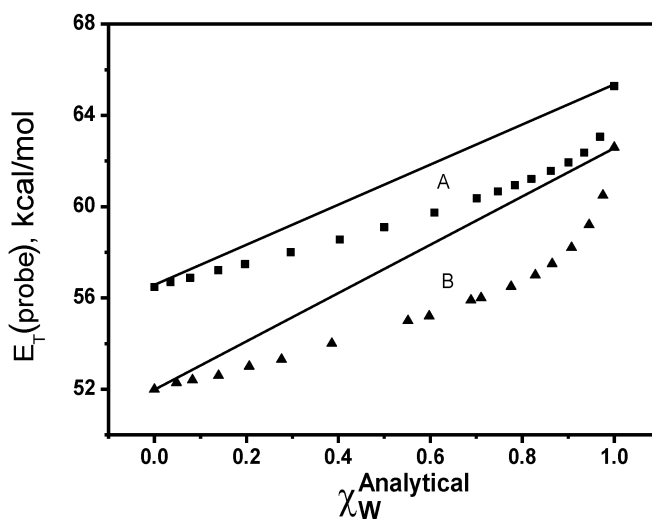


Fig. 5 Dependence of $E_T(\text{probe})$ on the analytical mole fraction of water, $\chi_W^{\text{analytical}}$, at 25 °C, for mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate with water. The straight lines were plotted to guide the eye, they represent ideal solvation of the probe by the mixture. The curves are for RB (A; ■) and MePMBr₂ (B; ▲). In order to avoid overlap of some data points, all $E_T(\text{MePMBr}_2)$ were decreased by 0.5 kcal/mol.

The reason for non-ideality is that most binary mixtures are micro-heterogeneous, as exemplified by the sequence of events that occur when acetonitrile, MeCN, is mixed with water. When the organic solvent is added, it replaces the uncoordinated water molecules. The limit of χ_W beyond which MeCN cannot be accommodated within the cavities of water is $\chi_W \approx 0.85$. Below this value, solvent micro-heterogeneity sets in, and there exists two “microdomains”, one highly structured consisting predominantly of coordinated water molecules, and a relatively disordered one containing mostly MeCN, hydrogen-bonded to water. Addition of more MeCN leads to a change in the relative concentrations of the two microdomains but their compositions do not vary appreciably. At $\chi_W \leq 0.3$, the water clusters have become few and so far apart that new interactions set in. W-MeCN interactions become important, this results in the formation of complexes, e.g., $(\text{MeCN})_m\text{-W}$ where $m = 1$ to 4. At still lower χ_W values, the structure of MeCN dominates, and species such as $(\text{MeCN})_m$ are abundant. It should be borne in mind, however, that the onset of formation of the different regions is not sharp, and is dependent on the method used to study the binary mixture [16,17].

The most important consequence of micro-heterogeneity of binary and tertiary solvent mixtures is that the composition, hence the polarity, of the solvation shell of the species of interest; probe, reactant or transition state is different from that of bulk solvent. That is, there is almost always a preferential solvation by one of the components of the mixture. Understanding and quantifying preferential solvation is important for reactions that are sensitive to medium polarity. For example, in mixtures of water and alcohols, the preferential solvation is by the organic component. Consequently, it is advantageous to carry out S_N2- or E2-type reactions in aqueous 1-propanol than in aqueous methanol, because preferential solvation is stronger by the former alcohol, leading to less solvation of the attacking (ionic) base/nucleophile.

The use of probes has led to a better understanding of preferential solvation. An “inventory” is carried out for the molecules that exist in the solvation shell of the probe. We have shown that it is realistic to treat an aqueous binary mixture as composed of W, S, and the “complex” hydrogen-bonded solvent species S-W [3a]. The 1:1 stoichiometry is a convenient working assumption that makes calculations of solvent exchange equilibria tractable. Solvent species with stoichiometry other than 1:1 may be treated, to a good approximation, as mixtures of the 1:1 structure plus excess solvent (S or W) [18]. The validity of this assumption is based on the fact that the 1:1 model has been successfully employed to fit the data of spectroscopic techniques that are particularly suitable to determine the stoichiometry of S-W aggregates; including the dependence on [W] of ^1H NMR chemical shifts; the IR wave number and peak width at half-height of $\tilde{\nu}_{\text{OH}}$ of water [19]. Additionally, using ^1H NMR spectroscopy, the stoichiometry of mixtures of dipolar aprotic solvents and water has been calculated; both 1:1 and 2:1 S-W complexes were considered. The ratios K_{1-1}/K_{2-1} were found to be 10, 26, and 132 for acetone, MeCN, and DMSO, respectively [20]. Thus, the assumption of 1:1 stoichiometry is convenient and is based on spectroscopic data; its appropriateness has been successfully tested for many binary mixtures of water with protic and aprotic solvents, and an IL (1-butyl-3-methylimidazolium tetrafluoroborate) [3,10,13].

Based on this approach, the following solvent exchange equilibria can be written [21]:



The values of the equilibrium constants of eq. 9, at different temperatures, have been conveniently determined from density measurements [21]. The equilibrium constants for eqs. 10–12 have been termed solvent “fractionation factors”, φ ; and are given by $\varphi_{\text{W/S}}$ (water substituting the organic solvent), $\varphi_{\text{S-W/S}}$ (complex solvent substituting the organic solvent), and $\varphi_{\text{S-W/W}}$ (complex solvent substituting water), respectively. The occurrence of preferential solvation can be inferred from the values of these equilibrium constants. For example, $\varphi_{\text{W/S}} < 1$ means that the solvation shell is richer in (S) than bulk solvent; the converse is true for $\varphi_{\text{W/S}} > 1$, i.e., the probe is preferentially solvated by water. A solvent fractionation factor of unity indicates an ideal behavior, i.e., the solvation shell and bulk solvent have the same composition. The same line of reasoning applies to $\varphi_{\text{S-W/S}}$ and $\varphi_{\text{S-W/W}}$, respectively. For example, $\varphi_{\text{S-W/W}} > 1$ means that the complex solvent is more efficient than water in solvating the probe.

The conclusions of several studies of binary mixtures at different temperatures, i.e., thermosolvatochromism, are the following [3,10,13,21]: Preferential solvation is always by (S) and (S-W), the latter is much more efficient than the former. The reason that $\varphi_{\text{W/S}} < 1$ is that the solvation of the probes by water is mainly due to hydrogen bonding to the phenolate oxygen. On the other hand, alcohols can solvate the probes by hydrogen-bonding and by solvophobic interactions. The efficiency of (S-W) in displacing both W and S depends on the $\text{p}K_{\text{a}}$ of the protic solvent, its lipophilicity, and the molecular structure of the probe. For example, for several probes, $\varphi_{1\text{-propanol-W}/1\text{-propanol}}$ and $\varphi_{1\text{-propanol-W/W}}$ are larger than the corresponding values for aqueous methanol, although the latter alcohol is a stronger acid in water ($\text{p}K_{\text{a}} = 15.5$) than the former one ($\text{p}K_{\text{a}} = 16.1$). The only exception is aqueous DMSO; the efficiency of DMSO-W in displacing the precursor solvents is noticeably less than the corresponding efficiency of mixtures of water and other aprotic solvents, e.g., acetone-W. This may be attributed to the fact that the interaction of DMSO with W is very strong; this attenuates the solvation efficiency of DMSO-W [22].

Figure 6 shows a typical solvent polarity-temperature-solvent composition contour for MePMBr_2 in mixtures of water and the IL 1-butyl-3-methylimidazolium tetrafluoroborate, in the temperature range from 10 to 60 °C. These contours are similar to those observed for binary mixtures of water with protic or with aprotic solvents [21,22]. The preferential solvation by the less polar components, IL and

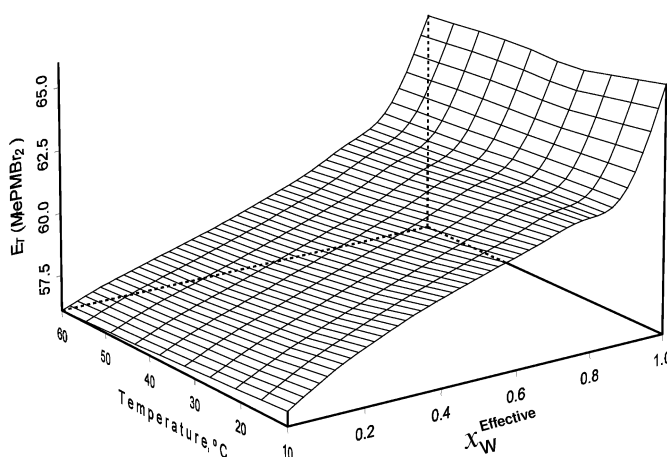


Fig. 6 Solvent polarity-temperature-solvent composition contour for MePMBr₂ mixtures of water and the IL 1-butyl-3-methylimidazolium tetrafluoroborate, in the temperature range from 10 to 60 °C, taken from [3b].

IL-W, is evident, as well as the gradual decrease in $E_T(\text{probe})$ as a function of increasing the temperature. The reason is that increasing temperature perturbs the structure of the binary mixture, leading to a decreased interaction with the ground state of the probe.

The relevance of thermo-solvatochromism to chemical kinetics is the following: Although desolvation of reactants and activated complexes is known to contribute to temperature effects on reaction rates, there is no obvious way to calculate its contribution to ΔH^\ddagger from the Arrhenius plot. This desolvation energy is readily calculated from thermo-solvatochromism. Our results have shown that the magnitude of this energy, expressed as ΔE_T , is sizeable (e.g., range from 2.1 to 3.7 kcal mol⁻¹ over a 50 °C range for WB in aqueous alcohols) relative to the activation enthalpies of many organic reactions [23]. ΔE_T for IL-W is less, ca. 0.54–1.2 kcal/mol over a 50 °C range, because the binary solvent is more structured than, say, an aqueous alcohol. Therefore, the interactions with the probe ground state are less affected by temperature increase [3].

The examples given at the beginning of this account are now addressed. As stated, the structure of the transition state for the hydrolysis of 4-nitrophenyl chloroformate is independent of the molarity of water. Thus, the (nonlinear) dependence of (k_{obs}) on [W] reflects the response of the reaction to the changes in the structure, at the microscopic level, of the binary mixture as a function of increasing [W]. The curve for H2 of Fig. 2 indicates a decrease in the partial positive charge on the hydrogens of the imidazolium ring, due to L₂O-mediated hydrogen-bonding. The change in the slope of the curve for HOD indicates that another mechanism is operative, whose effect on $\Delta\delta_{\text{obs}}$ does not vary (increase or decrease) in a systematic manner as a function of increasing χ_{L_2O} , but becomes important at χ_{L_2O} of ca. 0.73, i.e., probably when micro-heterogeneity of the IL-W binary mixture sets in [3a]. Figure 3 is interesting because it is an example of “probes” (native and mercerized celluloses) whose response to the solvent is largely controlled by the accessibility of their functional groups, namely, the OH groups of the anhydroglucose units. Mercerization leads to a decrease in crystallite size, increase in pore volume, and increase in disorder of the hydroxymethyl groups of cellulose. Additionally, this treatment leads to the transformation of cellulose I to cellulose II, the latter has less inter-crystalline hydrogen bonding [6]. Thus the supramolecular structure of mercerized cellulose is more accessible to the solvent; this leads to less sensitivity to solvent properties, relative to its native counterpart [7].

CONCLUSIONS

The effects of solvents and solvent mixture on distinct chemical phenomena can be rationalized by a common reasoning, namely, analysis of the solvent effects in terms of a linear combination of properties such as solvent acidity, basicity, dipolarity/polarizability, and lipophilicity. Evaluation of the relative importance of these interactions requires studying the solvatochromism of probes of adequate structure, e.g., the series RPMBr₂, where the pK_a is kept constant while the hydrophobic character is increased. Solvatochromism and thermo-solvatochromism in binary solvent mixtures can be described by a general mechanism, based on solvent exchange equilibria between the species present in solution (W, S, and S-W, respectively) and their counterparts in the probe solvation shell. All probes studied are preferentially solvated by S and, much more efficiently by S-W; DMSO-W is an exception. The contributing interactions are hydrogen-bonding to the phenolate oxygen and solvophobic interactions. Values of E_T(probe) decrease as a function of increasing the temperature because of effects of the latter on the structures of water and the organic component, and on their mutual interactions. The dependence of E_T(probe) on the composition of the binary mixture, the properties of the probe, and the temperature can be fruitfully employed in order to better explain reactivity data, e.g., the (complex) dependence on medium composition of rate constants and activation parameters. Studies of solvatochromism and thermo-solvatochromism are becoming increasingly important because of the current interest in the use of "green" solvents, e.g., supercritical CO₂ [24a] and ILs [24b].

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