^{109}Ag NMR-Study of the Selective Solvation of the Ag^+ Ion in Solvent Mixtures of Water and the Organic Solvents: Pyridine, Acetonitrile, and Dimethyl Sulfoxide

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In mixtures of water (W) and one of the organic solvents pyridine, acetonitrile, and dimethyl sulfoxide (O), the silver ion forms the following solvate complexes: AgW_2, AgWO, and AgO_2. The chemical shift of ^{109}Ag is strongly affected by the ligating solvent molecules, and replacing the ligand W by one of the three organic ligands yields a higher Larmor frequency. In solvent mixtures, only a single resonance line has been observed because of rapid chemical exchange. The measured chemical shifts in the range up to 400 ppm are mean values of the chemical shifts of the different solvate species in a given mixture, weighted with their relative concentrations.

The ^{109}Ag chemical shifts were determined for 0.05 to 0.15 molal solutions of $AgNO_3$, as functions of the mole fractions of the solvent components. Using a Gaussian least squares fitting routine, the individual chemical shifts of the Ag^+ solvate complexes and the corresponding equilibrium constants were determined. This fit was successful for the whole mole fraction range of DMSO, while in the solvent systems with acetonitrile and with pyridine at higher concentrations of the organic component the chemical shift is influenced by more than two solvent molecules. In these cases equilibrium constants were calculated from chemical shift data for solutions of low mole fraction of acetonitrile and pyridine.

1. Introduction

Only for small and highly charged metal ions the number of solvent molecules in the primary solvation shell has been determined from nuclear magnetic resonance measurements. When the exchange of solvent molecules between primary solvation shell and bulk solvent is sufficiently slow, the corresponding solvent resonance frequencies have been observed separately. In mixed solvents, the NMR spectrum shows simultaneously signals of bulk and bound molecules of each solvent component, and sometimes it is possible to differentiate between ionic solvation shells of different composition. However, for univalent ions in pure or mixed polar solvents, this differentiation is impossible even when suitable paramagnetic ions are added in order to enlarge the chemical shift between bulk and bound solvent signals or when the samples are cooled down to low temperatures. Nevertheless, it is reasonable to assume that also these ions possess a distinct primary solvation shell and that the solvent exchange between ionic solvation shell and bulk solvent is too fast for separate resonance lines to appear in the NMR spectrum of either the ligand molecules or the ionic entity itself. Then the measured chemical shift is a weighted average and its variation with solvent composition results from a series of competitive solvation equilibria [1, 2].

Nuclear magnetic resonance investigations of the solvate complexes of the silver ion in mixed solvents by ^{109}Ag NMR studies give essentially more information than NMR investigations of the ligand protons, as the variation in the chemical shift of the silver ion is by more than two orders of magnitude larger than that of protons [3]. However, considerable experimental difficulties are involved in silver NMR studies: Both silver isotopes, ^{107}Ag and ^{109}Ag, have the spin $I = 1/2$ and high natural abundances (51.3% and 48.7%, respectively), but very low magnetic moments. Therefore, at a given magnetic field B_0, their NMR receptivities with respect to that of the proton are 3.4×10^{-5} and 4.9×10^{-5}, respectively. The isotope ^{109}Ag was chosen for the present investigation because of its slightly higher

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receptivity. Besides of the low receptivity, additional difficulty in ^{109}Ag NMR measurements arises from the fact that this nucleus has an extremely long relaxation time. For example this is demonstrated by the ^{109}Ag relaxation times for a 1 molal aqueous $AgNO_3$ solution of $T_1 \approx 1000$ s and $T_2 \approx 150$ s [4]. Since the silver ions have spin 1/2 nuclei and their magnetic interactions with the surroundings are small, the widths of the recorded NMR lines are governed by the inhomogeneity of the magnetic field B_0 (described by a decay time constant T_2^*). This results in an enormous loss of NMR signal amplitude using cw-technique or pulse technique, which starts from the thermal equilibrium before each RF-pulse. Because of this, until now only samples with silver salt concentration of 1 M (doped with paramagnetic substances) or higher concentration have been investigated with conventional techniques [5–10]. The loss in intensity of the NMR signal due to inhomogeneity of B_0 can be completely avoided without addition of a paramagnetic substance by using a steady-state technique, *e.g.* the Quadriga-Fourier-Transform technique [11]. It has been shown recently [12] that the signal to noise ratio in experiments using this technique can be improved by a factor $(T_2/T_2^*)^{1/2}$ over the results from usual pulse-FT experiments which start from the (approximate) thermal equilibrium before each RF-pulse. In the case of relatively large samples, *i.e.* a short T_2^* value, which is ≈ 30 ms in the field of our magnet, the signals are improved by a factor $(T_2/T_2^*)^{1/2}$ of 50 to 100. This gain in sensitivity enables the investigation of samples of relatively low Ag concentration (0.05 M or less) in a comparatively short measuring time ($\leqq 12$ h). Therefore it is now possible to study quantitatively the preferential solvation of silver ions in mixed aqueous solvents from ^{109}Ag experiments, and to determine the formation constants K_i with $i = 1, 2, \ldots, n$ in the solvation equilibria

$$AgW_{n+1-i}O_{i-1} + O \overset{K_i}{\rightleftharpoons} AgW_{n-i}O_i + W \,. \qquad (1)$$

The charge of the solvates has been omitted in equations on grounds of simplification.

In several studies using different experimental methods it was shown that the coordination number of Ag^+ is probably $n = 2$ in water, acetonitrile, and pyridine [13]. This result is supported by investigations of the preferential solvation of Ag^+ in mixed solvents, which show that in the linear complex formed between Ag^+ and two ligating molecules, the bonds are much stronger than the interaction of Ag^+ with additional molecules.

In the present investigation, the chemical shift of $^{109}Ag^+$ in aqueous solutions of dipolar aprotic solvents O (= acetonitrile – AN, pyridine – Py and dimethyl sulfoxide – DMSO) has been determined as a function of solvent mole fraction and salt concentration. An attempt is made to explain these experimental shifts by such a competitive solvation equilibrium model on the basis of the coordination number $n = 2$ (the model on the basis $n = 1$ is included with $K_2 = 0$). The success or the failure of this model in explaining the experimental results will support or contradict the assumption $n = 2$.

Since there is a rapid chemical exchange between at most three silver solvate complexes in a given binary solvent mixture, the ^{109}Ag NMR spectrum consists of one line, in which the chemical shift is the mean value of the chemical shifts δ_i of the complexes $AgW_{2-i}O_i$ ($i = 0, 1, 2$), weighted with the concentrations of the complexes. From a sufficiently large set of measured chemical shifts of samples with different solvent composition and with different silver salt concentrations, formation constants K_1 and K_2 (1) and also the individual chemical shifts δ_i have been determined using a Gaussian least squares fitting routine.

2. Experimental

The silver isotope ^{109}Ag has a relatively small magnetic moment $\mu = -0.129\,961\,5\,(10)\,\mu_N$ [14] and a Larmor frequency $\nu_L(^{109}Ag) \approx 4.190$ MHz in the field of our apparatus, $B_0 = 2.114$ T (corresponding to 90 MHz proton Larmor frequency). On the assumption that the longitudinal and transverse relaxation times are equal, $T_1 = T_2$ (a condition, which was never fulfilled for any Ag^+ sample under investigation), the ^{109}Ag NMR signal of a 1 molar sample of an Ag^+ salt should be about 7 orders of magnitude weaker than the proton NMR signal of water in the same magnetic field B_0 and with the same probe volume. In general, beyond it, the intensity of the NMR signal is reduced by the factor $(T_2/T_1)^{1/2}$.

All ^{109}Ag NMR measurements were performed with a pulse spectrometer described in [15]. This apparatus was developed for investigations of very weak NMR signals in the frequency range 1 to 4.5 MHz. The magnetic field B_0 was produced by a

Bruker B-E 45 electromagnet, externally stabilized by the Bruker NMR stabilizer B-SN 15. The spatial homogeneity of $|\Delta B_0| \leqq 10^{-6}$ T in the range of the relatively large sample (20 mm internal diameter and 40 mm filling height) was achieved by 12-gradient electric shims. The temperature of the samples was stabilized to (300 ± 1) K by a thermostat.

The NMR signal between the RF-pulses was accumulated in a time-averaging computer (Signal Analyzer 5480 A of Hewlett-Packard) to improve the signal/noise-ratio. All functions of this time averaging computer as well as of the frequency synthesizer (Schomandl MG 520 M) were controlled by a PDP 11/04 computer and its clock. The data (1000 channels of 24 bits) were transferred to a PDP 11/45 computer via a coaxial line with a speed of 10^5 baud. The Quadriga-Fourier-transform was performed by this computer in the floating mode. For all measurements of the ^{109}Ag Larmor frequencies and chemical shifts, the Quadriga-Fourier-Transform technique [11] was used. The shape of the NMR absorption line, recorded with this steady-state technique is given by

$$I(\nu) \sim \sin\{2\pi T(\nu_L - \nu)\}/\{2\pi T(\nu_L - \nu)\},$$

where ν_L is the Larmor frequency and T the pulse period. By this technique, the NMR line is broadened to a halfwidth $\Delta\nu_{1/2} = 0.6/T$ by saturation. This linewidth is independent of the magnetic field B_0 and its inhomogeneity as well as of the natural linewidth, if T is chosen such that $T \ll T_2^*$, T_2, T_1. In this case any loss of NMR signal amplitude due to the inhomogeneity of B_0 can be avoided, without adding paramagnetic substances to the sample. For the present investigations, a pulse repetition rate $(1/T) = 83$ Hz was used; the resulting halfwidth of the NMR line is 50 Hz.

The measuring times were from 6 min for the reference sample to 12 h for the samples with the lowest Ag^+ concentrations (0.05 molal). To determine the chemical shifts, the sample replacement technique was used. The uncertainties of the measured chemical shifts (standard deviation) are in the range of ± 2 ppm for the lowest Ag^+ concentrations (0.05 molal) to ± 0.7 ppm for the highest Ag^+ concentrations (0.15 molal).

3. Samples

All samples were contained in cylinders of 20 mm internal diameter. The filling height was 40 mm corresponding to the hight of the sample coil. No corrections for bulk susceptibility were made, as for these samples the corrections are smaller than the statistical uncertainty.

The reference sample had the same size and shape as the samples under investigation; for all chemical shift measurements a reference sample was used, which corresponds to sample Ref. No. 3: 8.3 molal aqueous solution of AgF, used in previous investigations [3, 14, 16]. Its chemical shift of the ^{109}Ag Larmor frequency ν_{Ref} referred to the Larmor frequency ν_0 of the Ag^+ ion in H_2O at infinite dilution is

$$\delta\,(\text{Ref. }3) = (\nu_{Ref} - \nu_0)/\nu_0 = (14.0 \pm 1.5)\ \text{ppm}$$

measured at a temperature of (300 ± 1) K.

To prepare the samples for the present investigations, $AgNO_3$ (Merck No. 1512) of analytical grade and the following solvents were used: pyridine (Merck No. 9728)of analytical grade, acetonitrile (Merck No. 16, Uvasol), dimethyl sulfoxide (Merck No. 2950, Uvasol), and H_2O with a conductivity of less than $10^{-6}\ \Omega^{-1}\ \text{cm}^{-1}$. The concentrations m_{Ag} of the samples in moles $AgNO_3$ per kg solvent or solvent mixture were determined by weighing the salt and the solvents. To avoid precipitation of metallic silver by exposure to light, the samples were prepared in a room with dimmed light. The samples were filled in glass ampoules and sealed at once. The chemical shifts were determined immediately after the preparation of the samples.

4. Results

4.1. ^{109}Ag *Chemical Shift*

The ^{109}Ag chemical shifts were determined in 0.05, 0.07, 0.1 and 0.15 molal $AgNO_3$ solutions in solvent mixtures of water, W, and the organic solvents, O = Py, AN, and DMSO. The composition of the solvent mixtures is characterized by the mole fraction of the solvent components

$$X_O = m_O/(m_O + m_W)\,, \qquad (2)$$

where m_O and m_W are the molal concentrations of the organic solvents and of water, respectively. Without loss of generality, the chemical shift of the solvate complex AgW_2 has been taken as zero, $\delta_0 = 0$. This means that the resonance frequency of Ag^+ at infinite dilution in water is taken as reference frequency. The chemical shifts were calculated from the measured Larmor-frequency ν_{Ag} of the sample and the reference frequency ν_0:

$$\tilde{\delta}(X_{\mathrm{O}}, m_{\mathrm{Ag}}) = (\nu_{\mathrm{Ag}} - \nu_0)/\nu_0 .$$

These chemical shifts are mostly due to a change of the concentration of the species AgW_2^+, AgWO^+, and AgO_2^+ with their different ^{109}Ag chemical shifts δ_i $(i = 0, 1, 2)$; to a minor amount the measured shifts $\tilde{\delta}(X_{\mathrm{O}}, m_{\mathrm{Ag}})$ result from the concentration dependence of the chemical shifts of the individual species. For the complex AgW_2 in water, this concentration shift was studied in detail: For Ag$^+$ concentrations $m_{\mathrm{Ag}} < 1$ m, the ^{109}Ag chemical shift of aqueous AgNO_3 solutions is proportional to m_{Ag}:

$$\delta_m(m_{\mathrm{Ag}}) = (-15.0 \text{ ppm/mol/kg}) * m_{\mathrm{Ag}} .$$

This variation may be interpreted to be predominantly the influence of the nitrate anion on the chemical shift of AgW_2. In the organic solvents, a concentration dependence $\delta_m(m_{\mathrm{Ag}})$ of similar magnitude is observed.

In the concentration range $m_{\mathrm{Ag}} \leqq 0.15$ m used in the present investigation, this concentration dependence of the ^{109}Ag chemical shifts of the individual solvate complex AgW_2

$$|\delta_m| \leqq 2.25 \text{ ppm}$$

is of comparable magnitude to the experimental uncertainty ±1.5 ppm of the measured shifts. Therefore the same concentration dependence was assumed for all three species of solvate complexes, and all experimental chemical shifts have been corrected with $\delta_m(m_{\mathrm{Ag}})$:

$$\delta(X_{\mathrm{O}}, m_{\mathrm{Ag}}) = \tilde{\delta}(X_{\mathrm{O}}, m_{\mathrm{Ag}}) - \delta_m(m_{\mathrm{Ag}}) . \quad (3)$$

Now the corrected chemical shift $\delta(X_{\mathrm{O}}, m_{\mathrm{Ag}})$ depends only on the change in solvation of the silver ions as a function of solvent composition (X_{O}) and salt concentration (m_{Ag}), and it is zero in water for any silver concentration: $\delta(X_0 = 0, m_{\mathrm{Ag}}) \equiv 0$.

These chemical shifts are plotted versus mole fraction in Figs. 1a, 1b, and 1c for mixtures of water with Py, AN and DMSO, respectively. In mixtures with Py and AN, the chemical shift values were determined with particular accuracy for mole fractions $X_{\mathrm{Py}} \leqq 0.02$ and $X_{\mathrm{AN}} \leqq 0.1$, since in preliminary experiments it was shown that the chemical shifts determined for samples with higher mole fractions differ from values calculated with formation constants for solvent replacement equilibria, derived from experiments done at lower mole fractions. In mixtures of water and DMSO, the chemical shifts were confirmed in the total mole fraction range, $0 \leqq X_{\mathrm{DMSO}} < 1$.

4.2. Evaluation of Equilibrium Constants and Chemical Shifts of Solvate Complexes

The experimental data have been analyzed under the assumption that only a primary solvation of Ag$^+$ by two solvent molecules has to be taken into account. The chemical shift, corrected for the concentration dependence, $\delta(X_{\mathrm{o}}, m_{\mathrm{Ag}})$, is taken to be the average value of the intrinsic chemical shifts δ_i of the solvate complexes $\mathrm{AgW}_{2-i}\mathrm{O}_i^+$ with $i = 0, 1, 2$, weighted by the average concentration.

$$\delta(X_{\mathrm{O}}, m_{\mathrm{Ag}}) = \{\delta_1[\mathrm{AgWO}] + \delta_2[\mathrm{AgO}_2]\}/m_{\mathrm{Ag}} \quad (4)^*$$

The concentrations of the various solvate species are interrelated by the mass balance equations for salt, water and organic component i.e. by the two equilibria (1) with the corresponding equilibrium constants

$$K_i = \frac{[\mathrm{AgW}_{2-i}\mathrm{O}_i]\,\gamma_i\,\gamma_i^*\,[\mathrm{W}]\,\gamma_{\mathrm{W}}}{[\mathrm{AgW}_{3-i}\mathrm{O}_{i-1}]\,\gamma_{i-1}\,\gamma_{i-1}^*\,[\mathrm{O}]\,\gamma_{\mathrm{O}}}, \quad i = 1, 2 . \quad (5)$$

γ_i, γ_{i-1} are activity coefficients for the solvated species, which tend towards unity with decreasing electrolyte concentration in a given solvent mixture. Their ratio is equal to unity within the range of the Debye-Hückel theory including extended equations. γ_i^*, γ_{i-1}^* are medium activity coefficients for the differently solvated ionic species which tend to unity in pure water. The medium activity coefficient of an ionic species in a given solvent mixture or pure organic solvent is related to its free energy of transfer from water to that medium through

$$\Delta G_{\mathrm{tr}}^0 = 2.30\,RT \log \gamma^* .$$

γ_{W}, γ_{O} are the solvent activity coefficients which are unity when the corresponding mole fraction is equal to one. Ratios of solvent activity coefficients, $\gamma_{\mathrm{W}}/\gamma_{\mathrm{O}}$, were calculated from data in the literature [17, 18, 19, 21] and intermediate values were interpolated from three neighbouring points, using a quadratic Newtonian polynomial [20]. The results are given in Fig. 2 as logarithmic plot.

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* In this work, the symbol [XXX] defines molal concentration, i.e. moles XXX per kg solvent mixture, as weighed in.

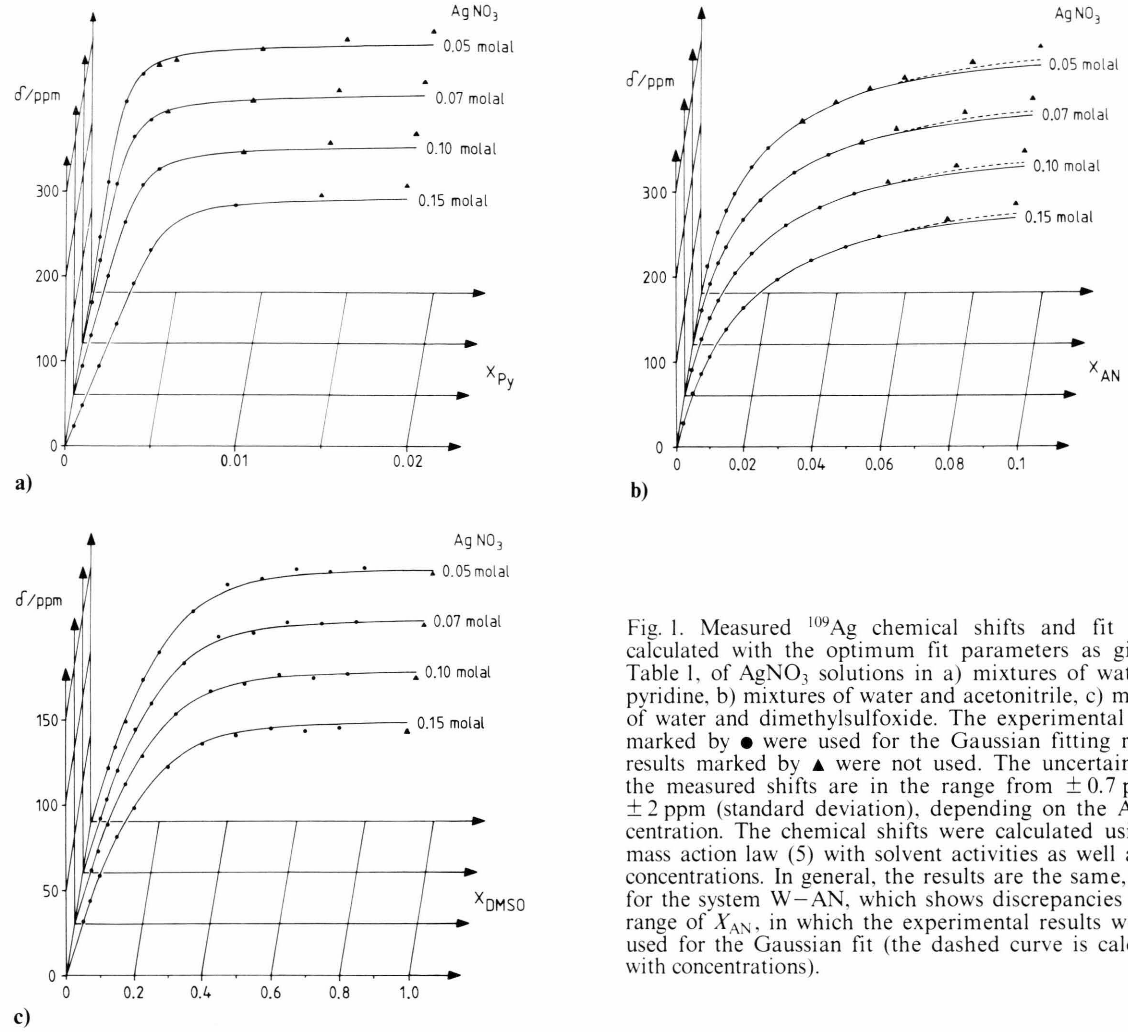

Fig. 1. Measured ^{109}Ag chemical shifts and fit curves, calculated with the optimum fit parameters as given in Table 1, of $AgNO_3$ solutions in a) mixtures of water and pyridine, b) mixtures of water and acetonitrile, c) mixtures of water and dimethylsulfoxide. The experimental results marked by ● were used for the Gaussian fitting routine; results marked by ▲ were not used. The uncertainties of the measured shifts are in the range from ± 0.7 ppm to ± 2 ppm (standard deviation), depending on the Ag concentration. The chemical shifts were calculated using the mass action law (5) with solvent activities as well as with concentrations. In general, the results are the same, except for the system W–AN, which shows discrepancies in that range of X_{AN}, in which the experimental results were not used for the Gaussian fit (the dashed curve is calculated with concentrations).

The clearest way to evaluate the unknown quantities

$$K_1, K_2, \delta_1, \text{ and } \delta_2$$

from the experimental chemical shifts $\delta(X_O, m_{Ag})$ corrected according to Eq. (3), would be an extrapolation of these shifts towards zero concentration of $AgNO_3$, i.e. $m_{Ag} \to 0$. For $m_{Ag} \to 0$, the concentration [O] of the organic solvent and [W] of water are the initial concentrations m_O and m_W of the solvents, respectively, as weighed for preparing the sample.

However, such an extrapolation of the measured shifts to zero concentration of $AgNO_3$ ($m_{Ag} \to 0$) is difficult to perform in the case of a strongly selective solvation of the Ag^+ ion. If the concentration of the dipolar aprotic solvent component and of $AgNO_3$ are of similar magnitude, a change in silver salt concentration at constant mole fraction will lead to changes in the distribution of the species AgW_2, $AgWO$, and AgO_2 and therefore to a complicated dependence of the chemical shift on salt concentration. This is demonstrated in Fig. 3: For solvent mixture of W and Py, the measured and corrected shifts δ are plotted versus the silver concentration m_{Ag} for some mole fractions X_{Py}. The drawn curves are the chemical shifts calculated with the aid of the evaluated formation constants K_i and the shifts δ_i of the individual species. It is easily seen that an extrapolation of the measured shifts

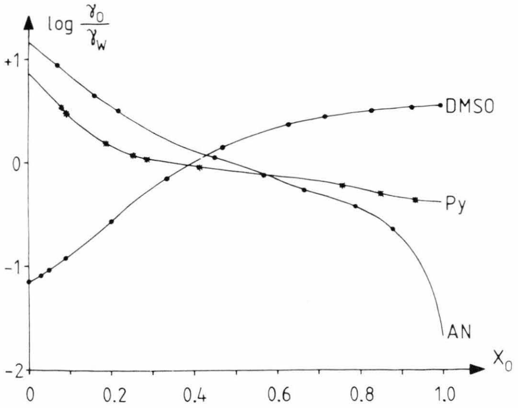

Fig. 2. Common logarithms of the ratios of the activity coefficients γ_O/γ_W as a function of the mole fraction X_O of the pure solvent mixture. To get continuous functions, the results from literature [17, 18, 19, 21] were fitted by quadratic Newtonian interpolation polynomials for each triplet of adjacent experimental results.

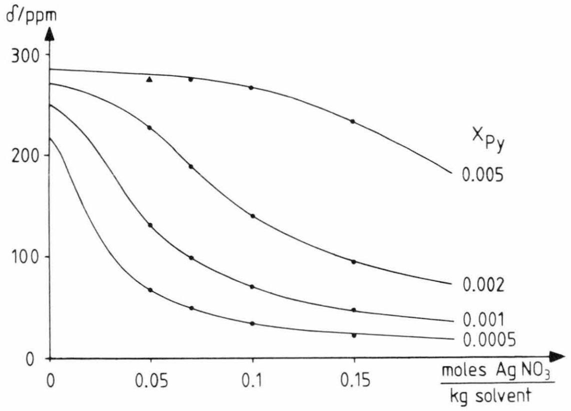

Fig. 3. Measured ^{109}Ag chemical shifts and fit curves of AgNO$_3$ solutions in mixtures of water and pyridine, plotted versus the silver concentration m_{Ag} for some mole fraction X_{Py}. The meaning of the symbols ● and ▲ is the same as in Figure 1. This plot shows clearly the impossibility to extrapolate the experimental shifts δ towards silver concentration zero ($m_{Ag} \to 0$).

towards vanishing silver concentration would lead to incorrect results. For the solvent mixture W–AN such an extrapolation is impossible in the same way, whereas for the solvent mixture W–DMSO, such an extrapolation is possible within the limits of error of the experimental results.

As it is impossible to determine the chemical shifts $\delta(X_O, m_{Ag} \to 0)$ of the Ag$^+$ ion in solvent mixtures for vanishing silver concentration, the shifts δ must be calculated for arbitrary silver concentrations. In addition to (5), with $\gamma_i = \gamma_{i-1}$, the following mass balance equation

$$[O] = m_O - [AgWO] - 2\,[AgO_2] \qquad (6)$$

must be fulfilled, whereas for low silver concentrations ($m_{Ag} \ll m_W + m_O$) and $X_O \leqq 0.8$ the following approximation can be made

$$[W] = m_W\,. \qquad (7)$$

The problem is now to evaluate the four unknown concentrations

$$[O] \quad \text{and} \quad [AgW_{2-i}O_i] \quad (i = 0, 1, 2)\,.$$

This is achieved by calculating the roots of a cubic polynomial, and therefore (somewhat extensive) analytical expressions may be given for these quantities.

Since the medium activity coefficients for the solvated silver ion species are unknown, the experimental data have been treated in two different ways: First, the ratio of medium activity coefficients in (5) was taken to be one

$$\gamma_i^*/\gamma_{i-1}^* = 1 \quad (i = 1, 2) \qquad (8)$$

otherwise it was assumed, that the ratio of the medium activity coefficients in (5) is compensated exactly by the ratio of the solvent activity coefficients, i.e.

$$\gamma_i^*/\gamma_{i-1}^* = \gamma_O/\gamma_W \quad (i = 1, 2)\,; \qquad (9)$$

in this case (5) contains only concentrations and no activities.

Taking now into account, that the ratios of the activity coefficients γ_O/γ_W are empirical functions of the concentration ratios of the bulk solvents (solvents not being participated in the solvation of the Ag$^+$ ions), the concentrations [O] as well as $[AgW_{2-i}O_i^+]$ must be calculated with the aid of an iterative routine in the case of assumption (8).

With the result of this calculation of the concentrations $[AgW_{2-i}O_i^+]$, the chemical shift of the sample, i.e. the mean value of the chemical shifts δ_i of the solvate complexes weighted with the relative concentrations $[AgW_{2-i}O_i^+]/m_{Ag}$ can be calculated with the aid of (4).

The four unkown quantities K_1, K_2, δ_1, and δ_2 in this calculation may be determined from a sufficiently large set of measured chemical shifts $\delta(X_O, m_{Ag})$ with the aid of a Gaussian least squares fitting routine (see e.g. [20]). Only those chemical shifts $\delta(X_O, m_{Ag})$ were used for the Gaussian fit, which had a low Ag^+ concentration:

$$m_{Ag}/(m_O + m_W) < 1\% \,,$$

so that simplification (7) is justified. For each sample the ratio $\alpha = [O]/m_{Ag}$ was calculated, i.e. the ratio of bulk organic solvent molecules per silver ion. The Gaussian fit procedure was started with a set of about 10 chemical shifts $\delta(X_O, m_{Ag})$ having the least values of α, then the set was extended to results with increasing α, as long as the standard deviation between the experimental shifts and the chemical shifts calculated with the aid of Eqs. (4–7) and the optimum fit parameters K_1, K_2, δ_1, and δ_2 was less than the experimental uncertainty. For the solvents Py and AN, a rapid increase of this standard deviation has been detected, if the set of experimental results $\delta(X_O, m_{Ag})$ used for the Gaussian fit, was extended to samples with $\alpha > 1.7$ or $\alpha > 0.8$, respectively, whereas the chemical shifts δ of all samples with aqueous DMSO, except those with $X_{DMSO} = 1$, which were not stable (a small amount of brown precipitate dropped out), could be used for the Gaussian fit.

The results of these Gaussian fits for the organic solvents Py, AN, and DMSO are given in Table 1, calculated on the basis of activities (assumption (8)) as well as on the basis of concentrations (assumption (9)). Using the same set of experimental results δ, the standard deviation between the measured and the calculated shifts is nearly the same under both assumptions. For the organic solvents AN and especially Py, it is not surprising, from a mathematical point of view, that a Gaussian fit is possible using either the activities of the solvents or their concentrations, since the ratio of the activity coefficients γ_O/γ_W is used only in a small interval of X_O, in which the ratio may be assumed to be constant. Comparing the two results for the water – DMSO solvent mixtures from Table 1, the fit based on concentrations yields $\delta_1 > \delta_2 > \delta_0 = 0$, whereas the fit based on activities yields the chemical shifts $\delta_2 > \delta_1 > \delta_0 = 0$, in agreement with all other results.

The results in Table 1 prove a highly selective solvation for all organic solvents under investigation: The theoretical shifts, calculated with the aid of the results of Table 1, are inserted into Figs. 1a, 1b, and 1c as drawn curves. In Figs. 4a, 4b, and 4c, the relative concentrations $[AgW_{2-i}O_i]/m_{Ag}$ ($i = 0, 1, 2$) are plotted for 0.1 molal $AgNO_3$ solutions as a function of the mole fraction X_0 of the pure solvent mixture for the organic solvents O = Py, AN, and DMSO, respectively. For the solvents AN and especially DMSO, there are striking discrepancies between these relative concentrations calculated with solvent activities ($\gamma_i^*/\gamma_{i-1}^* = 1$ (8)) (drawn curves) and those calculated with concentrations, i.e. calculated under the assumption ($\gamma_i^*/\gamma_{i-1}^* = \gamma_O/\gamma_W$ (9)) (dashed curves), whereas the chemical shifts derived from these relative concentrations (curves in Figs. 1b and 1c) show only minor differences.

Table 1. Resolvation constants (K_1, K_2) and intrinsic chemical shifts (δ_1, δ_2) from a Gaussian least squares fit, calculated with solvent activities ($\gamma_i^*/\gamma_{i-1}^* = 1$) in the mass action law (5), and calculated with solvent concentrations ($\gamma_i^*/\gamma_{i-1}^* = \gamma_O/\gamma_W$) ⟨results in brackets⟩. Standard deviation between the experimental chemical shifts used for the fit and the shifts calculated with the aid of the optimum fit parameters. α_{max} is the maximum value of the ratio of free O molecules per Ag^+ ion ($\alpha = [O]/m_{Ag}$) in samples of which the shift $\delta(X_O, m_{Ag})$ was used for the Gaussian fit.

Organic solvent	Py	AN	DMSO
K_1	2313 ± 680 $\langle 16\,920 \pm 5062 \rangle$	15.5 ± 1.8 $\langle 195.7 \pm 18 \rangle$	93.9 ± 7.3 $\langle 3.77 \pm 0.14 \rangle$
K_2	412 ± 35 $\langle 3037 \pm 264 \rangle$	2.20 ± 0.11 $\langle 35.4 \pm 1.7 \rangle$	5.5 ± 0.9 $\langle 2.70 \pm 0.48 \rangle$
δ_1/ppm	128.0 ± 1.6 $\langle 128.1 \pm 1.6 \rangle$	108.7 ± 9.3 $\langle 116.8 \pm 8.2 \rangle$	93.7 ± 4.5 $\langle 176.5 \pm 6.7 \rangle$
δ_2/ppm	259.8 ± 2.1 $\langle 259.3 \pm 2.1 \rangle$	377.5 ± 4.3 $\langle 319.4 \pm 1.9 \rangle$	147.9 ± 0.6 $\langle 144.4 \pm 1.5 \rangle$
Standard deviation	1.4 ppm	0.8 ppm	1.7 ppm
α_{max}	1.7	0.8	∞

The fact that not only extrapolated shifts $\delta(X_O, m_{Ag} \rightarrow 0)$ but all experimental shifts $\delta(X_O, m_{Ag})$ with sufficiently low α for arbitrary m_{Ag} are well represented, within the limits of the experimental uncertainty, by theoretical curves, is an excellent indication for the validity of the competitive solvation equilibrium model.

4.3. *Higher Solvation*

In mixtures of water and DMSO, the calculated chemical shift $\delta(X_O, m_{Ag})$ is in excellent agreement with the experimental results within the total mole fraction range. However, in the systems water – Py and water – AN, only the experimental shifts of

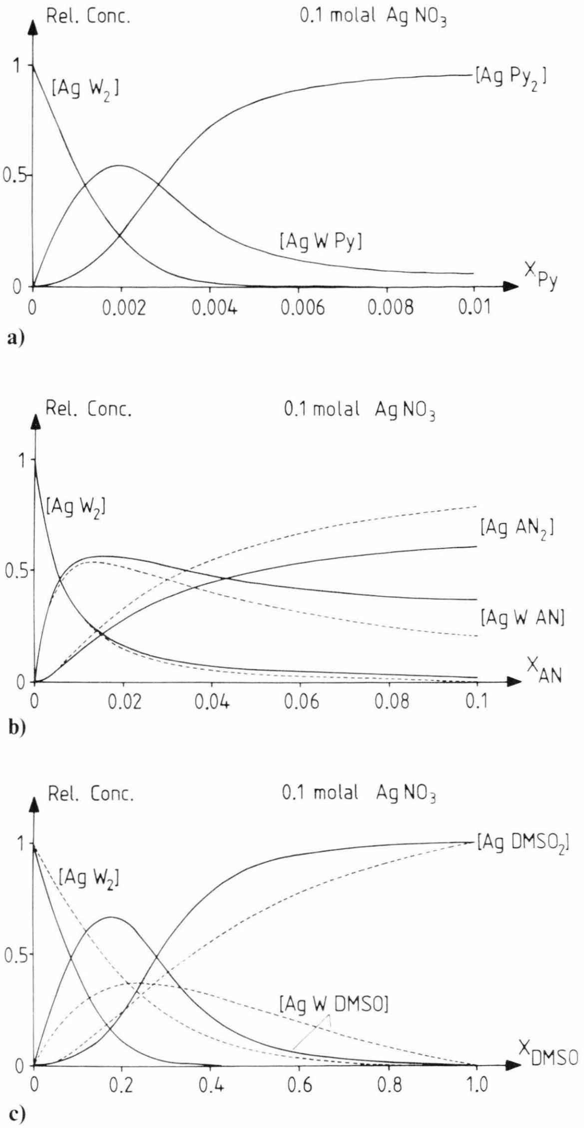

Fig. 4. Relative concentrations $[AgW_{2-i}O_i]/m_{Ag}$ ($i = 0, 1, 2$) of the three silver solvate complexes in 0.1 molal $AgNO_3$ solution as a function of the mole fraction X_O of the solvent mixture a) O = Py, b) O = AN, and c) O = DMSO. The drawn curves are calculated using solvent activities in the mass action law and the corresponding results for the optimum fit parameters from Table 1. The dashed curves are calculated with solvent concentrations and the optimum fit parameters in brackets from Table 1.

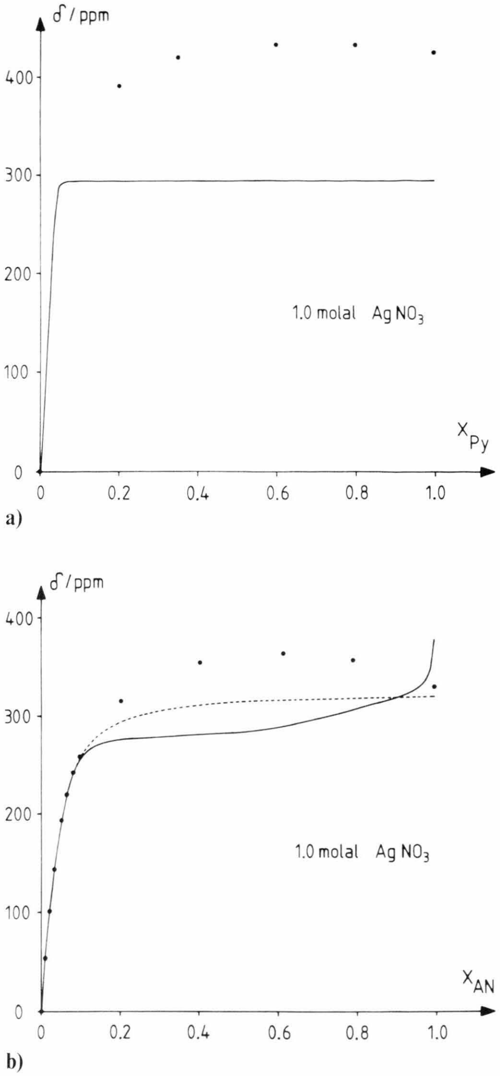

Fig. 5. Comparison of the ^{109}Ag chemical shifts of 1 molal $AgNO_3$ solutions a) in water – Py mixtures and b) in water – AN mixtures with the chemical shifts calculated from the results in Table 1. Drawn curves were calculated with solvent activities and the dashed curve with solvent concentrations. In the system water – Py (a) both calculations yield the same result. Agreement between experimental shifts and results of calculation is only achieved for sufficiently low mole fractions X_O. The discrepancies for higher X_O are due to a higher solvation sphere in addition to the solvate complexes $AgW_{2-i}O_i$ ($i = 0, 1, 2$).

those samples with $\alpha \leqq 1.7$ and $\alpha \leqq 0.8$, respectively (marked by dots in Figs. 1a and 1b) are in agreement with the theoretical curves. At higher values of α, the experimental chemical shifts (triangles in Figs. 1a and 1b) deviate obviously from the calculated curves even at these low concentrations of $AgNO_3$. The discrepancy between experiment and calculation in the two solvent systems is by no means negligible and its magnitude is demonstrated for 1 molal $AgNO_3$ solutions in Figs. 5a and 5b.

The decrease of (γ_{AN}/γ_W) towards $X_{AN} = 1$ is the reason why the theoretical curve in Fig. 5b, calculated with solvent activities, increases steeply near pure AN. This effect is all the larger the higher the concentration of $AgNO_3$ is.

The fact, that the ^{109}Ag Larmor frequency of the complexes $Ag(Py)_2^+$ and $Ag(AN)_2^+$ is shifted additionally towards higher values, if there is more than 1 free organic molecule per Ag^+ ion available, shows the existence of a higher (secondary) solvation in addition to the coordination with the coordination number 2, because the ^{109}Ag chemical shift may be influenced also by solvent molecules not belonging to the two of the silver solvate complex. However, the $^{109}Ag^+$ NMR data in the water − DMSO system give no indication for the existence of a higher solvation sheath.

5. Discussion

It has been shown recently that also solvation of an univalent ion in mixed solvents can be treated in terms of coordination, when one solvent component solvates the ion more strongly than the other [21, 22]. Since the silver ion interacts quite strongly with Lewis base molecules and even partly covalent [23, 24] with nitrogen atoms in polar molecules, the solvation of Ag^+ has been long investigated by different experimental methods. So the sensitive and uncomplicated handling of the silver metal/silver ion electrode made it possible to study the stepwise resolvation reactions of Ag^+ in solvent mixtures by potentiometric measurements. Especially the solvation of Ag^+ by acetonitrile has been investigated extensively and, using experimental methods from all sections of physical chemistry, the results indicate equivocally that the interaction of Ag^+ with acetonitrile is much more pronounced than with water. Therefore the solvation of Ag^+ in mixtures of water and acetonitrile shall be treated first together with remarks and discussions which may also concern the corresponding aqueous Ag^+ solutions with pyridine and DMSO.

The strength of interaction between Ag^+ and AN has been detected by Raman, IR and NMR spectroscopic methods [25, 26, 27] by conductance and transference numbers [28] and recently by ESR measurements at low temperatures [29] and the 1:1 and 1:2 complexes of Ag^+ with AN have been isolated by the cooling of concentrated solutions [30]. The stabilities of $Ag(AN)^+$ and $Ag(AN)_2^+$ in water have been presented by Pawelka [31] and by Koch [32], respectively, assuming the existence of only one type of the complexes. More thorough investigations using vapour pressure [33], NMR [34] and also potentiometric experiments [21, 35−37] have shown that both complexes coexist in aqueous silver salt solutions of AN. The corresponding stability constants are listed in Table 2 together with results of the present investigation. The agreement is much better than one would expect considering the different concentration ranges and ionic strengths.

In the potentiometric studies, different extra-thermodynamic assumptions have been applied in order to present changes in EMF or corresponding free energies of transfer which depend only on the preferential solvation of Ag^+. Manahan and Iwamoto [35] assumed the liquid junction potential to be constant during potentiometric titrations, i.e. independent on changes in mole fraction, and Koepp et al. [37] measured the potential of the Ag/Ag^+ electrode against a ferrocene-ferricinium ion electrode, whose standard potential is presumed to remain constant independent of the solvent. The derivation of formation constants from $CH_3{}^{13}CN$ NMR chemical shifts by Fromon et al. [34] was only possible when the intrinsic chemical shifts of the two acetonitrile molecules in $Ag(AN)_2^+$ were taken to be equal to the chemical shift in $Ag(AN)^+$.

In the treatment of the ^{109}Ag NMR chemical shift data presented in this paper individual cationic chemical shifts of the species $Ag(AN)^+$ and $Ag(AN)_2^+$ could be derived in addition to the equilibrium constants, because of the large variation in resonance frequency of the ^{109}Ag nucleus on changes in the environment of the ion. On the other hand, this sensitivity is the reason why in mixtures of water and acetonitrile at high mole fractions X_{AN}, the influence of a so called secondary solvation is observed, which concerns more than the two dominating solvating molecules.

Previous workers have plotted functions of the chemical shift against either mole fraction or volume fraction or activities of the solvent components [22, 37a, 37b, 41] in order to determine equilibrium constants for ion solvation in mixed solvents. In the present treatment of the ^{109}Ag NMR chemical shifts both, mole fraction and solvent activities have been used in the calculation of

Table 2. Equilibrium constants for the solvation of Ag$^+$ in mixtures of water with some organic solvents and related transfer-free energies between water and the nonaqueous solvents at 25 °C.

Solvent	K_1	K_2	ΔG^0_{tr} [kJ mol^{-1}]	Method	m_{Ag} [m]	I [M]	Ref.
CH_3CN	150	61	−23	EMF	0.01	0.1 (KNO_3)	[37]
CH_3CN	110	61	−22	EMF		0.01 ($LiClO_4$)	[35]
CH_3CN	144	128	−24	EMF		0.1 ($NaClO_4$)	[36]
CH_3CN	80	195	−24	^{13}C NMR	< 1.0	–	[34]
CH_3CN	196	35	−22	^{109}Ag NMR	≦ 0.15	–	[a]
CH_3CN	15.5	2.2	− 9	^{109}Ag NMR	≦ 0.15	–	[b]
C_6H_5N	16920	3037	−44	^{109}Ag NMR	≦ 0.15	–	[a]
C_6H_5N	2313	412	−34	^{109}Ag NMR	≦ 0.15	–	[b]
$(CH_3)_2SO$	3.77	2.70	− 6	^{109}Ag NMR	≦ 0.15	–	[a]
$(CH_3)_2SO$	93.9	5.5	−16	^{109}Ag NMR	≦ 0.15	–	[b]

[a] this work, calculation based on solvent concentrations.
[b] this work, calculation based on solvent activities.

equilibrium constants. The results are given in Tables 1 and 2 and are of rather different magnitude, whereby the constants of the mole fraction calculation are in good agreement with the constants from EMF and ^{13}C NMR experiments. It is quite a simple test to calculate the free energies of transfer of Ag$^+$ from water to acetonitrile:

$$\Delta G^0_{tr}(\mathrm{Ag}^+, \mathrm{W} \rightarrow \mathrm{AN}) = -2.3\,RT \log (K_1 K_2)\,. \quad (10)$$

A comparison of the ΔG^0_{tr} values calculated from ^{109}Ag shifts with (10) shows that the calculations based on the mole fraction representation are in excellent agreement with the ΔG^0_{tr} data from other experiments. In addition they are consistent with transfer-free energies for Ag$^+$ from water to pure AN, which were determined independently using various extra-thermodynamic assumptions. From the numerous experiments done in this system only few recent results shall be quoted: $\Delta G^0_{tr} = -21.8$ kJ/mol (Ph_4AsBPh_4 assumption) [38, 39], $\Delta G^0_{tr} = -22.8$ kJ/mol (ferrocene-ferricinium ion assumption) [40]. Obviously the contribution of higher solvation to the free energy is of little consequence.

The comparison of equilibrium constants and transfer-free energies from different studies has shown that the utilization of the mole fraction in the treatment of the chemical shift data is more appropriate than taking into account solvent activities. This result is supported by the more monotonous variation of the calculated chemical shift (dashed curve in Fig. 5b) and by experiments and calculations of Covington et al. [22, 41]. They have found that the ratio of solvent activity coefficients of molecules pertaining to the bulk and to the solvation shell is for one component compensated by the corresponding ratio for the second component and corresponds to (9) when the properties of the various solvates of an ion are related by statistical requirements.

Since K_1, K_2 and δ_1 correspond within 15%, 17% and 37%, respectively, to values calculated with

$$K_{i,\mathrm{stat}} = (K_1 K_2)^{1/2} \cdot (3-i)/i\,, \quad i = 1, 2\,, \quad (11)$$

$$\delta_{1,\mathrm{stat}} = \tfrac{1}{2}\,\delta_2 \quad (12)$$

which are based on a statistical distribution of the solvated species and the additivity of the shielding contributions [41], the success of taking into account only the mole fraction is reasonable.

Resolvation equilibria of Ag$^+$ have been determined by potentiometric measurements only in Py-propylene carbonate mixtures [42]. It is known for a long time that $AgNO_3$ in pyridine forms a solvate [43] and spectroscopic studies have shown the existence of a strongly coordinated complex $Ag(Py)_2^+$ in aqueous pyridine solution [44]. The equilibrium constants for the solvation of Ag$^+$ in aqueous pyridine calculated from ^{109}Ag NMR chemical shifts are given in Table 2. They are much larger than those for acetonitrile, but also here K_1, K_2 and δ_1 are within 15%, 18% and 1%, respectively, in agreement with statistical values calculated from (11) and (12). The free energy of transfer of Ag$^+$ from water to pyridine, which is calculated (10) using the mole fraction dependent constants is in good agreement with $\Delta G^0_{tr} = -46$ kJ/mol determined by Mukherjee [45]. To obtain this value, they have done potentiometric measurements and applied the ferrocene-ferricinium ion assumption. Also in this solvent system the constants have been calculated from ^{109}Ag chemical shifts in a restricted mole fraction range, but the effect of secondary solvation on ΔG^0_{tr} is of little importance just as in the acetonitrile system.

The interpretation of the results on the solvation of Ag^+ in mixtures of water and DMSO is less straight forward than that for aqueous solutions of acetonitrile and pyridine, because different experimental studies show a more complicated behaviour and to some extent lacking agreement. A bisdimethyl sulfoxide complex of $AgClO_4$ has been prepared and analyzed by X-ray diffraction [46, 47]. In the crystal of $Ag(DMSO)_2ClO_4$, the silver ion is coordinated to four DMSO molecules. This is also likely to be the case in water-DMSO solutions, because in acetone-DMSO and nitromethane-DMSO mixtures, the silver ion is found to be surrounded by four DMSO molecules [48]. However, in aqueous DMSO solutions of $AgNO_3$, the NMR chemical shifts of water protons and of DMSO protons change only insignificantly with solvent composition at mole fractions $X_{DMSO} \leqq 0.2$ [49]. Only at higher concentrations of DMSO, the chemical shift variation is as pronounced as it corresponds to the preferential solvation of Ag^+ by DMSO. The indifference of Ag^+ towards DMSO in aqueous mixtures of mole fraction $X_{DMSO} \leqq 0.2$ and its selectivity for DMSO at higher mole fractions is observed also in the variation of the solvent transference number of Ag_2SO_4 and in the free energy of transfer of Ag^+ with solvent composition [49, 50]. A further indication to the nonselective solvation of Ag^+ in highly aqueous DMSO solutions is the result of a potentiometric titration of Ag^+ with DMSO at $X_{DMSO} \leqq 0.1$, namely that no complexes with DMSO are formed in water [47]. However, Cox et al. [21] have determined four equilibrium constants from the transfer-free energies of Ag^+ from water to water-DMSO mixtures up to pure DMSO using as extra-thermodynamic assumption the negligibility of the liquid junction potential. These constants are, when solvent concentrations are replaced by their activities, $\log K_1 = 2.24$, $\log K_2 = 1.69$, $\log K_3 = 1.13$ and $\log K_4 = 0.57$. Thus the free energy of transfer from water to DMSO of

$$\Delta G^0_{tr} = -2.3\,RT \log (K_1 K_2 K_3 K_4) = -32.3 \text{ kJ/mol}$$

is in excellent agreement with results based on other extra-thermodynamic assumptions:

$\Delta G^0_{tr} = -33.5$ kJ/mol (Ph_4AsBPh_4 assumption) [38, 39], and $\Delta G^0_{tr} = -32.5$ kJ/mol (ferrocene-ferricinium ion assumption) [51]. However, much smaller transfer-free energies follow from the two sets of equilibrium constants for Ag^+ solvation in water-DMSO (Table 2), although they both reproduce excellently the experimental chemical shifts throughout the whole mole fraction range. No indication of higher solvation could be observed, and an attempt to change the coordination number and to analyze the ^{109}Ag chemical shifts with a model where each water molecule in $Ag(W)_2^+$ is replaced simultaneously by two DMSO molecules failed, because a much more unfavourable standard deviation resulted.

Since in water-Py and water-AN mixtures the resolvation constants derived from electrochemical and from ^{109}Ag NMR experiments are in good agreement, the unexpected discrepancy in water-DMSO points to specific properties of Ag^+ in this solvent system. There is a difference in the interaction of Ag^+ in aqueous solution with nitrogen (Py, AN; backbonding) on one hand and with oxygen on the other, which may help in explaining why in highly aqueous solutions no complexes of Ag^+ with DMSO [48], dimethylformide [52] and hexamethylphosphotriamide [53] have been detected in potentiometric studies although the solvation of Ag^+ in these solvents alone is much stronger than in water. This change in selectivity of Ag^+ from hydration to solvation by DMSO at low mole fractions has in fact not been observed as an inflection point in the chemical shift variation, but whether this behaviour is responsible for the low resolvation constants shall be investigated in further NMR studies on Ag^+ solvation by polar molecules with an oxygen donor site.

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