Preferential Solvation of Silver(I), Copper(I) and Copper(II) Ions in Aqueous Acetonitrile

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The preferential solvation of Ag^+, Cu^+ and Cu^{2+} ions in the mixed solvent water + acetonitrile has been examined on the basis of spectroscopic and other relevant data from the literature and calculated according to the quasi-lattice quasi-chemical method. This study confirms that the monovalent ions are strongly preferentially solvated by the acetonitrile component of the mixtures, whereas the divalent ion is strongly preferentially solvated by the water component.

The phenomenon of preferential solvation of a solute in a mixed solvent is well known, and it has important implications regarding the chemical, kinetic, thermodynamic, spectroscopic and other properties of the system. This is true, of course, also in the case where the solute is an ion, and a great variety of information is available in the literature concerning the preferential solvation of ions in binary mixtures of solvents, generally where one of the components is water. Some information has also been published concerning the structure and other properties of the binary solvent mixtures themselves, and this is the case in the present instance, dealing with mixtures of water and acetonitrile.[1] Such mixtures were shown to have a potential application in the hydrometallurgy (or better, solvatometallurgy) of silver and copper.[2] This application is due to the preferential solvation of silver(I) and copper(I) ions by acetonitrile and of copper(II) and other base-metal ions by water in such mixtures. However, the quantitative description of this preferential solvation has so far been incomplete, and it is the purpose of the present paper to provide a fuller description.

The specification of the number and distances (and orientations) of the solvent molecules, both those acting as ligands around the central metal ion and the more remote ones that still affect its properties in the solution, would constitute a complete description of the preferential solvation. Such information could, eventually, be obtained from neutron diffraction measurements on isotopically substituted species in the solution, but such measurements have not yet been feasible. As a first step, the numbers of ligand-solvent molecules in the first solvation shell around the central cation can be accepted as an approximation to the complete description. This requires knowledge of the total co-ordination number of the cation and of the local mole fraction of one of the solvents in the first solvation shell as functions of the bulk composition of the solvent. A further compromise is made when it is assumed that if the co-ordination number is the same in both the pure solvents, then it would also be the same in the mixtures.

The quasi-lattice quasi-chemical (QLQC) method provides the means for the calculation of the local mole fraction $x^L_{A(S)}$ of solvent component A (in a mixture of solvents A + B) around the solute S, based on thermodynamic data.[3] Necessarily, $x^L_{A(S)} + x^L_{B(S)} = 1$, and if $Z_A = Z_B = Z$ is the co-ordination number of S, then the numbers of A and B solvent ligands are $n_{A(S)} = x^L_{A(S)}Z$ and $n_{B(S)} = x^L_{B(S)}Z$, respectively. The following set of equations leads to values of $x^L_{A(S)}$. There are N_{AS} neighbouring pairs of solvent A and solute S and N_{BS} neighbouring pairs of solvent B and solute S, so that equation (1) can be written. Each

$$x^L_{A(S)} = N_{AS}/(N_{AS} + N_{BS}) = 1/(1 + N_{AS}/N_{BS}) \quad (1)$$

of the quantities N_{AS} and N_{BS} can be expressed by the quasi-chemical formula,[3] *e.g.* equation (2) for N_{AS}. Hence, we obtain

$$N_{AS} = 2\,N_{AA}^{\frac{1}{2}}\,N_{SS}^{\frac{1}{2}} \exp(\Delta e_{AS}/2kT) \quad (2)$$

expression (3). The interaction-energy difference $\Delta e_{ter} = (\Delta e_{BS} -$

$$x^L_{A(S)} = 1/[1 + (N_{AA}/N_{BB})^{\frac{1}{2}} \exp(\Delta e_{ter})] \quad (3)$$

$\Delta e_{AS})/2kT$ equals the difference in the standard molar Gibbs energies of transfer of S from some reference solvent W (which could be one of the two components of the mixture, *e.g.* water) to the two solvents: $\Delta_{tr}G^\circ(S, W \longrightarrow A)$ and $\Delta_{tr}G^\circ(S, W \longrightarrow B)$, divided by $2ZRT$.[3] This quantity thus depends strongly on the properties of the solute S with respect to its interactions with the two individual solvents A and B. On the other hand, the ratio N_{BB}/N_{AA} depends only on the properties of the binary solvent system, equations (4) and (5) where $S = N_{AA} + N_{BB} + N_{AB}$ (at

$$N_{BB}/N_{AA} = [(x_B - N_{AB}/2S)/(x_A - N_{AB}/2S)] \quad (4)$$

$$N_{AB}/2S = (1 - \{1 - 4x_Ax_B[1 - \exp(-\Delta e_{AB}/kT)]\}^{\frac{1}{2}})/2[1 - \exp(-\Delta e_{AB}/kT)] \quad (5)$$

infinite dilution of the solute S), *i.e.* the total number of neighbours of all kinds, equation (6) where $G^E_{AB}(x = 0.5)$ is the

$$\exp(\Delta e_{AB}/kT) = \{2\exp[-2G^E_{AB}(x = 0.5)/ZRT] - 1\}^2 \quad (6)$$

excess molar Gibbs free energy of mixing of the two solvent components *in the absence of the solute* at the equimolar composition.[3] The quantities that are required for the complete evaluation of the dependence of the local composition near the solute on the bulk composition of the solvent mixture are, thus, $\Delta_{tr}G^\circ(S, W \longrightarrow A)$, $\Delta_{tr}G^\circ(S, W \longrightarrow B)$ and $G^E_{AB}(x = 0.5)$, and the lattice constant (co-ordination number) Z.

Once the local solvent composition is known from this calculation, the resulting effects on other properties, such as the dependence of $\Delta_{tr}G^\circ(S, W \longrightarrow A + B)$ or spectral properties of the solutions on the bulk solvent composition, can be evaluated and compared with the experimentally determined quantities. This comparison is a check on the applicability of the QLQC method with the model on which it is based to the present instances, as well as a rationalization of the observed thermodynamic and spectral data.

The Data Employed

The relevant co-ordination number of Ag^+ ions is $Z = 4$, both for aqueous solutions[4] and for solutions in acetonitrile.[5] No direct structural information is available concerning the co-ordination number of Cu^+ in solutions, but it can be safely assumed that $Z = 4$ also for this cation, in analogy with Ag^+. In the gas phase, the four-co-ordination of Cu^+ with water is somewhat more pronounced than that of Ag^+.[6] The Cu^{2+} cation in aqueous solution under the Jahn–Teller effect has a total co-ordination number of $Z = 6$, but has four short and two long bonds to the water molecules.[7] No direct structural information on the co-ordination number of Cu^{2+} in acetonitrile is available, but the spectroscopic evidence[8] (see below) is compatible with $Z = 6$ in this solvent too.

For the purpose of equation (3), $\Delta e_{ter} = \Delta_{tr}G°(S, W \longrightarrow MeCN)/2ZRT$, where W is water and MeCN is acetonitrile. The standard molar Gibbs free energy of transfer $\Delta_{tr}G°$ of the ions $S = Ag^+$, Cu^+ or Cu^{2+} from water to pure acetonitrile was reported by many authors in several publications and was summarized by the present author.[9] In these latter summaries, values were 'selected', representing the weighted average of the more reliable data that are consistent with the TATB extrathermodynamic assumption, *i.e.* that $\Delta_{tr}G°(AsPh_4^+) = \Delta_{tr}G°(BPh_4^-)$ for transfer of these tetraphenyl ions between any two solvents. These values pertain to 298.15 K and to the mol dm^{-3} (molar) concentration scale, as do the data shown below. It was stressed, however, that such selections were open to revision in the light of additional information.

The value $\Delta_{tr}G°(Ag^+, W \longrightarrow MeCN) = -31.4$ kJ mol^{-1} was obtained from the transfer activity coefficients reported by Parker and Alexander[10] for the transfer of Ag^+ from methanol to water and to acetonitrile. This was later revised by Parker and his co-workers to ≈ -22 kJ mol^{-1}. The value -23.2 kJ was selected[9] as the weighted average of several further reported data, but it appears that the earlier value, *i.e.* -31.4 kJ mol^{-1} is more consistent with other data, including those discussed in the present work.

Only one value $\Delta_{tr}G°(Cu^+, W \longrightarrow MeCN)$ was reported in the review,[9b] but several values have been published or can be derived (-47.7,[11a] -48.1,[11b] -48.6,[11b,c] -50.0,[11d,e] -50.4[11f] kJ mol^{-1}) from the work of independent authors. The difference between $\Delta_{tr}G°(Cu^+, W \longrightarrow MeCN)$ and $\Delta_{tr}G°(Ag^+, W \longrightarrow MeCN)$, however, is -30.5 kJ mol^{-1},[11b] and this quantity is independent of the extrathermodynamic assumption employed [it pertains, *e.g.*, also to $\Delta_{tr}G°(CuCl, W \longrightarrow MeCN) - \Delta_{tr}G°(AgCl, W \longrightarrow MeCN)$[12]], hence is more reliable than the individual ionic values. If this difference is deducted from the average, -49 kJ mol^{-1}, of the values reported for $\Delta_{tr}G°(Cu^+)$, the much too low value of -18.5 kJ mol^{-1} is obtained from $\Delta_{tr}G°(Ag^+)$. If this difference is added to the tentatively accepted value of -31.4 kJ mol^{-1} for $\Delta_{tr}G°(Ag^+)$, the value -62 kJ mol^{-1} is obtained for $\Delta_{tr}G°(Cu^+)$. This point is elaborated further in the Discussion.

The values reported for $\Delta_{tr}G°(Cu^{2+}, W \longrightarrow MeCN)$ cover a considerable range: 50,[11e] 53.0,[11c] 55.2,[11b] 59.4,[11a] and 68.0[2,11d] kJ mol^{-1}. It is difficult to select among them, but the higher values appear to be more consistent with the other information discussed in the present paper. It is significant that whereas $\Delta_{tr}G°(Cu^+)$ and $\Delta_{tr}G°(Ag^+)$ are negative, $\Delta_{tr}G°(Cu^{2+})$ is positive. The monovalent d^{10} ions prefer the acetonitrile, whereas the divalent d^9 ion prefers water. As is discussed below, this pertains not only to the energetics regarding the pure solvents but also to the near environment of these ions in the mixtures.

Standard molar Gibbs free energies were also reported by several authors for the transfer of the ions Ag^+, Cu^+ and Cu^{2+} from water to mixtures of water with acetonitrile at 298.15 K, on the mol dm^{-3} scale, and compatible with the TATB assumption. The relative values, *i.e.* $\Delta_{tr}G°(S, W \longrightarrow W + MeCN)/\Delta_{tr}G°(S, W \longrightarrow MeCN)$, reported by the different authors are shown in Figs. 1–3 as functions of the composition of the solvent mixture.

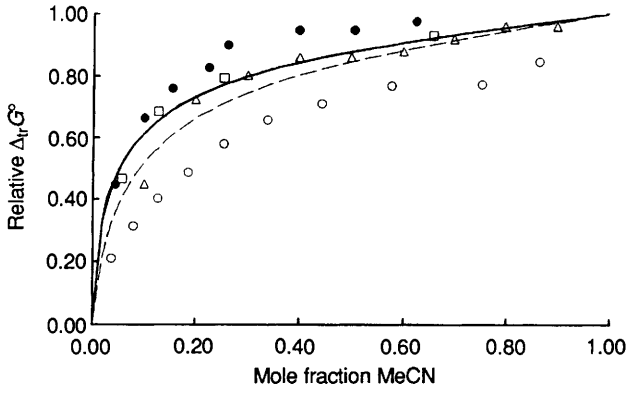

Fig. 1 The relative $\Delta_{tr}G°(Ag^+, W \longrightarrow W + MeCN)/\Delta_{tr}G°(Ag^+, W \longrightarrow MeCN)$ for transfer of silver ions from water to aqueous acetonitrile: (□) ref. 11*d*; (△) ref. 13*a*; (○) ref. 13*b*; (●) ref. 11*b*. Calculated from the QLQC model: ——, with $\Delta_{tr}G°(Ag^+, W \longrightarrow MeCN) = -31.4$ kJ mol^{-1}; – – – –, with $\Delta_{tr}G°(Ag^+), W \longrightarrow MeCN) = -23.2$ kJ mol^{-1}

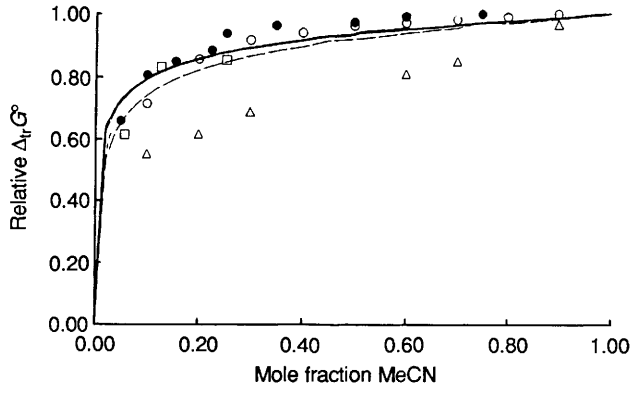

Fig. 2 The relative $\Delta_{tr}G°(Cu^+, W \longrightarrow W + MeCN)/\Delta_{tr}G°(Cu^+, W \longrightarrow MeCN)$ for transfer of copper(I) ions from water to aqueous acetonitrile: (□) ref. 11*d*; (△) ref. 11*f*; (○) ref. 11*a*; (●) ref. 11*b*. Calculated from the QLQC model: ——, with $\Delta_{tr}G°(Cu^+, W \longrightarrow MeCN) = -62$ kJ mol^{-1}; – – – –, with $\Delta_{tr}G°(Cu^+, W \longrightarrow MeCN) = -49$ kJ mol^{-1}

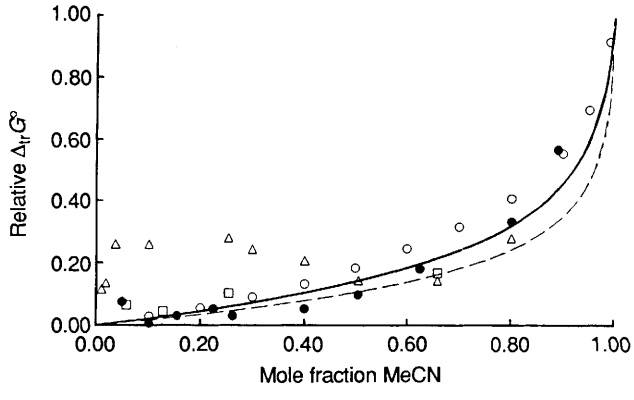

Fig. 3 The relative $\Delta_{tr}G°(Cu^{2+}, W \longrightarrow W + MeCN)/\Delta_{tr}G°(Cu^{2+}, W \longrightarrow MeCN)$ for transfer of copper(II) ions from water to aqueous acetonitrile: (□) ref. 11*d*; (△) ref. 11*e*; (○) ref. 13*a*; (●) ref. 11*b*. Calculated from the QLQC model: ——, with $\Delta_{tr}G°(Cu^{2+}, W \longrightarrow MeCN) = 50$ kJ mol^{-1}; – – – –, with $\Delta_{tr}G°(Cu^{2+}, W \longrightarrow MeCN) = 68$ kJ mol^{-1}

These data provide direct information on the preferential solvation of the ions by the two solvents. Unfortunately, the agreement between the different sets of data for a given ion is rather poor.

Additional information is derived from spectroscopic data. NMR chemical shifts δ (in ppm *vs.* an external standard) of the

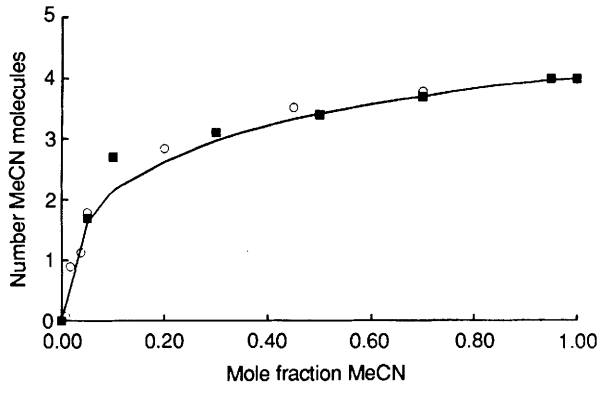

Fig. 4 The number of nearest-neighbour acetonitrile molecules near silver ions in aqueous acetonitrile solutions as obtained from proton NMR data of Schneider and Strehlow[14] (○) and of Cox *et al.*[11b] (■) and from the QLQC model (——) with $\Delta_{tr}G^{\circ}(Ag^{+}, W \longrightarrow MeCN) = -31.4$ kJ mol^{-1}

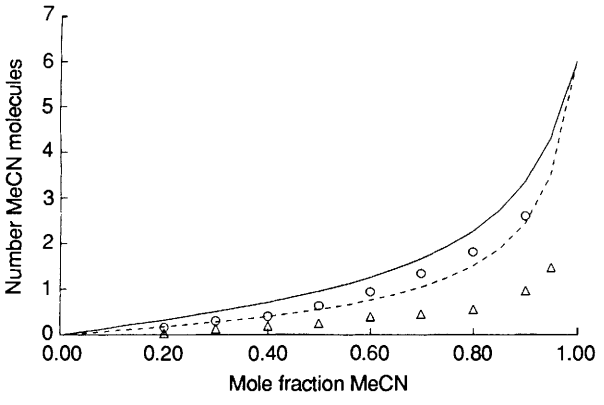

Fig. 5 The number of nearest-neighbour acetonitrile molecules near copper(II) ions in aqueous acetonitrile solutions as obtained from spectroscopic data[8] at 0.5 mol dm^{-3} (○), extrapolated to infinite dilution (△) and calculated from the QLQC model with $\Delta_{tr}G^{\circ}(Cu^{2+}, W \longrightarrow MeCN) = 50$ kJ mol^{-1} (——) and with $\Delta_{tr}G^{\circ}(Cu^{2+}, W \longrightarrow MeCN) = 68$ kJ mol^{-1} (– – – –)

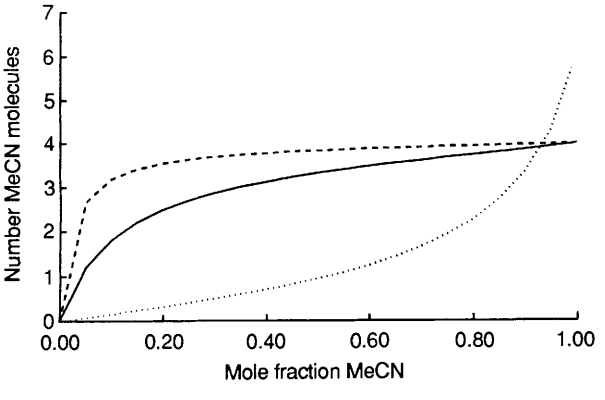

Fig. 6 The number of nearest-neighbour acetonitrile molecules near silver(I) (——), copper(I) (– – – –) and copper(II) (•••••) ions in aqueous acetonitrile solutions as obtained from the QLQC model

acetonitrile protons in aqueous acetonitrile containing silver(I) nitrate[14] or perchlorate[11b] have been determined. The relative shift, $\Delta\delta$, with respect to the solvent mixture without the salt is divided into the contributions from the acetonitrile molecules that are near the cation and those near the anion as in equation (7), where δ^{+} and δ^{-} are the shifts characteristic of acetonitrile

$$\Delta\delta = p^{+}\delta^{+} + p^{-}\delta^{-} \quad (7)$$

protons in the vicinities of the cation and anion, and p^{+} and p^{-} are the fractions of this solvent in the respective environments. It is assumed that δ^{+} and δ^{-} are not sensitive to the composition of the environment near the ions. They are obtained from data in pure acetonitrile containing the silver salt and in concentrated solutions of the silver salt in a relatively poorly solvating solvent containing a low concentration of acetonitrile. At a given constant concentration of the silver salt (0.5 mol dm^{-3}) the values of $\Delta\delta$ then lead to values of $n_{CH_3CN(Ag^{+})} = Zx^{L}_{CH_3CN(Ag^{+})}$, *i.e.* the number of acetonitrile molecules in the first co-ordination shell of the silver ions. The results are shown in Fig. 4 and are compared there with the results from the QLQC model.

Rather than NMR data for the protons of the acetonitrile, signals from ^{63}Cu and ^{65}Cu in solutions of copper(I) perchlorate were measured in aqueous acetonitrile.[15] However, quadrupolar line broadening permits the detection of the signal of only the highly symmetrical (presumed[16] tetrahedral) species $[Cu(CH_3CN)_4]^{+}$ but not of the less-symmetrical mixed solvent-ligand species. Even so, the presence of water in the mixtures causes line broadening and decreased intensities of the signals. A quantitative evaluation of the results in terms of the average environment of the copper ions was not attempted.[15]

The spectra of solutions of copper(II) perchlorate in aqueous acetonitrile were measured in the visible region (the electronic spectrum of Cu^{2+}) and in the infrared region (the O–D stretching of deuteriated water and the C–N stretching of acetonitrile).[8] The position of the band maximum in the visible spectrum changes with the composition of the solvent, but is independent of the copper concentration in dilute solutions. The infrared spectrum in the C–N stretching region shows a new band, at 2328 cm^{-1}, in the presence of Cu^{II} that is not seen in its absence. This is the wavenumber at which –C≡N polarized by cations absorbs.[17] The intensity of this band is proportional to the concentration of the acetonitrile that is bonded to the copper. Difference spectra were created in the O–D stretching region of the infrared, by subtracting the spectrum of acetonitrile containing 2 mole % water from the spectra of solutions containing also copper, weighted to obtain near zero absorbance at 2650 cm^{-1}. The absorbance at 2450 cm^{-1} is then assigned to $Cu^{2+} \cdots OD \cdots NCCH_3$ and is proportional to the concentration of such species.[8] The results, in terms of $n_{CH_3CN(Cu^{2+})} = Zx^{L}_{CH_3CN(Cu^{2+})}$ and $n_{H_2O(Cu^{2+})} = Zx^{L}_{H_2O(Cu^{2+})}$, are shown in Fig. 5 and are compared there with the results of the calculations by means of the QLQC model.

Discussion

Figs. 1–3 show that the QLQC model can represent the transfer data into the mixtures well, considering the scatter in the data originating from different publications. The calculated curves are sensitive to the value of $\Delta_{tr}G^{\circ}(S, W \longrightarrow MeCN)$ selected for obtaining Δe_{ter}, but not very strongly (they are more sensitive to the selected value of Z). The best fit in the case of the silver ions is between the curve calculated with $\Delta_{tr}G^{\circ}(Ag^{+}, W \longrightarrow MeCN) = -31.4$ kJ mol^{-1} and the data of Singh *et al.*[11d] and of Kundu and Parker.[13a] In the case of the copper(I) ions the best fit is between the curve with $\Delta_{tr}G^{\circ}(Cu^{+1}, W \longrightarrow MeCN) = -62$ kJ mol^{-1} and the data of Coetzee and Istone.[11a] In the case of copper(II) ions the best fit is between the curve with $\Delta_{tr}G^{\circ}(Cu^{2+}, W \longrightarrow MeCN) = 50$ kJ mol and the data of Cox *et al.*[11b] and of Coetzee and Istone,[11a] but even with these data the fit is not so good. The mutual agreement of these two sets of data is not very good either, however. A somewhat lower Δe_{ter} would have provided a better fit, but is incompatible with the data for transfer into pure acetonitrile, $\Delta_{tr}G^{\circ}(Cu^{2+}, W \longrightarrow MeCN)$.

On the whole, Figs. 1–3 show that the QLQC model is capable of describing the thermodynamic data for transfer, and therefore should also provide valid values of the local solvent composition near the ions according to equations (1)–(6). These

values, in the form of $n_{CH_3CN(Ag^+)}$, $n_{CH_3CN(Cu^+)}$ and $n_{CH_3CN(Cu^{2+})}$, are shown in Fig. 6. Specifically, in Fig. 4 the values of $n_{CH_3CN(Ag^+)}$ obtained from the QLQC model are compared with the values reported by Schneider and Strehlow[14] and by Cox *et al.*[11b] from their NMR data. The agreement is seen to be good. It should be noted, however, that the NMR data pertain to a moderate concentration (0.5 mol dm^{-3}) of the silver salts whereas the QLQC values, calculated from the thermodynamic transfer data, pertain to infinite dilution of the ions.

The comparison of the results for copper(II) solvation from the spectroscopic measurements[8] and the QLQC model presented in Fig. 5 shows, again, the difference between the solvation at finite concentrations and at infinite dilution. In this case measurements were made at several copper(II) concentrations, so that extrapolation of the spectroscopic data to infinite dilution could also be carried out. It is interesting that these data for infinite dilution represent considerably lower solvation by acetonitrile than those at 0.5 mol dm^{-3}, and that the latter are the ones that conform most closely to the predictions of the QLQC model, as Fig. 5 shows. Both the spectroscopic data and the model depend on the assumption that $Z = 6$ for the mixtures as well as for solutions in pure acetonitrile, but their detailed dependence on Z differs. A lower Z for the acetonitrile-rich solutions would bring the calculated curves nearer to the spectroscopic data extrapolated to infinite dilution. However, the molar absorptivity of the C≡N stretching peak at 2328 cm^{-1} is consistent with the value $Z = 6$ more than with, say, $Z = 4$, indicating, though not proving, that the choice of this value was reasonable.[8]

The solvation numbers by acetonitrile of Ag^+, Cu^+ and Cu^{2+} in the aqueous mixtures, shown in Fig. 6, confirm the earlier qualitative reports on the preferential solvation of these ions. It is not surprising that the d^{10} ions Cu^+ and Ag^+ are preferentially solvated by acetonitrile in the order shown. The back bonding from the metal orbitals to empty non-bonding π orbitals of the nitrile should depend on the electron density, which is larger in the smaller Cu^+. The distance of Cu^+ to the ligands acetonitrile and pyridine is shorter by 26 pm than the corresponding distance of Ag^+ and the standard enthalpy of solvation of Cu^+ in acetonitrile is more negative by 150 kJ mol^{-1} than that of Ag^+.[18] Still, there exists contradictory information concerning the geometry of the solvation shell around these ions in neat acetonitrile. The bonding does not seem to be along the C–C–N axis but rather so as to make the C≡N π-electron system available to the metal ion, *i.e.* this axis is perpendicular to the bond.[15,19] This does not tally with the X-ray diffraction results for Ag^+ (0.97 mol dm^{-3} silver perchlorate in acetonitrile),[5] that, furthermore, indicate tetrahedral geometry whereas electron-spin echo data from X-ray-irradiated frozen acetonitrile solution of silver perchlorate indicate a square-planar geometry.[19] The present approach cannot shed light on this problem.

Another point worth of note is that the structure of the aqueous acetonitrile medium itself[1] is not taken into account in the present considerations. The fact of the existence of a microheterogeneous structure over an intermediary range of compositions, say $x_{MeCN} = 0.2$–0.6, is not reflected in the experimental data shown in Figs. 4 and 5 as deviations from the smooth curve that the QLQC model prescribes. This model does not involve the structure of the mixed solvent beyond the magnitude of the positive Gibbs free energy of mixing at the equimolar composition (that no doubt depends on the micro-heterogeneity, but in an implicit manner). In this respect the insight that this model can provide is limited, but so is that provided by the presently available experimental data.

A minor point is that if the value of $\Delta_{tr}G^\circ(Ag^+, W \longrightarrow MeCN) = -31.4$ kJ mol^{-1} does indeed represent the Gibbs free energy of transfer of silver ions from water to acetonitrile, as tentatively emerges from the present work, better than the 'selected'[9] value of -23.2 kJ mol^{-1}, then the value for the softness parameter of acetonitrile[20] should be modified to $\mu = 0.43$ from the earlier value of 0.35. This is in the wrong direction, considering other measures of its softness, so that the less-negative value of $\Delta_{tr}G^\circ(Ag^+, W \longrightarrow MeCN)$ may, after all, be the better estimate.

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