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Characterization of binary solvent mixtures: the water–acetonitrile mixture

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Binary mixtures of water and acetonitrile (W/AN) were characterized in the light of the pure solvent scales, using suitable probe/homomorph couples. Various thermodynamic (vapour pressure, softness parameter, excess molar Gibbs energy and enthalpy of mixing) properties, surface tension, viscosity, and spectroscopic (IR, Raman and NMR) properties of the mixtures, and the distribution of molecular structures (*viz.* free CH_3CN and $CH_3CN–H_2O$ complexes) are described in terms of their polarity, acidity and basicity, and the descriptions examined in relation to a potential physical significance.

Introduction

The obvious interest of water as a solvent, its efficiency in solvating ionic and dipolar solutes, and its poor ability to solvate non-polar molecules, have fuelled vast efforts to understand the properties of aqueous solutions. These properties of water have a large bearing on biological systems and other chemical systems of practical significance, and are related to the highly associating nature of this solvent through its ability to form hydrogen bonds.[1] This type of interaction results in a structure of liquid water the boundary image of which is ice. The structure of liquid water is believed to be significantly altered on mixing with another substance. This concept has gradually evolved to what is currently known as the "hydrophobic effect".[2,3] Hydrophobic interactions can be of two types, namely: hydrophobic hydration of the solute (*i.e.* iceberg formation) and hydrophobic association of the solute molecules. As shown below, water–acetonitrile (W/AN) mixtures have been the subject of much interest and controversy in this context.

W/AN mixtures are a recurring reaction medium in physical organic chemistry,[4] play a central role in atmospheric chemistry,[5] are an effective choice for recovering charged ion-pair complexes that cannot be extracted into conventional organic solvents such as trichloromethane,[6] and have gained practical significance through use in reversed-phase liquid chromatography (RPLC).[7] While acetonitrile is completely water-soluble throughout the mole fraction range, it appears to form heterogeneous mixtures with water, the physico-chemical properties of which suggest that they consist of structurally different regions. The nature of the structural changes potentially occurring when the mixture composition is altered has been discussed in detail.[1,8–20]

In the early 1980s, authors seemingly agreed that W/AN mixtures comprised various composition regions.[8–11] In such regions, structural changes in the mixture are induced on raising its acetonitrile content. Thus, acetonitrile molecules added to water were assumed to occupy cavities in the water network structure, which remained intact while the cavities were filled. At a 15–20 mol% content of acetonitrile, the water became saturated with it and further addition triggered a marked structural change.

In 1981, Balakrishman and Easteal[12] reasoned that, because acetonitrile was less polar than pure water, the "polarity" of the mixture should decrease upon addition of former and would be dictated by the fact that the water molecule was more polar in isolation than as a part of a cluster. In order to confirm this hypothesis, they estimated the "polarity" of W/AN mixtures using Dimroth and Reichardt's $E_T(30)$ probe.[21] The description derived from the behaviour of this probe seemingly supported the hypothesis and led them to infer the presence of two "microphases" in the mixture, namely: a highly structured microphase consisting predominantly of water (denoted by α), in which all water molecules were coordinated, and a disordered microphase, β, containing mostly acetonitrile. Based on excess volumes, viscosity, dielectric constants and acid–base properties, Douhéret *et al.*[10,22–24] inferred the presence of three structurally different regions over the W/AN mixture composition range. The bounds for such regions, in mole fractions of acetonitrile, were $0 \le x \le 0.2$, $0.2 \le x \le 0.75$ and $0.75 \le x \le 1.0$.

The literature contains abundant, significant spectroscopic information about W/AN mixtures. Based on Raman spectroscopic results, von Kabisch[25] concluded that acetonitrile does not stabilize the water structure over the range $0 \le x_{AN} \le 0.2$. Kamogawa and Kitagawa,[13] Rowlen and Harris,[14] Gorbunov and Naberukhin,[26] Jamroz *et al.*,[16] and Bertie and Lan[17] found evidence of structural changes in W/AN mixtures. Takamuku *et al.*[20] contributed an interesting bank of IR, UV–Vis and X-ray spectroscopic data. Thus, they determined the O–D and $C\equiv N$ stretching frequencies with a view to establishing the distribution of free acetonitrile and W/AN complexes. Also, they contributed UV–Vis spectroscopic information for the whole composition range that they determined using the $E_T(30)$ and Z scales. Based on X-ray data, they found each molecule in pure acetonitrile to interact with two nearest neighbours via antiparallel dipole–dipole interaction, and also a small shift in the two molecular centres and two acetonitrile molecules in the second-neighbour shell to interact with a central molecule through parallel dipole–dipole interaction. Thus, acetonitrile molecules were alternately aligned, forming a zigzag cluster. Venables and Schmuttenmaer[19] found a loss in tetrahedral water structure upon mixing; however, water molecules have a strong tendency to aggregate, especially in mixtures with acetonitrile.

Based on careful analysis of reported thermodynamic information, Marcus and Migron[15] determined Taft and Kamlet[41]'s parameters α, β and π^* and concluded that acetonitrile is solvated by water at low acetonitrile mole fractions, that microheterogeneity sets in above $x_{AN} = 0.22 \pm 0.11$ and that discrete complexes of water with one or two acetonitrile molecules exist at high acetonitrile concentrations. Above an acetonitrile mole

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fraction of 0.95, the mixture inclines towards the structure of neat acetonitrile and contains the 1 : 1 H_2O–AN complex as solute.

If one accepts that W/AN mixtures are highly structured in water- and AN-rich regions, and that raising the proportion of either component in them results in marked destructuring, then those descriptions assuming that the two components interact with each other by forming a complex must be reconsidered-notwithstanding the accurate description of surface tension thus obtained by Cheong and Carr,[27] or that of $E_T(30)$ reported by Skwierczynski and Connors.[28]

W/AN mixtures have also been examined in molecular dynamic simulations. Thus, Kovacs and Laaksonen[29] and Mountain[30] concluded that these mixtures exhibit microheterogeneity. Venables and Schmuttenmaer[19] found increased structuring in the mixtures relative to ideal ones but no evidence of microheterogeneity.

In summary, the abundant, varied experimental information available on the thermodynamic (p_v, mixing excesses, Marcus softness[31]) properties, viscosity, surface tension, and spectroscopic (IR, NMR, UV–Vis) properties of W/AN mixtures as determined by analysing signals of either their own components (ν_{OH}, ν_{CN}, δ_N) or molecular probes [$E_T(30)$, Z, δ_{Xe}] dissolved in them, was examined in this work with a view to characterizing the mixtures in the light of the pure solvent scales.

Specifically, we characterized the W/AN mixtures by their acidity (SA), basicity (SB) and dipolarity/polarizability (SPP), using a previously reported approach that has so far provided excellent results in the interpretation of the properties of binary solvent mixtures, the solvolysis kinetics of *tert*-butyl chloride,[32] the decarboxylation of 3-carboxybenzisoxazoles[33] and the characterization of solvent mixtures of DMSO with water and other cosolvents,[34] as well as in the study of the preferential solvation model.[35]

The acidity, basicity and dipolarity/polarizability of W/AN mixtures must be the result of molecular interactions in their bulk; consequently, they could be of assistance in interpreting changes in their physical properties with the mole fraction. In this work, the W/AN mixture was characterized in this respect in the light of the pure solvent scales recently developed by our group.[36–40]

The pure solvent scales were established from suitable probe/homomorph couples. Thus, the dipolarity/polarizability scale of a pure solvent can be characterized in terms of the solvatochromism of the probe 2-dimethylamino-7-nitrofluorene and its homomorph 2-fluoro-7-nitrofluorene: SPP values range from 0 in the absence of solvent (*i.e.* the gas phase) to 1 for DMSO.[36] The SB scale is based on the solvatochromism of the probe 5-nitroindoline and its homomorph 1-methyl-5-nitroindoline; SB values range from 0 for the gas phase to 1 for tetramethylguanidine.[39] Finally, SA is evaluated from the solvatochromism of the probe *o-tert*-butylstilbazolium betaine dye and its homomorph *o,o′*-di-*tert*-butylstilbazolium betaine dye, and encompasses values from 0 for the gas phase to 0.4 for ethanol. The acidity of solvents more acidic than methanol (SA = 0.605) is evaluated by applying the solvent comparison method[41] to solvatochromic measurements of the probe 3,6-diethyl-1,2,4,5-tetrazine.[40]

In principle, any molecular property of a mixture can be analysed by using an equation of the type

$$P = s\mathrm{SPP} + a\mathrm{SA} + b\mathrm{SB} + P_0 \qquad (1)$$

where SPP, SB and SA are typical of the mixture; and coefficients s, a and b pertain to the property in question (P) and describe its sensitivity to the dipolarity/polarizability, basicity and acidity, respectively, of the mixture. The use of eqn. (1) in applying the pure solvent scales is discussed elsewhere;[42] the three scales are linearly independent.

Experimental section

All solvents used were of the highest available purity and purchased from Merck in Uvasol or similar grade. Solvent mixtures were prepared from freshly opened bottles, using Brand II 25.00 mL burettes to transfer the liquids.

Polarity (SPP) and basicity (SB) values were obtained from the wavenumbers of the absorption maxima for the probe/homomorph couple 2-dimethylamino-7-nitrofluorene/2-fluoro-7-nitrofluorene[36,37] and 5-nitroindoline/1-methyl-5-nitroindoline,[39] respectively. The acidity (SA) of the W/AN mixture was estimated by using 3,6-diethyl-1,2,4,5-tetrazine[40] over the $0.0 \leq x_{AN} \leq 0.7$ range and pyridazine[34] over the $0.7 \leq x_{AN} \leq 1.0$ range.

UV–Vis measurements were made on a Shimadzu 2100 spectrophotometer the monochromator of which was calibrated by using the 486.0 and 656.1 nm lines from a deuterium lamp. The instrument was routinely checked for wavelength accuracy by using holmium oxide and didymium filters. All spectral measurements were made at 25 °C, using a matched pair of quartz cells of 1 cm light path.

SA, SB and SPP data were fitted using the multiparameter analysis software MINITAB,[43] which provided an equation containing the previous three parameters as variables.

Results and discussion

Characterization of the W/AN mixture

Fig. 1 shows the variation of the polarity, acidity and basicity of the W/AN mixture throughout the mole fraction range. As can be seen, the three parameters exhibit a non-ideal behaviour. Thus, SB exhibits positive deviations from linearity throughout the mole fraction range, whereas SPP exhibits negative deviations. The most salient behaviour, however, is that of SA, which exhibits negative deviations over the range $0.0 \leq x_{AN} \leq 0.53$ and positive ones at $0.53 \leq x_{AN} \leq 1.0$.

The dipolarity/polarizability (SPP) of the mixture behaves quite acceptably for two solvents of virtually identical polarity (0.895 and 0.962). Thus, as acetonitrile is added to water, SPP initially decreases and reaches the value for acetonitrile at an

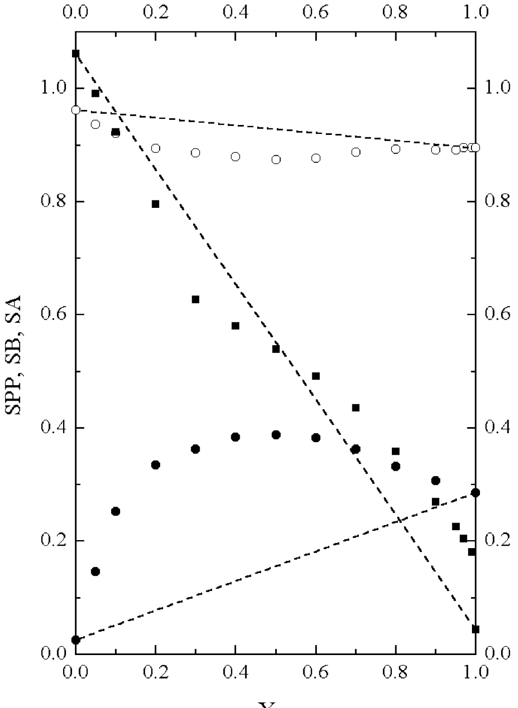

Fig. 1 Plot of the SPP (○), SB (●) and SA (■) parameters against the mole fraction X_{AN} for the water/AN mixture.

AN mole fraction as low as 0.2; it then continues to rise as the AN mole fraction is increased, to a minimum (SPP = 0.875) around $x_{AN} = 0.5$. Further enrichment with acetonitrile shifts the polarity of the mixture towards that for neat acetonitrile, where it levels off over the range $0.75 \le x_{AN} \le 1.0$. Notwithstanding the above-described changes, all mixtures are highly polar, with SPP values between those for water (0.962) and acetonitrile (0.895).

The basicity (SB) of the mixture is invariably higher than the ideal value. The departure is maximal around an AN mole fraction of 0.3. The basicity rises gradually as water is added, from the value for pure AN (SB = 0.286), which is not regained up to $x_{AN} = 0.13$. Further water addition causes it to drop to the virtually negligible value for water (SB = 0.025).

The acidity of the mixture varies in a manner that depends on whether AN or water predominates in its composition. With AN as the major component, the acidity exhibits positive deviations from the ideal behaviour that are maximal over the range $0.80 \le x_{AN} \le 0.99$. On the other hand, with water as the major component, the acidity exhibits negative deviations, with a maximal departure around $x_{AN} = 0.3$. It should be noted that the inversion with respect to the ideal behaviour occurs at a *quasi*-equimolar fraction (*viz.* $x_{AN} = 0.53$). As can be seen from Fig. 1, the acidity of the mixture decreases strongly as acetonitrile is added to pure water in the region $0.0 \le x_{AN} \le 0.3$, it then, continues diminishing over the range $0.3 \le x_{AN} \le 0.98$, beyond which it drops abruptly to the value for pure acetonitrile (SA = 0.044).

From Fig. 1 it clearly follows that SA, SB and SPP for W/AN mixtures do not change monotonically between the values for pure water (SA = 1.062, SB = 0.025, SPP = 0.962) and acetonitrile (SA = 0.044, SB = 0.286, SPP = 0.895); rather, they seem exhibit three different variation patterns corresponding to as many regions. Thus, in the water-rich region ($0 \le x_{AN} \le 0.3$), the acidity of the mixture decreases by 43% of the difference between the two pure solvents, and so does its polarity (by 115% of the difference between the two neat solvents); by contrast, the basicity of the mixture increases by 141% of the difference between the values for water and acetonitrile. In the acetonitrile-rich region ($0.8 \le x_{AN} \le 1.0$), the mixture polarity remains constant while its basicity increases slightly and its acidity drops abruptly at an acetonitrile mole fraction around 0.99. In the intermediate region, the polarity of the mixture remains virtually constant but slightly below that for the less polar pure component, the acidity decreases very strongly but in a monotonic manner, and the basicity remains above the value for the more basic solvent throughout the composition range.

Because W/AN mixtures contain an extremely acid solvent (water) and a negligibly acid one (acetonitrile), they can be used to span the whole solvent acidity range simply by changing their mole fraction. Also, their acidity may be associated to their water character and their basicity to their acetonitrile character, whether the two mixture components occur in isolation or as complexes.

The behaviour of SA, SB and SPP illustrated in Fig. 1 departs strongly from that observed by Marcus and Migron,[15] who found the following: (a) the polarity of the mixture decreased monotonically between π^* for water (1.14) and acetonitrile (0.73); (b) its acidity varied in three distinct regions between α for water (1.13) and acetonitrile (0.31), with a water-rich ($x_{AN} \le 0.2$) and an acetonitrile-rich region ($0.7 \le x_{AN}$) where the acidity decreased, and an intermediate region ($0.2 \le x_{AN} \le 0.7$) where the acidity remained virtually constant; (c) its basicity decreased only slightly, from the value for water ($\beta = 0.52$) to that for acetonitrile ($\beta = 0.47$). Obviously, the pure solvent scales provide an interpretation of the behaviour of both W/AN mixtures and its pure constituents that departs markedly from that based on the Taft and Kamlet scales.[15]

Let us now examine the potential structural implications of the changes in the SA, SB and SPP values for W/AN mixtures with their composition. The following conclusions can be drawn as regards the structural behaviour of the mixtures in the water-rich region: (*a*) the dramatic decrease in acidity of the mixture upon addition of acetonitrile suggests that, contrary to the widespread belief, acetonitrile molecules do not occupy available cavities in the water structure (and interact weakly with it), but rather must interact highly effectively with it and decrease the number of water sites responsible for the acidity of the mixture (whether these occur on the surface of the water structure or, more likely, as free water); and (*b*) the fact that the addition of acetonitrile raises the basicity and lowers the polarity of the mixture to values close to those for neat acetonitrile suggests that, in this region, free acetonitrile or the complexes formed endow the mixture with basicity and polarity similar to those of pure acetonitrile. The facts that the basicity in the intermediate region is higher than that of the more basic component and that the polarity decreases below that for pure acetonitrile allow us to conclude that the structures involved are rather different from those in the water- and acetonitrile-rich regions.

Once SA, SB and SPP for the W/AN mixture have been examined, let us analyse other properties in the light of the multiparameter eqn. (1) with a view to establishing the potential physical significance of its fitting coefficients.

Thermodynamic properties

In 1987, French[44] measured the vapour pressure (P_v) at 308.15 K for 22 different W/AN mixtures and the two pure solvents, and found the results to depart strongly from the ideal values.

$$P_v/\text{kPa} = (187.5 \pm 95.2)\text{SPP} + (72.7 \pm 19.6)\text{SB} - (5.3 \pm 1.7)\text{SA} - (168.9 \pm 90.5) \quad (2)$$

Eqn. (2) accurately reproduces the vapour pressure of the mixture ($n = 24$, $r = 0.977$, sd = 1.03 kPa, $F = 139.3$) in terms of its polarity, basicity and acidity.

In a mixture such as this, where the two components possess a virtually identical dipolarity/polarizability, one can expect changes in surface tension, γ, to be governed by specific interactions between the components. This is, in fact, the case, as shown by eqn. (3),

$$\gamma^{25^\circ\text{C}}/\text{dyn cm}^{-1} = -(85.8 \pm 10.8)\text{SB} + (11.4 \pm 4.9)\text{SA} + (54.1 \pm 6.0) \quad (3)$$

which reproduces the behaviour of the data measured by Cheong and Carr[27] with $n = 13$, $r = 0.967$, sd = 3.7 dyn cm^{-1} and $F = 71.8$. Based on this equation, the surface tension of the mixture decreases with increasing basicity (*i.e.* with increasing acetonitrile character) and increases with increasing acidity (*i.e.* with increasing water character).

In theory, the viscosity of a mixture should increase with increasing interaction between its components. The equation

$$\eta^{20\ ^\circ\text{C}}/\text{P} = (396.7 \pm 312.50)\text{SB} + (917.9 \pm 122.2)\text{SA} + (109.2 \pm 154.6) \quad (4)$$

reproduces the viscosity values for the W/AN mixture measured by Vierk[45] with $n = 12$, $r = 0.948$, sd = 94.8 P and $F = 39.7$. Consequently, increasing the basicity and, especially, the acidity of the mixture, increases its viscosity.

The mixing process is energetically similar to dissolution, so it encompasses a non-negligible energy term that arises from the cohesive energy of the liquid mixture involved in the formation of a cavity. The variation of this property cannot be accurately described if such a contribution is ignored. Because the cohesive energy for each mixture was unknown, we approximated it to the boiling point (bp), the values for which were taken from the literature.[46]

Let us analyse some thermodynamic properties of interest for this mixture. One of the thermodynamic properties of the W/AN mixture most strongly deviating from ideality is the excess molar Gibbs energy, G. Based on eqn. (5),

$$G/\mathrm{J\,mol^{-1}} = -(30500 \pm 3929)\mathrm{SPP} + (1533.8 \pm 144)\mathrm{SA} + (2004 \pm 1379)\mathrm{bp} + (25673 \pm 2548) \qquad (5)$$

which reproduces the experimental results with $n = 24$, $r = 0.957$, sd = 139 J mol^{-1} and $F = 71.3$, the Gibbs energy of mixing for the W/AN mixture comprises an endothermic contribution corresponding to the formation of a cavity and an exothermic one encompassing general and specific interactions between the mixture components.

Surprisingly, the enthalpy of mixing of the W/AN mixture cannot be accurately described by this procedure throughout the mole fraction range; however, for such a wide range as that spanning acetonitrile mole fractions from 0 to 0.7 (*i.e.* most of the water-rich region), the enthalpy of mixing is highly accurately described by the following equation:

$$H/\mathrm{J\,mol^{-1}} = -(2809 \pm 919)\mathrm{SPP} - (1837 \pm 81)\mathrm{SA} + (1143 \pm 252)\mathrm{bp} + (3515 \pm 612) \qquad (6)$$

which reproduces the experimental results with $n = 47$, $r = 0.997$, sd = 31.29 J mol^{-1} and $F = 2099$. The enthalpy of mixing of the W/AN mixture comprises an endothermic contribution corresponding to the formation of a cavity and an exothermic one encompassing general and specific interactions between the mixture components. This result confirms that the addition of acetonitrile to water does not merely result in the occupation of cavities in the water structure and virtually no interaction with it, and also that, only when such cavities are filled up with acetonitrile molecules do they interact with the water structure and destroy it.

The composition region excluded in the previous analysis, $0.7 \le x_{\mathrm{AN}} \le 1.0$, can also be accurately described. However, as can be inferred from eqn. (7)

$$H/\mathrm{J\,mol^{-1}} = (8677 \pm 1028)\mathrm{SB} + (1555 \pm 364)\mathrm{SA} - (2555 \pm 516) \qquad (7)$$

which reproduces the experimental results with $n = 14$, $r = 0.988$, sd = 66 J mol^{-1} and $F = 226$, only the specific terms are significant, and the cavity term is not, which suggests that the zigzag structures of acetonitrile may form cavities to accommodate water molecules.

In 1994, Marcus[47] used the softness parameter, μ, for the W/AN mixture to deviate from the ideal behaviour in the region around $x_{\mathrm{AN}} = 0.2$, where the microheterogeneous mixture of the two components regains microscopic homogeneity, acetonitrile molecules taking up voids in the structured water. Marcus used three different ions (*viz.* silver, sodium and potassium) as probes to measure μ and determined the standard molar Gibbs energy of their transfer from water into the mixture, expressed in kJ mol^{-1}. The softness parameter is given by

$$\mu/\mathrm{kJ\,mol^{-1}} = \{\Delta_{\mathrm{tr}}G^0(\mathrm{Ag^+}) - [\Delta_{\mathrm{tr}}G^0(\mathrm{Na^+}) + \Delta_{\mathrm{tr}}G^0(\mathrm{K^+})]/2\}/100 \qquad (8)$$

The μ values for the W/AN mixture shown in Fig. 4 of the paper by Marcus[47] are described in terms of SA, SB and SPP by eqn. (9)

$$\mu/\mathrm{kJ\,mol^{-1}} = (3.15 \pm 1.14)\mathrm{SPP} + (0.77 \pm 0.25)\mathrm{SB} - (0.35 \pm 0.02)\mathrm{SA} - (2.66 \pm 1.09) \qquad (9)$$

with $n = 12$, $r = 0.993$, sd = 0.01 kJ mol^{-1} and $F = 189.5$. As can be seen from Fig. 1, the acidity is the most significant fitting term, so much so that the softness of the W/AN mixture is described by an equation based on acidity alone

$$\mu/\mathrm{kJ\,mol^{-1}} = -(0.33 \pm 0.02)\mathrm{SA} + (0.39 \pm 0.01) \qquad (10)$$

with $n = 12$, $r = 0.983$, sd = 0.02 kJ mol^{-1} and $F = 281.5$.

This result seriously questions the physical significance of the softness parameter for the W/AN mixture.

Spectroscopic properties

Let us begin by analysing the spectroscopic signals for the mixture components, which are bound to provide information about the structural changes observed as the mixture composition is altered.

In 1965, Loewenstein and Margalit[48] determined the chemical shift for the ^{14}N resonance in acetonitrile as a function of its mole fraction in W/AN mixtures of variable composition. The equation

$$\delta^{14}\mathrm{N/ppm} = (33.7 \pm 19.9)\mathrm{SPP} + (10.9 \pm 1.4)\mathrm{SA} + (72.9 \pm 17.3) \qquad (11)$$

reproduces the behaviour of δ ^{14}N with $n = 10$, $r = 0.979$, sd = 0.88 ppm and $F = 81.7$.

In 1986, Kamogawa and Kitagawa[13] reported the observed frequency shift, $\Delta\nu_{\mathrm{obsd}}$, for C–H vibrations in AN

$$\Delta\nu_{\mathrm{obsd}}/\mathrm{cm^{-1}} = -(4.86 \pm 0.37)\mathrm{SB} + (3.25 \pm 0.13)\mathrm{SA} + (0.74 \pm 0.18) \qquad (12)$$

reproduces their experimental results with $n = 14$, $r = 0.997$, sd = 0.1 cm^{-1} and $F = 982.6$. They resolved their $\Delta\nu_{\mathrm{obsd}}$ values into two contributions arising from perturbations of other acetonitrile molecules in the mixture ($\Delta\nu_{\mathrm{AA}}$) and those of water molecules ($\Delta\nu_{\mathrm{AB}}$)

$$\Delta\nu_{\mathrm{AA}}/\mathrm{cm^{-1}} = -(34.87 \pm 1.73)\mathrm{SB} + (9.67 \pm 0.63)\mathrm{SA} + (8.29 \pm 0.85) \qquad (13)$$

reproduces the experimental results with $n = 14$, $r = 0.997$, sd = 0.46 cm^{-1} and $F = 878$. On the other hand, eqn. (14)

$$\Delta\nu_{\mathrm{AB}}/\mathrm{cm^{-1}} = (13.70 \pm 6.24)\mathrm{SPP} + (3.07 \pm 0.63)\mathrm{SA} - (11.95 \pm 5.33) \qquad (14)$$

reproduces them with $n = 14$, $r = 0.951$, sd = 0.4 cm^{-1} and $F = 51.6$.

In 1998, Takamuku *et al.*[20] reported the stretching frequencies for the O–D bond in water and the C≡N bond in acetonitrile throughout the composition range of the W/AN mixture. Eqn. (15)

$$\nu(\mathrm{O{-}D})/\mathrm{cm^{-1}} = -(293.0 \pm 39.9)\mathrm{SA} + (2808.0 \pm 24.7) \qquad (15)$$

reproduces the experimental results with $n = 11$, $r = 0.926$, sd = 36.7 cm^{-1} and $F = 51.6$, and eqn. (16)

$$\nu(\mathrm{C{\equiv}N})\ (\mathrm{cm^{-1}}) = (7.51 \pm 1.02)\mathrm{SA} + (2252.3 \pm 0.6) \qquad (16)$$

with $n = 11$, $r = 0.925$, sd = 0.81 cm^{-1} and $F = 53.6$. Including basicity and polarity in eqns. (15) and (16) results in no appreciably improved fitting ($r = 0.939$ and 0.940, respectively).

Both vibrations are subject to similar effects from their environment.

Takamuku *et al.*[20] used the previous spectroscopic data to estimate the proportion of acetonitrile molecules remaining free [*i.e.* uncomplexed, $\mathrm{CH_3CN_{(free)}}$] in the mixture and that of molecules bound to water (*i.e.* complexed, $CH_3CN–H_2O$) throughout the mole fraction range. The following equation

$$\mathrm{CH_3CN(free)} = (21.1 \pm 11.7)\mathrm{SPP} + (12.0 \pm 4.1)\mathrm{SB} - (2.1 \pm 0.38)\mathrm{SA} - (20.8 \pm 11.6) \quad (17)$$

reproduces the proportion of free acetonitrile with $n = 10$, $r = 0.975$, sd = 0.12 and $F = 38$, and

$$\mathrm{CH_3CN–H_2O} = -(2.49 \pm 1.06)\mathrm{SB} + (3.37 \pm 0.23)\mathrm{SA} - (0.24 \pm 0.43) \quad (18)$$

that of complexed acetonitrile/water with $n = 9$, $r = 0.990$, sd = 0.14 and $F = 147$.

Let us now analyse the spectroscopic information available for the molecular probes (Xe, bis-(2,4-pentanedionato)oxovanadium(IV) {VO(acac)$_2$}, 2,6-diphenyl-4-(2,4,6-triphenylpyrido)phenoxide {$E_T(30)$} and 1-ethyl-4-(methoxycarbonyl)-pyridinium iodide ion-pair {Z}added to W/CH_3CN mixtures.

In 1984, Stengle *et al.*[49] introduced the chemical shift for Xe as a probe for the hydrophobic effect and measured it throughout the mole fraction range for the W/AN mixture.

$$\delta^{124}\mathrm{Xe/ppm} = -(21.47 \pm 2.08)\mathrm{SA} - (172.3 \pm 1.56) \quad (19)$$

Eqn. (19) reproduces their experimental results with $n = 11$, $r = 0.960$, sd = 0.60 ppm and $F = 107$. This questions whether δ^{124}Xe can accurately describe the hydrophobic effect in this mixture.

In 1998, Takamuku *et al.*[20] characterized the W/AN mixture in terms of $D_{II,I}$,[50] which reflects both electron-donating ability and electron-accepting ability of a solvent molecule; this parameter is related to solvation of both oxygen and vanadium atoms within the VO(acac)$_2$ complex by acceptor and donor atoms in the solvent molecules, respectively.

$$D_{\mathrm{II,I}}/\mathrm{kJ\ mol^{-1}} = (30.17 \pm 2.41)\mathrm{SA} + (33.56 \pm 1.50) \quad (20)$$

Eqn. (20) reproduces the experimental results of $D_{II,I}$ with $n = 11$, $r = 0.972$, sd = 2.23 kJ mol^{-1} and $F = 156$.

Two well-known molecular environment probes, *viz.* Kosower's Z[51] and Dimroth and Reichardt's $E_T(30)$,[21] have been used to characterize the W/AN mixture.[12,20,28,52,53] The following equations fit the solvatochromism of these probes to the pure solvent parameters:

$$Z/\mathrm{kcal\ mol^{-1}} = (17.23 \pm 3.17)\mathrm{SB} + (24.51 \pm 1.13)\mathrm{SA} + (65.20 \pm 1.45) \quad (n = 11,\ r = 0.992,\ \mathrm{sd} = 0.89\ \mathrm{kcal\ mol^{-1}},\ F = 259) \quad (21)$$

$$\mathrm{E_T(30)/kcal\ mol^{-1}} = (13.79 \pm 0.46)\mathrm{SA} + (47.31 \pm 0.31) \quad (n = 75,\ r = 0.961,\ \mathrm{sd} = 1.1\ \mathrm{kcal\ mol^{-1}\ and}\ F = 881). \quad (22)$$

We should note that these equations introduce some novelties in relation to the behaviour of the probes towards pure solvents. Thus, based on eqn. (21), the solvatochromism of Z depends only on SA and SB, whereas that of pure solvents depends additionally on SPP.[42] Whereas based on eqn. (22), the solvatochromism of $E_T(30)$ depends on SA only, whereas that of pure solvents depends additionally on SPP.[42]

Conclusions

As shown in this work, the solvents scales are efficient tools with a view to characterizing binary mixtures of solvents. The absence of methods allowing the SA, SB and SPP values for a solvent mixture to be estimated from those for the pure solvents calls for experimental measurements of the mixture. These parameters provide interesting information about the molecular interactions that govern the properties of the mixtures. The proven fact that accurately describing the enthalpy of mixing in the mole fraction range $0.0 \leq x_{AN} \leq 0.6$ entails using cavity terms questions the widespread belief that, in the water-rich region, acetonitrile molecules added to water occupy cavities in its structure. The favourable results obtained for this mixture encouraged us to address alcohol/water mixtures, which have so far provided highly interesting but as yet uninterpreted results in relation to protein folding.[54–60]

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