^{109}Ag NMR-Studies of the Selective Solvation of the Ag$^+$-Ion in Water-Ethylamine-Mixtures and of the Coordination of Halide-Anions to the Silver-Ethylamine Solvate Complexes

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^{109}Ag chemical shift measurements of 0.02 up to 3 molar solutions of $AgNO_3$, AgCl, and AgBr in solvent mixtures of H_2O (W) and ethylamine (ea) were performed. The extremely long relaxation times T_1 and T_2 were determined with new techniques.

The Ag$^+$-ion in solvent mixtures of W and ea shows a strongly selective solvation by ea. The ^{109}Ag chemical shift of the solvate complex $[Ag\,ea_2]^+$ surrounded solely by W is $\delta_2 = (335 \pm 2)$ ppm (referred to the Ag$^+$-ion in W). A further solvation in addition to the inner solvation sphere was determined; this solvation is not or only weakly selective. There is a rapid chemical exchange; the lifetime of the inner solvation sphere is long compared with the Larmor period, whereas the solvation outside this sphere is changed in times shorter than the Larmor period.

In contrast to the NO_3^--anion, the halide anions Cl^- and Br^- are partly coordinated to the $[Ag\,ea_2]^+$ complex. The equilibrium constants for this coordination were determined as well as the chemical shifts of the $[Ag\,ea_2 \cdot Cl]$ and the $[Ag\,ea_2 \cdot Br]$ complexes. The bromine ion is coordinated for shorter times than the Larmor period, whereas the time of the coordination of the chlorine ion may be comparable to the Larmor period or shorter.

1. Introduction

The silver ion Ag$^+$ dissolved in mixtures of water and organic solvents shows a selective solvation, which has been studied by a variety of techniques [1] including NMR applied to the protons of the ligand molecules [2]. Unfortunately the chemical shifts of these ligand protons are relatively small (some ppm), and thus information taken from such experiments is limited. In the last few years, however, special steady-state pulse techniques have become available and enabled systematic NMR investigations of the nuclei ^{107}Ag and ^{109}Ag [3, 4]. The silver chemical shifts are found to be in the range of some hundreds of ppm and suggest investigations on the central atom of the solvate complex.

All previous experiments [5] show the coordination number 2 of the Ag$^+$-ion for water as well as for ethylamine. Therefore in solvent mixtures of water (W) and ethylamine (ea) the solvate complexes $[Ag\,W_2]^+$, $[Ag\,W\,ea]^+$, and $[Ag\,ea_2]^+$ are possible. There is a dynamic equilibrium:

$$[Ag\,W_2]^+ + ea \overset{K_1}{\rightleftarrows} [Ag\,W\,ea]^+ + W$$

and

$$[Ag\,W\,ea]^+ + ea \overset{K_2}{\rightleftarrows} [Ag\,ea_2]^+ + W\,,$$

governed by the mass action law:

$$K_1 = \frac{[[Ag\,W\,ea]^+]\cdot[W]}{[[Ag\,W_2]^+]\cdot[ea]}$$

and

$$K_2 = \frac{[[Ag\,ea_2]^+]\cdot[W]}{[[Ag\,W\,ea]^+]\cdot[ea]}\,.$$

The equilibrium constants, determined by a variety of techniques (see p. 43 of [5]) to be $K_1 \approx 1.1 \cdot 10^5$ and $K_2 \approx 3.5 \cdot 10^5$, are extremely high compared to those with other organic solvents. This means that e. g. in a solvent with the original mole fraction $X_{ea} = 5.6 \cdot 10^{-3}$ more than 99% of the Ag$^+$-ions are solvated by 2 ea molecules.

In general there is a rapid chemical exchange between the three solvate complexes and the NMR spectrum consists of one line, of which the chemical shift is the mean value of the chemical shifts δ_i of the complexes $[Ag\,W_{2-i}\,ea_i]^+ (i = 0, 1, 2)$, weighted with the concentrations of the complexes. Therefore NMR investigations of the central nucleus of such solvate complexes are an excellent tool to study the formation of these complexes, and to determine their chemical shifts δ_i as well as the equilibrium constants.

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The influence of the anions of the silver salt can be studied in that mixture of solvents, which guarantees the predominance of only one solvate complex; in other words, the predominance of this complex must not be changed by varying the concentration of the silver salt. For H_2O-ea solvent mixtures a sufficiently high mole fraction X_{ea} guarantees the predominance of the $[Ag\,ea_2]^+$ complex.

In contrast to the NO_3^--anion, which yields a nearly linear dependence of the ^{109}Ag chemical shift on the $AgNO_3$ concentration, it was pointed out in a recent paper [4] that the ^{109}Ag chemical shifts of solutions of the silver halides AgF, AgCl, AgBr, and AgI are spread over a range from 430 ppm to 790 ppm (related to the resonance of the Ag^+-ion in H_2O at infinite dilution), whereas the shift of each of the halides is only slightly depending on the Ag-concentration in the range >0.5 molal. Particularly there is no convergence of the four chemical shifts to a common value for Ag-concentration $\rightarrow 0$. From this behaviour, the conclusion must be drawn that at least a fraction of the halide anions is coordinated to the $[Ag\,ea_2]^+$ complex. To study this coordination phenomenon in detail, very time consuming ^{109}Ag chemical shift measurements were performed in the Ag-concentration range 0.025 to 0.5 molal. From these, quantitative results about the anion coordination were to be deduced.

The dynamic behaviour of the solvate complexes, i. e. their lifetimes, may be evaluated from the ^{109}Ag relaxation times. As the ^{109}Ag nucleus has the spin $I=1/2$ and only a small magnetic moment, no quadrupolar and only a weak magnetic interaction of this nucleus with its environment is possible. This yields very long relaxation times T_1 and T_2, which are mostly due to chemical exchange. Therefore the ^{109}Ag nucleus is an excellent probe to study very fast chemical exchange processes. Unfortunately there is not only an exchange in the first solvation sphere but also outside this sphere; a further exchange process, the anion coordination complicates the situation. As these individual contributions to the relaxation rates are not to be separated, not the lifetimes of the complexes, but only upper limits for these values may be evaluated.

2. Experimental

The silver isotope ^{109}Ag has an abundance of 49% in the natural mixture. The spin of this nucleus is $I=1/2$ [6] and it has a relatively small magnetic moment $\mu=-0.129\,961\,5(10)\,\mu_N$ [3]. This yields a Larmor frequency $\nu_L(^{109}Ag)\approx 4.190$ MHz in our field $B_0=2.114$ T (corresponding to 90 MHz proton Larmor frequency). On the assumption that the longitudinal and transverse relaxation times are equal (a condition, which is never fulfilled for any sample), the NMR signal of ^{109}Ag in a 1 molar sample of an Ag salt is 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. The lack of an electric quadrupole moment and the small magnetic moment yield very long relaxation times up to some ten minutes.

All ^{109}Ag measurements were performed with a pulse spectrometer described in [7]. This apparatus was especially developed for investigations of very weak NMR signals in the frequency range 1 ... 4.5 MHz. The magnetic field B_0 was produced by a Bruker B-E 45 magnet, 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 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. The data (1000 channels of 24 bits) were transferred to a PDP 11/04 computer via a coaxial line with a speed of 10^5 baud. From this computer, the data were to be transferred via a telephone line to the CDC 3300 computer of the Zentrum für Datenverarbeitung, Tübingen, for further evaluation.

For all measurements of the ^{109}Ag Larmor frequencies and of chemical shifts, the Quadriga Fourier-Transform technique [8] 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 inhomogeneity of the magnetic field B_0 as well as of the natural line width if $T\ll T_2^*$, T_2, T_1 is chosen (T_2^* is the time constant which describes the decay of the NMR signal due to the inhomogeneity of B_0). In this case any

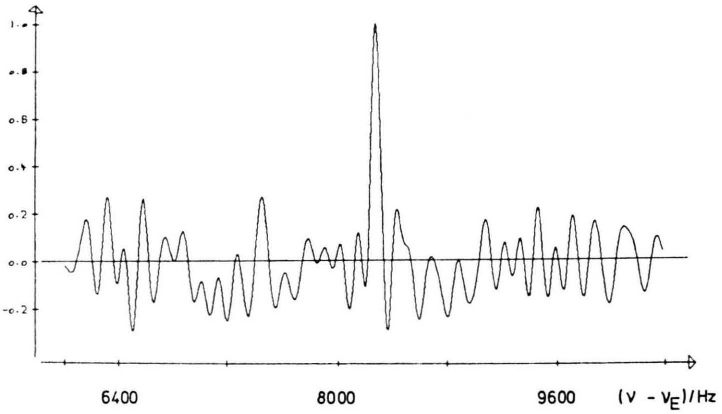

Fig. 1. NMR absorption spectrum of ^{109}Ag in a 0.02 molar $AgNO_3$ solution in 70% aqueous ea solution. The pulse repetition rate was $1/T = 80$ Hz and the irradiation frequency of the rf-field $\nu_E = 4.182274$ MHz. In a measuring time of 77 hours a signal/noise-ratio of about 7 was to be achieved.

loss of NMR signal due to the inhomogeneity of the field B_0 can be avoided, without paramagnetic admixtures to the sample with its well known disadvantages.

For the present investigations, pulse repetition rates $1/T = 80$ Hz and 83 Hz were used; the resulting halfwidths of the absorption lines are 48 Hz and 50 Hz, respectively. The measuring times were from 6 minutes for the reference sample to 77 hours for the samples with the weakest silver concentrations (0.020 molar ≙ 0.025 molal). In Fig. 1, the absorption spectrum of such a weak sample is given.

Usually, during such long measuring times a spurious signal, produced by the time-averaging computer itself, is superimposed to the NMR signal; this troublesome effect was to be avoided totally by inverting the phase of the input-signal to the time-averaging computer after the first half of the measuring time and by subtracting the data, accumulated during the two halves of the experiment.

To determine chemical shifts, the sample replacement technique was used. The uncertainties of the measured chemical shifts (3 times the standard deviation) are ± 2 ppm for Ag-concentrations $\leqq 0.1$ molal and ± 1 ppm for higher silver concentrations.

To measure the relaxation times T_1 and T_2, a combination of two steady-state experiments, the T_1/T_2-experiment and the $T_1 + T_2$-experiment, was used as is described in detail in Ref. [9]. By these techniques, any waiting time for the thermal equilibrium as well as for the buildup of the magnetization can be avoided, and therefore maximum information can be reached in a given measuring time. The block-averaging technique, which is necessary for the $T_1 + T_2$-experiment, was performed in the memory of the PDP 11/04 computer. All functions of the time-averaging computer were controlled by the PDP 11/04 and its clock.

The parameters for these two relaxation experiments were: Pulse-repetition rate: $1/T = 198$ Hz, in order to achieve nearly the same free precession angle Φ for all spin-isochromats. Irradiation frequency of the rf-field: $\nu_E = \nu_L - 1/(2\,T)$, this yields a free precession angle $\Phi = \pi$. The pulse width for the flip angle $\theta = \pi$ was about 200 μs. In the $T_1 + T_2$-experiment, the duration τ_A of the data acquisition and the number of rf-pulses in this interval were governed by the buildup time constant $T^* = (T_1 + T_2)/2$ of the steady-state. This buildup of the NMR signal was recorded during ten acquisition intervals; therefore τ_A was chosen to fulfil the conditions

$$0.75\,T^* \leqq 10\,\tau_A < 1.5\,T^* \quad \text{and} \quad \tau_A = 2^n\,T\,,$$

i. e. 2^n rf-pulses were applied during this interval. n was chosen in the range from 11 for $T^* < 100$ s up to 14 for $T^* > 800$ s. The $T_1 + T_2$-experiment was repeated $K = 2^{(16-n)}$ times and the NMR signal block-averaged, i. e. the NMR signal of 2^{16} pulse cycles was summed up for each acquisition interval, independent of the relaxation times.

Additional ^{14}N, ^{35}Cl, and ^{79}Br NMR-investigations were performed with a commercial Fourier-pulse spectrometer SXP 4 – 100 of Bruker-Physik AG.

3. Samples

All samples with an Ag-concentration > 1 molal were contained in spheres of 17 mm internal diameter, in order to avoid corrections for bulk susceptibility, all samples with Ag-concentrations $\leqq 1$ molal were contained in cylinders of 20 mm internal diameter with a filling height of 40 mm. No corrections for bulk susceptibility were made, as for these samples the corrections are smaller than the statistic uncertainty.

The reference sample always had the same size and shape as the sample under investigation. For the chemical shift measurements, the following reference samples were used:

Ref. No. 3: 8.3 molal aqueous solution of AgF and

Ref. No. 5: 14 molal solution of $AgNO_3$ in a mixture of 90 wt.% acetonitrile (CH_3CN) and of 10 wt.% D_2O.

Both reference samples had been used in previous investigations [3, 4, 10]. The chemical shifts of the ^{109}Ag Larmor frequencies $\nu_{\text{Ref.}}$ of these samples referred to the Larmor frequency ν_0 of the Ag^+-ion in H_2O at infinite dilution are

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

and

$$\delta(\text{Ref. 5}) = (\nu_{\text{Ref. 5}} - \nu_0)/\nu_0 = (148.0 \pm 1.5)\,\text{ppm},$$

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

For preparing the samples for the present investigations, the following silver salts and solvents were used: $AgNO_3$ (Merck No. 1512 and J. T. Baker No. 1182, both analytical grade), AgCl (Merk No. 10486, Selectipur), AgBr (Merck No. 10485, Selectipur), 70% solution of ethylamine (C_2H_7N) in H_2O (Merck No. 820024) and H_2O with a conductivity of less than $10^{-6}\ \Omega^{-1}\ \text{cm}^{-1}$. The concentrations of the samples were determined by weighing salt and solvent or solvents, respectively. The concentration of the ea solutions was determined from their density. In order to avoid evaporation of ea, the aqueous ea solution was stored and handled at temperatures below 278 K, and the heat of solution was removed carefully by cooling with ice water. The solvents H_2O and acetonitrile used for the samples for relaxation measurements were degassed by bubbling purified N_2 into the solvent for about 30 minutes. The sample solutions were degassed in the same manner for some minutes at room temperature; the samples were sealed at once.

4. Results and Discussion

4.1. Selective Solvation of the Ag^+-Ion by H_2O and Ethylamine

To study this selective solvation, the chemical shifts of 0.15 molal, 0.375 molal, and 0.75 molal $AgNO_3$ solutions in solvent mixtures of H_2O and ea in the range of the mole fraction $0.0056 \leqq X_{\text{ea}} \leqq 0.444$ were determined. The results and an extrapolation to vanishing silver concentrations are given in Figure 2.

For small mole fractions $X_{\text{ea}} \rightarrow 0.0056$, the ^{109}Ag chemical shifts of all silver concentrations seem to converge to the chemical shift

$$\delta_2 = (335 \pm 2)\,\text{ppm}\,.$$

This is the chemical shift of the $[Ag\,ea_2]^+$ complex solely surrounded by H_2O molecules. For higher

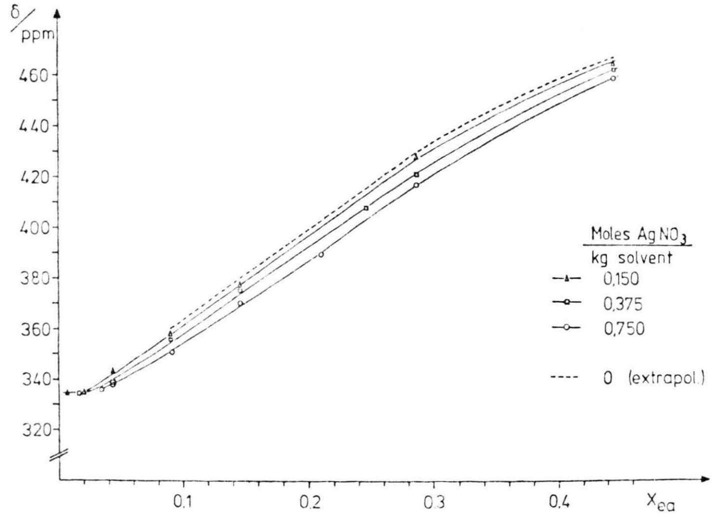

Fig. 2. ^{109}Ag chemical shift of $AgNO_3$ in H_2O-ea solvent mixtures referred to the Larmor frequency of the Ag^+-ion in H_2O at infinite dilution, i.e. of the $[Ag\,W_2]^+$ complex in H_2O. The uncertainty of the measured shifts is $\pm$ 2 ppm.

mole fractions X_{ea}, there is a nearly linear increase of the chemical shift. This increase of the shift is obviously due to the replacement of H_2O molecules in the environment of the $[Ag\,ea_2]^+$ complexes by ea molecules. It is not to be deduced from this result, whether there is a further solvation in addition to the inner coordination sphere. But if such a second or higher solvation sphere exists, this solvation is not or only weakly selective, in contrast to the inner solvation sphere.

Unfortunately in solvent mictures of H_2O and ea with mole fractions in the range $X_{ea} < 0.0056$, a 0.15 molal $AgNO_3$ solution is not possible: a black or brown precipitate drops out, probably Ag_2O. Calculating the concentration of the silver complexes $[Ag\,W_{2-i}\,ea_i]^+$ $(i = 0, 1, 2)$ with the aid of the mass action law and the equilibrium constants cited in Sect. 1, the product of the concentration of the $[Ag\,W_2]^+$ and the OH^- concentration is $> 2 \cdot 10^{-8}$ $(mol/l)^2$, the solubility product of AgOH, for mole fractions $X_{ea} < 0.0056$. By this, also the maximum concentration of $[Ag\,W\,ea]^+$ is too low as to get a suitable NMR signal in a reasonable measuring time, i. e. any results about the chemical shift of the mixed solvate complex are impossible in this way.

There is another way to dissolve the $[Ag\,W\,ea]^+$ complex, used by Carlson et al. [11] for a potentiometric determination of the equilibrium constants K_1 and K_2: By adding the same stoichiometric amount of a strong acid (HNO_3) and further ethylamine, the pH of the sample is lowered, but the concentration of free ea is not changed, as the equilibrium of the reaction

$$H^+ + ea \rightleftarrows eaH^+$$

is shifted nearly quantitatively to the right site, because of the large equilibrium constant $k = 10^{10.8}$ l/mol (see [11]).

In samples 0.22 molal in HNO_3 and 0.2 molal in $AgNO_3$, no precipitate dropped out for all mole fractions X_{ea}. In the range of mole fraction $0.0041 \leqq X_{ea} \leqq 0.0115$, no NMR signal was to be detected, although the measuring time was extended by a factor of 100 compared with the samples of higher mole fraction X_{ea}. This result is due to a very high ratio T_1/T_2 of the relaxation times (see Section 4.3). For $X_{ea} > 0.0115$, the chemical shift of the $[Ag\,ea_2]^+$ complex $\delta_2 = 335$ ppm was determined. This is the same shift as in the samples not acidified.

4.2. Coordination of the Halide Anions to the Silver Solvate Complexes

For all samples used for these coordination investigations, a mixture of ea and H_2O with the mole fraction $X_{ea} = 0.444$ (in the following called 70% ea solution) was used. The chemical shifts of solutions of the salts $AgNO_3$, AgCl, and AgBr were determined in the silver-concentration range 25 millimolal to 4 molal. The results are plotted in Fig. 3: The ^{109}Ag chemical shift of $AgNO_3$ in this 70% ea solution is a nearly linear function of the molality of the silver salt, the chemical shift decreases with increasing silver concentration. This chemical shift curve may be easily extrapolated to $AgNO_3$-concentration $\rightarrow 0$. The extrapolated chemical shift is $\delta^* = 470$ ppm, in good agreement with the result of Fig. 2 (dashed curve, extrapolated to vanishing Ag-concentration, for mole fraction $X_{ea} = 0.444$).

At this high mole fraction of the solvent, the only Ag-solvate complex to occur is $[Ag\,ea_2]^+$, and this extrapolated chemical shift δ^* is the shift of this complex in a H_2O-ea mixture with $X_{ea} = 0.444$. For high $AgNO_3$ concentrations, solvent molecules near the $[Ag\,ea_2]^+$ complex may be replaced by NO_3^--anions, which yields a lower chemical shift. A selective solvation of the NO_3^--anions by ea-molecules would lower the ratio {ea-molecules/H_2O-molecules} in the solvent and also change the solvation outside the inner solvation sphere to a lower ea-concentration, and therefore a lower ^{109}Ag Larmor frequency would result.

The chemical shift curves of the silver halides AgCl and AgBr are in striking contrast to this behaviour. Both curves increase with increasing Ag-concentration; they show a steep slope for low Ag-concentrations and a small gradient for higher Ag molality. A quantitative extrapolation of these curves for vanishing Ag-concentration would require measuring points in the range $[Ag] < 0.025$ molal; enormous measuring times would be necessary for such samples. The given measuring points show the trend of the halide curves to converge to the same shift δ^* for Ag-concentration $\rightarrow 0$ as the NO_3-curve. These results confirm the assumption that the halide anions Cl^- and Br^- are partly coordinated to the $[Ag\,ea_2]^+$ complexes in contrast to the NO_3^--anions, which do not show such an effect.

A further confirmation to this assumption comes from a NMR investigation of the anion nuclei: In 4 molal samples of the Ag salts $AgNO_3$, AgCl, and

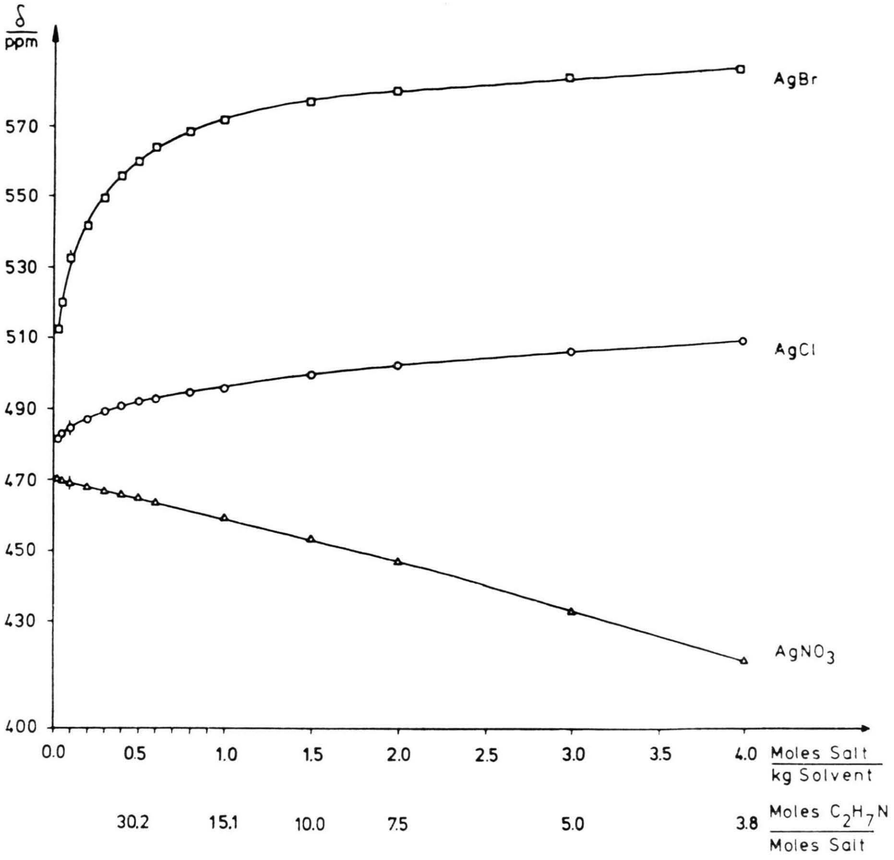

Fig. 3. ^{109}Ag chemical shifts of $AgNO_3$, AgCl, and AgBr in 70% aqueous ea solution as a function of the concentration of the silver salt, referred to the resonance frequency of the Ag^+-ion in H_2O at infinite dilution. In a second abszissa scale, the total number of ea solvent molecules in the sample per Ag^+-ion is given. The uncertainty of the measured shifts is ± 2 ppm for [Ag] < 0.1 molal and ± 1 ppm for higher concentrations of silver.

AgBr dissolved in 70% ea solution, the NMR signals of ^{14}N, ^{35}Cl, and ^{79}Br, respectively, were recorded. Each of these nuclei has an electric quadrupole moment in the range $(0.01 \text{ to } 0.3) \cdot 10^{-24}\,\text{cm}^2$. These nuclei in free anions show relatively narrow NMR lines: The linewidths of ^{14}N, ^{35}Cl, and ^{79}Br in 4 molal aqueous solutions of $NaNO_3$, NaCl, and NaBr are about 15 Hz, 30 Hz, and 700 Hz, respectively.

Anions, which are coordinated to a molecule or a complex, however, are in general not in a spherically symmetric environment, i. e. at the places of these nuclei there is an electric field gradient. The interaction of the quadrupole moments of the nuclei under investigation with this field gradient yields short relaxation times and broad NMR lines will result, which may be too broad as to be detected in some cases. Indeed the NMR signals of ^{35}Cl and ^{79}Br in the 4 molal solutions of AgCl and AgBr in 70% ea solution were not to be detected, even in measuring times which exceed those used for the aqueous samples by a factor of 500 to 1000. On the other hand, the ^{14}N NMR line of the $AgNO_3$ sample had a width of 22 Hz and nearly the same intensity as that of the aqueous sample. This shows that the halide anions Cl^- and Br^- are coordinated to the $[Ag\,ea_2]^+$ complex, at least for a fraction of the time, in contrast to the NO_3^--anion.

As the ^{109}Ag NMR spectrum consists of one single line for all samples, there must be a rapid chemical exchange between solvate complexes in silver halide solutions in 70% ea solution of the type

$$[Ag\,ea_2]^+ + X \overset{K_x}{\rightleftarrows} [Ag\,ea_2 \cdot X],$$

where X stands for the anions Cl^- or Br^-.

A coordination of the halide anions in the manner

$$[\mathrm{Ag\,ea_2}]^+ + \mathrm{X} \rightleftarrows [\mathrm{Ag\,ea\cdot X}] + \mathrm{ea}$$

may be excluded by the fact that AgCl and AgBr can not be dissolved quantitatively in an aqueous ea-solution which contains the same number of ea molecules as silver halide molecules to be dissolved.

Not only the coordinated anions, but also the free ones yield a chemical shift of the ^{109}Ag NMR line in the same manner as the NO_3^--anion. For the following, the assumption is made, that the ^{109}Ag chemical shift due to these free anions is the same for the $[\mathrm{Ag\,ea_2}]^+$ and the $[\mathrm{Ag\,ea_2\cdot X}]$ complexes. Let be $[\mathrm{X}]$ the concentration of the free halide anions in mol/l, then the chemical shift caused by these free anions is $\delta_\mathrm{X}\cdot[\mathrm{X}]$; here δ_X is the slope of the shift curve vs. concentration, this constant has the unit ppm · l/mol. With the further quantities:

$\delta_{K\mathrm{X}}$: ^{109}Ag chemical shift between the $[\mathrm{Ag\,ea_2}]^+$ and the $[\mathrm{Ag\,ea_2\cdot X}]$ complexes at vanishing silver concentration.

P : Relative abundance of the $[\mathrm{Ag\,ea_2}]^+$ complex $P = [[\mathrm{Ag\,ea_2}]^+]/[\mathrm{Ag}]$,

P_X : Relative abundance of the $[\mathrm{Ag\,ea_2\cdot X}]$ complex $P_\mathrm{X} = [[\mathrm{Ag\,ea_2\cdot X}]]/[\mathrm{Ag}]$

with $[\mathrm{Ag}] = [[\mathrm{Ag\,ea_2}]^+] + [[\mathrm{Ag\,ea_2\cdot X}]]$ (the total silver concentration in the sample) the chemical shift of the sample (related to the Larmor frequency of the $[\mathrm{Ag\,ea_2}]^+$ complex at vanishing Ag-concentration) is

$$\delta = \delta_{K\mathrm{X}}\cdot P_\mathrm{X} + \delta_\mathrm{X}\cdot[\mathrm{X}].$$

The concentrations of the complexes may be calculated with the aid of the mass action law:

$$[[\mathrm{Ag\,ea_2\cdot X}]] = [\mathrm{Ag}] + 1/(2\,K_\mathrm{X}) - R$$

and

$$[\mathrm{X}] = [[\mathrm{Ag\,ea_2}]^+] = R - 1/(2\,K_\mathrm{X})$$

with

$$R = \sqrt{1/(4\,K_\mathrm{X}^2) + [\mathrm{Ag}]/K_x}\,.$$

Now the chemical shift of the sample under investigation is

$$\delta = \delta_{K\mathrm{X}}\left\{1 + \frac{1}{2[\mathrm{Ag}]\cdot K_\mathrm{X}} - \frac{R}{[\mathrm{Ag}]}\right\} + \delta_\mathrm{X}\,\{R - 1/(2\,K_\mathrm{X})\}$$

with $\mathrm{X} = \mathrm{Cl}^-$ or Br^-.

Both chemical shift curves for the halides in Fig. 3 must be represented by this formula (neglecting the shift δ^* of the $[\mathrm{Ag\,ea_2}]^+$ complex at vanishing Ag-concentration). By a Gaussian least squares fitting routine, the optimum values for the parameters $\delta_{K\mathrm{X}}$, δ_X, and K_X were determined. These optimum parameters are given in Table 1; the relatively large uncertainties of the equilibrium constants are due to the fact that no shifts were to be measured for $[\mathrm{Ag}] < 0.02$ mol/l because of the weak ^{109}Ag NMR signals.

With these optimum parameters, the two contributions to the chemical shift δ : $P_\mathrm{X}\cdot\delta_{k\mathrm{X}}$ by the $[\mathrm{Ag\,ea_2\cdot X}]$ complex, and $\delta_\mathrm{X}\cdot[\mathrm{X}]$ by the free anions were to be calculated. Together with the total shift δ, these contributions are plotted in Figs. 4 a and 4 b for the anions Cl^- and Br^-, respectively.

Within the experimental uncertainties of ± 1 ppm, as marked in Fig. 4 a, there is an excellent agreement between the experimental result and the fitted curve for the AgCl samples. However there are slight differences for the AgBr samples in Fig. 4 b, which may be due to the fact that the assumption of an equal influence of the free halide anions on the $[\mathrm{Ag\,ea_2}]^+$ and the $[\mathrm{Ag\,ea_2\cdot X}]$ complexes is not entirely correct.

4.3. *Relaxation Investigations and Lifetimes of the Solvate Complexes*

All results of the relaxation measurements are contained in Table 2. The first conclusion, which may be drawn by comparing the relaxation rates of the 1 molal $AgNO_3$ solutions in H_2O and D_2O, is the fact that the spin-lattice relaxation rate $1/T_1$ and especially the transverse relaxation rate $1/T_2$ are only to a small part due to the interaction of the ^{109}Ag nucleus with the magnetic moments of the nuclei in the solvent molecules, as the magnetic

Table 1. Optimum fitting parameters for the coordination of the halide anions to the $[\mathrm{Ag\,ea_2}]^+$ complex. The uncertainties given here, are the standard deviations of the results.

X	δ_{K_X} / ppm	δ_X / ppm · l/mol	K_X / l/mol
Cl^-	13.1 ± 0.7	317 ± 71	421 ± 171
Br^-	107 ± 5	80 ± 24	39 ± 6

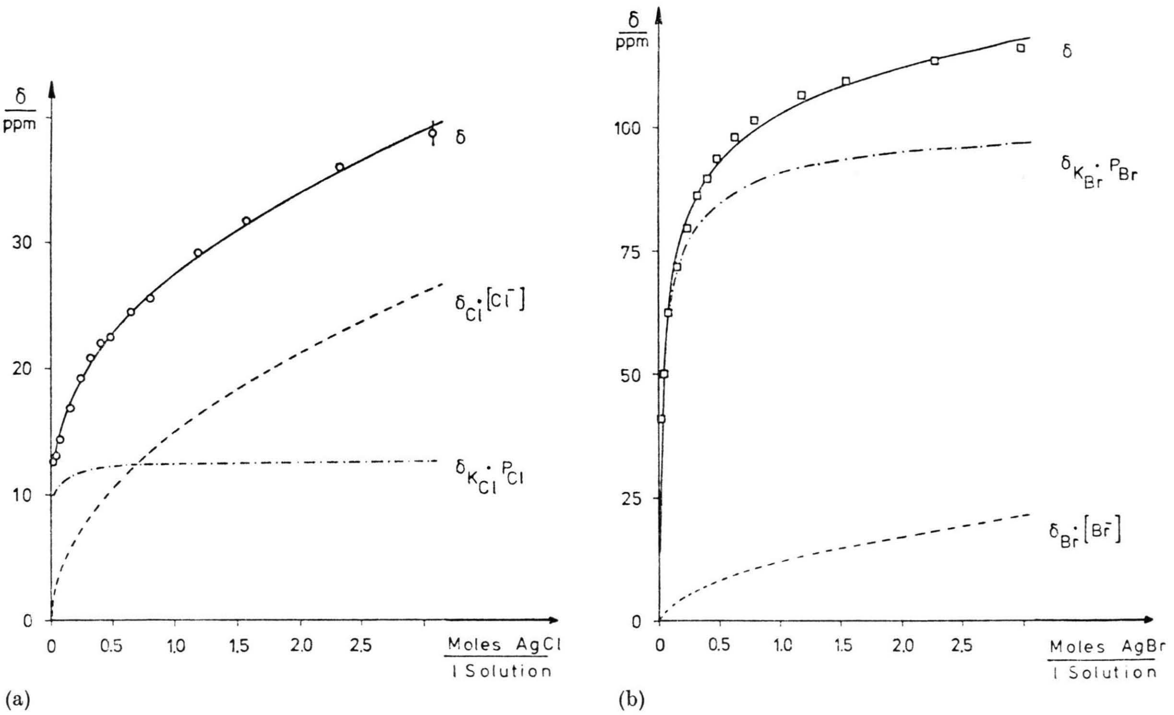

Fig. 4. Chemical shifts of (a) AgCl and (b) AgBr in 70% aqueous ea solution as a function of the concentration of the silver salt, referred to the Larmor frequency of the $[Ag\,ea_2]^+$ complex in 70% ea solution (the ordinate scales of Fig. 3 and Fig. 4 differ by the additive constant δ^*). The contributions to the chemical shift by the coordination of the anions — — — and by the free anions - - - - were calculated with the optimum parameters given in Table 1. The curve ——— is the sum of these two calculated contributions. The measured shifts are marked by circles and squares for the Cl^- and Br^- anions, respectively. The experimental uncertainty of ± 1 ppm is indicated in (a) and it corresponds to the size of the squares in (b).

Table 2. Results of relaxation measurements of ^{109}Ag in different samples. The uncertainties of the relaxation times T_1 and T_2 are $< \pm 7\%$.

Sample	Experimental results		Relaxation times		Transverse relaxation rate by chemical exchange	
	$\{T_1/T_2\}/s$	$T_1 + T_2$	T_1/s	T_2/s	upper bond $\{1/T_2\}/s^{-1}$	lower bond $\{1/T_2 - 1/T_1\}/s^{-1}$
$AgNO_3$ 0.15 molal in H_2O-ea mixture with the mole fraction						
$X_{ea} = 0.0076$	7.1					
$X_{ea} = 0.0063$	12.4					
$X_{ea} = 0.0056$	27.7					
$AgNO_3$ 1 molal in D_2O	7.6	1261	1115	146	$6.85 \cdot 10^{-3}$	$5.95 \cdot 10^{-3}$
$AgNO_3$ 1 molal in H_2O	6.1	1119	962	157	$6.37 \cdot 10^{-3}$	$5.33 \cdot 10^{-3}$
$AgNO_3$ 4 molal in H_2O	6.5	787	682	105	$9.52 \cdot 10^{-3}$	$8.06 \cdot 10^{-3}$
$AgNO_3$ 4 molal in acetonitrile	2.3	543	380	163	$6.13 \cdot 10^{-3}$	$3.50 \cdot 10^{-3}$
$AgNO_3$ 4 molal in 70% ea sol.	2.8	112	83	30	$33.3 \cdot 10^{-3}$	$21.3 \cdot 10^{-3}$
AgCl 4 molal in 70% ea sol.	2.0	190	127	63	$15.9 \cdot 10^{-3}$	$8.00 \cdot 10^{-3}$
AgBr 4 molal in 70% ea sol.	2.3	200	139	61	$16.4 \cdot 10^{-3}$	$9.20 \cdot 10^{-3}$

moments of the proton and of the deuteron differ by a factor 3.3. Rather the relaxation is due to fluctuating chemical shift, which may result from an anisotropy of the shielding of the ^{109}Ag nucleus in the solvate complex, from chemical exchange in this complex, and from fluctuating shielding by the different solvent molecules and the anions in the surrounding of the silver solvate complex.

It is obvious that the ^{109}Ag relaxation rates of $AgNO_3$ in the solvent mixture ea-H_2O are considerably higher than those of $AgNO_3$ in the pure solvents H_2O and acetonitrile (CH_3CN). Unfortunately pure ea is a gas at room temperature and cannot be used as solvent. These higher relaxation rates in the solvent mixture H_2O-ea may be due to a solvation in addition to the inner coordination sphere. Even if this solvation in the higher solvation spheres is not selective (as pointed out in Sect. 4.1); this coordination guarantees a dwelling time of the solvent molecules near the $[Ag\,ea_2]^+$ complex considerably longer than it would be due to the thermal motion of the molecules. The change of such a ligand molecule must be regarded as chemical exchange rather than thermal motion.

The ^{109}Ag relaxation rates $1/T_1$ and $1/T_2$ of the silver halides AgCl and AgBr 4 molal in 70% ea solution are smaller by a factor of about 2 than those of $AgNO_3$ in the same solvent. By the coordination of the halide anions to the $[Ag\,ea_2]^+$ complexes the solvation outside the inner solvation sphere is changed in comparison with the NO_3^--anion.

The contribution $1/T_2 - 1/T_2^\circ$ of a rapid chemical exchange between the two sites A and B to the transverse relaxation rate was pointed out by Meiboom [12] and by Allerhand and Gutowsky [13]. Here T_2° is the transverse relaxation time, which would occur if there were no chemical exchange. If T_1 is not influenced by chemical exchange and in the extreme narrowing case, $T_2^\circ = T_1$ may be assumed. For very rapid chemical exchange (lifetime of at least one site $\leqq$ Larmor period), T_1 is influenced by the exchange, and it is surely

$$T_1 \leqq T_2^\circ < \infty\,.$$

Specialized to the silver halides in 70% aqueous ea-solution, site A may be the $[Ag\,ea_2]^+$ complex and site B the $[Ag\,ea_2 \cdot X]$ complex. With the lifetimes $\tau_{[Ag\,ea_2]^+}$ and $\tau_{[Ag\,ea_2 \cdot X]}$, respectively, the contribution of the exchange to the transverse relaxation rate is

$$1/T_2 - 1/T_2^\circ = P \cdot P_x (2\,\pi\,\nu_L \cdot \delta_{KX})^2 \cdot \tau_X$$

with

$$\tau_X^{-1} = \tau_{[Ag\,ea_2]^+}^{-1} + \tau_{[Ag\,ea_2 \cdot X]}^{-1}\,.$$

It must be emphasized, however, that this is not the only chemical exchange process which contributes to the transverse relaxation rate of the sample. Therefore, inserting the measured relaxation time T_2 into the Gutowsky formula, the result will not be the real lifetimes of the complexes, but their upper bonds. To estimate this upper bond, it is suitable to set $T_2^\circ = \infty$, i.e. the contribution of the chemical exchange to the transverse relaxation rate must be taken from the last but one column of Table 2. The results of the upper bonds for the lifetimes of the solvate complexes of 4 molal AgCl and AgBr solution in 70% aqueous ea-solution are given in Table 3.

Table 3. Calculation of upper bonds of the lifetimes of the solvate complexes in the chemical exchange

$$[Ag\,ea_2]^+ + X \rightleftarrows [Ag\,ea_2 \cdot X]$$

with $X = Cl^-$ or Br^-.

X	Cl^-	Br^-
P	0.027	0.088
P_X	0.973	0.912
δ_{KX}/ppm	13.1	106.6
τ_X/s	$< 5.1 \cdot 10^{-6}$	$< 2.6 \cdot 10^{-8}$
$\tau\ [Ag\,ea_2]$/s	$< 5.3 \cdot 10^{-6}$	$< 2.9 \cdot 10^{-8}$
$\tau\ [Ag\,ea_2 \cdot X]$/s	$< 18.5 \cdot 10^{-5}$	$< 2.9 \cdot 10^{-7}$

Surely, the bromine ion is coordinated to the $[Ag\,ea_2]^+$ complex for time intervals which are smaller than the Larmor period of ^{109}Ag, and therefore not only T_2 but also the longitudinal relaxation time T_1 is influenced by this exchange. For the chloride ion, the time interval of coordination may exceed the Larmor period of ^{109}Ag.

The exchange of the ligands H_2O and ea in the inner solvation sphere is considerably slower. This follows from the results of the ratios T_1/T_2 given in Table 2 for 0.15 molal $AgNO_3$ solutions as well as from the vanishing NMR signal of those acidified samples which contain the $[Ag\,W\,ea]^+$ complex (see Section 4.1.). If there is an exchange between the $[Ag\,W\,ea]^+$ and the $[Ag\,ea_2]^+$ complexes, the transverse relaxation rate $1/T_2$ is influenced much stronger than the spin-lattice relaxation rate $1/T_1$.

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