

# $^{109}\text{Ag}$ Nuclear Magnetic Resonance Studies of Organic and Inorganic Silver Complexes

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The NMR lines of  $^{109}\text{Ag}$  have been investigated in solutions of several silver salts in acetonitrile, propionitrile, pyridine, and ethylenediamine, and also in aqueous solutions of  $\text{Na}_2\text{S}_2\text{O}_3$  and ethylamine. In these solvents the  $\text{Ag}^+$ -ions form one or several complexes. In any case a single NMR line was to be detected, i. e. a rapid chemical exchange between different complexes in a sample may be assumed. The concentration dependence of the chemical shifts was determined with high accuracy for these solutions. From these results the chemical shift data of some defined complexes were derived. The chemical shifts of mixtures of  $\text{AgCl}$  and  $\text{AgBr}$  and also of  $\text{AgCl}$  and  $\text{AgI}$  dissolved in 70% aqueous solution of ethylamine are linear functions of the anions mole fraction. In two samples of  $\text{AgNO}_3$  dissolved in organic solvents, the ratio  $\nu(^{109}\text{Ag})/\nu(^{107}\text{Ag}) = 1.149\,640(1)$  was measured in good agreement with the value from silver salts in aqueous solutions; i. e. no primary isotopic effect was to be detected within these limits of error (0.9 ppm).

## 1. Introduction

Both silver nuclei  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$  are not easily accessible to NMR investigations, as they have both the nuclear spin  $I = 1/2$  (Ref.<sup>1</sup>) and relatively small magnetic moments. In our magnetic field of 1.807 Tesla, their Larmor frequencies are  $\nu(^{107}\text{Ag}) \approx 3.114$  MHz and  $\nu(^{109}\text{Ag}) \approx 3.579$  MHz. The natural abundances of these silver isotopes are 51% and 49% respectively.

Therefore the NMR signals of  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$  in a 1 molar solution of an Ag salt are 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. As the NMR signal of  $^{109}\text{Ag}$  is stronger by a small amount than that of  $^{107}\text{Ag}$ , the  $^{109}\text{Ag}$  nucleus is preferred for NMR investigations.

A further difficulty for silver NMR investigations results from the extremely weak interaction of the silver nuclei with their surroundings, due to the missing quadrupole moments ( $I = 1/2$ ) combined with the small magnetic moments. The consequence of this are very long relaxation times of the silver nuclei, e. g. relaxation times  $T_1$  of more than 5 minutes were measured for the  $^{109}\text{Ag}$  nucleus<sup>2</sup>.

These are probably the reasons for the few silver NMR investigations up until now: As far as we know there were two experiments<sup>3,4</sup> more than twenty years ago; both authors have used relatively concentrated aqueous  $\text{AgNO}_3$  solutions as samples

and they have added paramagnetic ions, in order to reduce the relaxation times  $T_1$  and  $T_2$ , i. e. to broaden the extremely narrow NMR lines beyond the line width caused by the inhomogeneity of the field  $B_0$ . Unfortunately such admixtures can cause considerable shifts of the NMR lines (see e. g.<sup>5</sup>), which are undesired in most cases.

The first systematic NMR investigations of  $\text{Ag}^+$ -ions in aqueous solutions of different silver salts<sup>6</sup> were performed with the Quadriga-technique<sup>7</sup>, a steady-state pulse technique, which avoids any loss of NMR signal due to the inhomogeneity of the field  $B_0$ , without any paramagnetic admixtures. In this earlier paper accurate measurements of the ratio of the Larmor frequencies  $\nu(^{109}\text{Ag})/\nu(^{107}\text{Ag})$  were reported and the hyperfine structure anomaly deduced. From systematical investigations of the chemical shifts of the silver salts as a function of the concentration of the aqueous solution, accurate values for the nuclear magnetic moments of the silver isotopes  $^{107}\text{Ag}$  and  $^{109}\text{Ag}$  ( $\text{Ag}^+$  solely surrounded by water) and for the shielding constant  $\sigma$  were determined.

Besides the solvent "pure water" there are several organic solvents and on the other hand water with thiosulphate or ethylamine admixtures, which form complexes with the  $\text{Ag}^+$ -ion. In the present work NMR investigations of such complexes will be reported.

## 2. Experimental

Our measurements were performed with a pulse spectrometer, described in<sup>8</sup>. This apparatus was

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especially developed to detect very weak NMR signals in the frequency range 1...4.5 MHz. The magnetic field  $B_0 \approx 1.807$  Tesla is stabilized with a  $^7\text{Li}$  - NMR probe<sup>9</sup>. The spatial homogeneity of the field ( $|\Delta B_0| \leq 5 \cdot 10^{-6}$  Telsa in the range of the relatively large NMR sample) is achieved by special nickel-shims. The temperature of the samples was held constant within a range of  $\pm 1$  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 measuring technique and the evaluation of the NMR signals were just the same as used for the investigation of the  $\text{Ag}^+$ -ions<sup>6</sup>; they are described in detail there. The Quadriga Fourier Transform technique was used for all silver measurements. The shape of the NMR absorption line recorded with this technique is given by

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

$\nu_L$  is the Larmor frequency and  $T$  the pulse period, which was chosen for all measurements:  $T = 11.1$  msec, i. e. the pulse repetition rate was 90 Hz. The halfwidth of the NMR line is  $\Delta\nu_{1/2} = 0.6/T = 54$  Hz, using the pulse repetition rate  $1/T = 90$  Hz. This line width is independent of the inhomogeneity of the magnetic field  $B_0$  as the pulse spacing is  $T \ll T_2^*$ , the time constant describing the decay of the NMR signal due to the inhomogeneity of the field  $B_0$ ; on the other hand the line width is independent of the natural width of the NMR line, i. e. of the relaxation times, as  $T \ll T_1, T_2$  holds.

To determine chemical shifts as well as ratios of Larmor frequencies, the sample replacement technique was used. The reference sample always had the same size and shape as the sample under investigation. Samples with higher silver concentration were measured in spheres of 18 mm internal diameter, in order to avoid corrections for bulk susceptibility. Samples with concentrations less than 2 molal were contained in cylinders of 21 mm internal diameter and 40 mm filling height. No corrections for bulk susceptibility were made for these samples as they are less than the statistical errors.

The measuring times for the different samples were in the range of 12 minutes for samples with the highest concentrations to 2 hours for the samples with the least concentrations (0.3 molal); within these times signal/noise-ratios of at least 20 were achieved for all samples. All measurements of

chemical shifts and ratios of Larmor frequencies were repeated at least 6 times at different days.

### 3. Samples

For the chemical shift measurements the following reference samples were used

Ref. No. 3: 8.3 molal aqueous solutions of  $\text{AgF}$  and  
Ref. No. 5: 14 molal solution of  $\text{AgNO}_3$  in a mixture of 90 wt.% acetonitrile ( $\text{CH}_3\text{CN}$ ) and of 10 wt.%  $\text{D}_2\text{O}$ .

The reference sample No. 3 had been used in our previous investigations of silver ions<sup>6</sup>; because of its considerably better NMR signal, reference sample No. 5 was preferred for the present investigations in most cases. The  $^{109}\text{Ag}$  Larmor frequency of Ref. 5 was referred to that of the deuteron in the same sample with the highest accuracy<sup>10</sup>.

The chemical shifts of the  $^{109}\text{Ag}$  Larmor frequencies  $\nu_{\text{Ref}}$  of these samples referred to the Larmor frequency  $\nu_0$  of the  $\text{Ag}^+$ -ion in  $\text{H}_2\text{O}$  at infinite dilution are

$$\delta(\text{Ref. 3}) = (\nu_{\text{Ref.3}} - \nu_0) / \nu_0 = (14.0 \pm 1.5) \text{ ppm}^6 \text{ and}$$

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

measured at a temperature of  $(300 \pm 1) \text{ K}$ . The uncertainties of these results are due to the extrapolation of the Larmor frequencies of aqueous solutions of silver salts to zero concentration.

For preparing the samples for the present investigations the following silver salts and solvents were used:  $\text{AgNO}_3$  (Merck No. 1512 and J. T. Baker No. 1182, both analytical grade),  $\text{AgF}$  (Merck No. 12333),  $\text{AgCl}$  (Merck No. 10486, Selectipur),  $\text{AgBr}$  (Merck No. 10485, Selectipur),  $\text{AgI}$  (Merck No. 12335),  $\text{AgNO}_2$  (Merck No. 12336),  $\text{CH}_3\text{COOAg}$  (Merck No. 1505),  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{ H}_2\text{O}$  (Merck No. 6516, analytical grade); acetonitrile  $\text{CH}_3\text{CN}$  (Merck No. 16, Uvasol) propionitrile  $\text{C}_2\text{H}_5\text{CN}$  (Merck No. 807068), 70% solution of ethylamine  $\text{C}_2\text{H}_7\text{N}$  in  $\text{H}_2\text{O}$  (Merck No. 820024), ethylenediamine  $\text{C}_2\text{H}_8\text{N}_2$  (Merck No. 800947), pyridine  $\text{C}_5\text{H}_5\text{N}$  (Merck No. 9728, analytical grade) and  $\text{H}_2\text{O}$  with a conductivity of less than  $10^{-6} \Omega^{-1} \text{ cm}^{-1}$ .

In general, the concentrations of the solutions were determined by weighing salt and solvent. Preparing the aqueous  $\text{AgF}$  solutions, used as reference, always some metallic  $\text{Ag}$  dropped out, which had to be filtered, therefore the concentration of

this solution was determined from their density by using the values of Jahn-Held and Jellinek<sup>11</sup>.

Dissolving the silver halides in ethylamine solution a considerable heat of solution appeared, which had to be removed in order to prevent a loss of ethylamine.

## 4. Results and Discussion

### 4.1 The Ratio of the Larmor Frequencies of $^{107}\text{Ag}$ and $^{109}\text{Ag}$

In a former work this ratio of Larmor frequencies was determined in four different samples, all of these were aqueous solutions of different silver salts. From 82 ratios measured, the following mean value results:

$$\nu(^{109}\text{Ag})/\nu(^{107}\text{Ag}) = 1.149\,639\,7(8).$$

This relative error of 0.7 ppm is three times the standard deviation of the result, and the results obtained from the four samples were all within these limits of error, i.e. a primary isotopic effect was not to be detected.

In order to search for such an effect, in two solutions of Ag salts in organic solvents, this ratio of Larmor frequencies was determined. In a 14 molal solution of  $\text{AgNO}_3$  in a mixture of 90 wt.% acetonitrile and 10 wt.%  $\text{D}_2\text{O}$  (Ref. No. 5) the ratio is:

$$\nu(^{109}\text{Ag})/\nu(^{107}\text{Ag}) = 1.149\,639\,6(10)$$

and in a 9 molal solution of  $\text{AgNO}_3$  in propionitrile:

$$\nu(^{109}\text{Ag})/\nu(^{107}\text{Ag}) = 1.149\,640\,4(10).$$

These results are the mean values of 13 ratios measured with each sample, and the errors of 0.9 ppm are three times the standard deviations of the results.

Both results are in good agreement with each other and with the ratio from the silver salts dissolved in water, i.e. there is no primary isotopic effect within these limits of error, a primary isotopic effect is surely less than 0.9 ppm.

### 4.2 Chemical Shifts of the Silver Complexes

In all samples only one single NMR line was to be detected, i.e. in all samples with more than one Ag-complex, a rapid chemical exchange must take place, and the measured Larmor frequency is a weighted mean of the Larmor frequencies of all

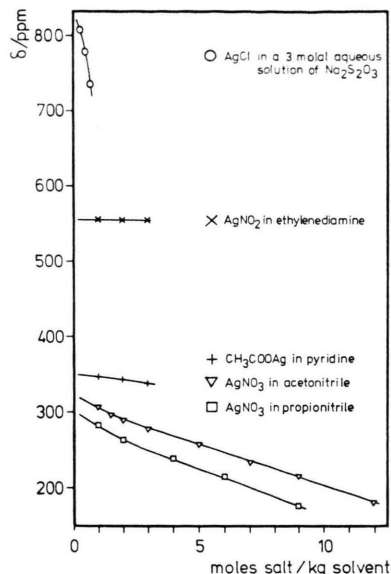


Fig. 1. Chemical shifts of the  $^{109}\text{Ag}$  NMR line in different solutions of silver salts in solvents, forming complexes with the  $\text{Ag}^+$ -ions, as a function of the concentration. The chemical shifts, plotted on the ordinate, are defined  $\delta = (\nu_x - \nu_{\text{Ag}^+})/\nu_{\text{Ag}^+}$ , where  $\nu_{\text{Ag}^+}$  is the Larmor frequency of the  $\text{Ag}^+$  ion in  $\text{H}_2\text{O}$  at infinite dilution. The uncertainties of the measured shifts in the range 1...2 ppm are less than the size of the symbols used by a factor 5...10.

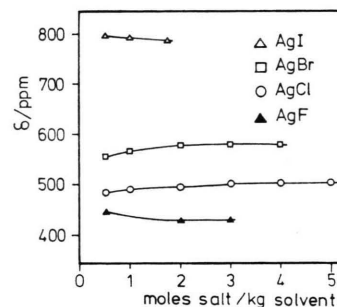


Fig. 2. Chemical shifts of the  $^{109}\text{Ag}$  Larmor frequency in solutions of silver halides in 70% aqueous ethylamine solution as a function of the concentration. The uncertainties of the measured shifts are considerably less than the size of the symbols used.

Ag-complexes in the sample. In Fig. 1 and Fig. 2 the chemical shifts of the  $^{109}\text{Ag}$  NMR lines in some solutions of silver salts in different solvents are plotted versus the concentrations of the solutions. The zero-point of the ordinate scale is the shift of the  $\text{Ag}^+$ -ion in aqueous solution at infinite dilution with the Larmor frequency  $\nu_{\text{Ag}^+}$ . The chemical shift is defined:

$$\delta(\text{sample}) = (\nu_{\text{sample}} - \nu_{\text{Ag}^+})/\nu_{\text{Ag}^+}.$$

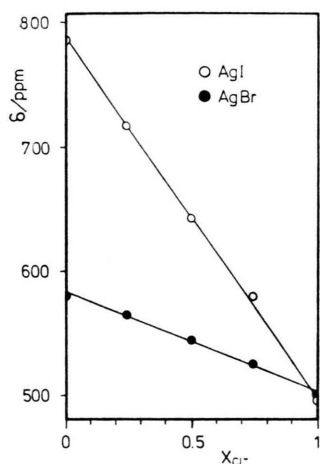


Fig. 3.  $^{109}\text{Ag}$  chemical shifts in solutions of mixtures of AgCl and AgBr and also of AgCl and AgI in 70% aqueous solution of ethylamine. The total Ag-concentration was held constant: 4 molal for the AgCl+AgBr and 2 molal for the AgCl+AgI mixtures. The abscissa scale is the mole fraction of the  $\text{Cl}^-$  anions in the solution:  $X_{\text{Cl}^-} = [\text{Cl}^-]/([\text{Br}^-] + [\text{Cl}^-])$  or  $X_{\text{Cl}^-} = [\text{Cl}^-]/([\text{I}^-] + [\text{Cl}^-])$  respectively.

All shifts plotted in Figs. 1, 2 and 3 were measured at a temperature of  $(300 \pm 1)\text{K}$ .

The uncertainties of the measured chemical shifts are about  $\pm 1$  ppm for the samples with Ag-concentrations  $\geq 1$  molal, for the less concentrated solutions the statistical error tends to  $\pm 2$  ppm. Likewise an uncertainty of  $\pm 2$  ppm must be assumed for the chemical shifts of the solutions of silver halides in 70% aqueous ethylamine solutions, plotted in Figs. 2 and 3, as the ethylamine concentrations may be lowered by the considerable heat of solution. These uncertainties are three times the standard deviations of the mean values of at least 6 shift measurements per concentration. An additional uncertainty arises from the measured chemical shift of the reference samples, as given in Sect. 3, however this error is the same for all measured points of one curve.

In the following these results will be discussed in detail:

#### 4.2.1 $\text{AgNO}_2$ in Ethylenediamine

Within the limits of error, the  $^{109}\text{Ag}$  chemical shift in the solution of  $\text{AgNO}_2$  in ethylenediamine (= en) is independent of the Ag-concentration. This is a hint for the predominance of one silver complex

in the solution. Schwarzenbach et al.<sup>12</sup> have pointed out the following complex ions in aqueous solutions of ethylenediamine and silver salts:  $[\text{Ag}_2\text{en}]^{2+}$ ,  $[\text{Ag en}]^+$ ,  $[\text{Ag}_2\text{en}_2]^{2+}$  and  $[\text{Ag en}_2]^+$ . The equilibrium constants given there, show that nearly all silver ions form the complex  $[\text{Ag en}_2]^+$  if there is an excess of en. If pure en is used as solvent, this is practically the only complex formed, with the chemical shift

$$\delta[\text{Ag en}_2]^+ = (554 \pm 2) \text{ ppm (in ethylenediamine)}.$$

Schwarzenbach<sup>13</sup> has pointed out two forms as well for the  $[\text{Ag en}]^+$  or the  $[\text{Ag}_2\text{en}_2]^{2+}$  complex as for the  $[\text{Ag en}_2]^+$  complex: a linear form and a chelate form, in which both N-atoms of the diamine are coordinated to the  $\text{Ag}^+$ -ion, forming a ring of five atoms. Probably the two forms of the  $[\text{Ag en}_2]^+$  complex will lead to different Larmor frequencies of the  $^{109}\text{Ag}$  NMR. As no dependence of the  $^{109}\text{Ag}$  resonance frequency on the concentration of the solution was observed, it must be assumed, that either one of the two forms of the  $[\text{Ag en}_2]^+$  complex appears in poor concentration compared with the other, or the ratio of the concentrations of both forms does not depend on the Ag-concentration of the solution.

#### 4.2.2 $\text{CH}_3\text{COOAg}$ in Pyridine

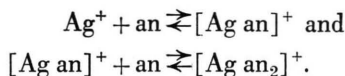
The  $^{109}\text{Ag}$  chemical shift of this solution is slightly depending on the Ag-concentration. In aqueous solutions of pyridine (= py) and silver salts, the following complexes  $[\text{Ag py}]^+$  and  $[\text{Ag py}_2]^+$  were found, and the complex formation constants were determined by a variety of authors (p. 74 of Ref. <sup>14</sup>) with potentiometric and calorimetric techniques and from the solubility. The logarithms of the equilibrium constants are  $\lg K_1 \approx 2.0$  and  $\lg K_2 \approx 2.2$ . This means for lower Ag-concentrations and for higher py-concentrations and especially for pure pyridine as solvent, the predominance of the  $[\text{Ag py}_2]^+$  complex ion. For higher Ag-concentrations the  $[\text{Ag py}]^+$  complex may appear with small abundance and contribute to the measured Larmor frequency. By extrapolation of the measured chemical shifts to Ag-concentration  $\rightarrow 0$ , the chemical shift of the  $[\text{Ag py}_2]^+$  complex ion in pyridine becomes

$$\delta[\text{Ag py}_2]^+ = (350 \pm 3) \text{ ppm}.$$



#### 4.2.3 $\text{AgNO}_3$ in Acetonitrile

The  $^{109}\text{Ag}$  chemical shift of this solution is considerably depending on the Ag-concentration, which can be extended to more than 14 molal. This dependence may be explained, regarding the results of infrared-, Raman- and proton NMR-spectroscopy by Janz et al.<sup>15-18</sup>, and the results of electric conductance-<sup>19</sup> and diffusion-measurements<sup>20</sup>. In the concentration range of the  $\text{AgNO}_3$  solutions in acetonitrile (=an) used for the present NMR investigations, there are the following complex ions:  $[\text{Ag an}]^+$  and  $[\text{Ag an}_2]^+$ . The average solvation number is decreasing from  $N=4$  for very poor Ag-concentrations ( $<0.5$  molar) via  $N=2$  in the moderate concentration range  $0.5 \dots 5$  molar ( $\cong 0.64 \dots 7.4$  molal) to  $N=1$  at higher concentrations ( $>5$  molar). This behaviour is due to the competition of Ag-ion – solvent and ion – ion interaction described by the equilibrium reaction formulae:



For higher Ag-concentrations both equilibria are shifted to the left. For Ag-concentrations  $<5$  molar ( $\cong 7.4$  molal) the predominant complex is  $[\text{Ag an}_2]^+$ , and for Ag-concentrations  $>5$  molar the complex  $[\text{Ag an}]^+$  predominates<sup>18</sup>.

The measured  $^{109}\text{Ag}$  NMR frequency is a weighted mean of the Larmor frequencies of the  $\text{Ag}^+$ -ion and the complex ions  $[\text{Ag an}]^+$  and  $[\text{Ag an}_2]^+$ . The extrapolation of the measured chemical shift curve to zero concentration of Ag leads to the shift of the  $[\text{Ag an}_2]^+$  complex in acetonitrile:

$$\delta[\text{Ag an}_2]^+ = (335 \pm 2) \text{ ppm}.$$

To improve this result, further measurements – not given in Fig. 1 – were performed.

From the negative gradient of the chemical shift curve vs. Ag-concentration in Fig. 1, a lower chemical shift  $\delta[\text{Ag an}]^+$  may be derived.

Janz et al.<sup>16</sup> have pointed out, the equilibria of the above reaction formulae being shifted to the right with decreasing and to the left with increasing temperature. From this and from the chemical shifts of the Ag complexes, discussed above, lower measured chemical shifts of the  $^{109}\text{Ag}$  NMR line are to be expected with increasing temperature. This is well confirmed by our experiments: In the range

275...323 K, the  $^{109}\text{Ag}$  chemical shift of a 12 molal solution of  $\text{AgNO}_3$  in an is a nearly linear function:

$$\delta(T) = \delta(300 \text{ K}) + C(T - 300 \text{ K})$$

with the gradient  $C = -(0.52 \pm 0.01) \text{ ppm/K}$ .

#### 4.2.4 $\text{AgNO}_3$ in Propionitrile

To investigate effects, combined with enlargement of the ligands, propionitrile (=pn) was used as solvent. The  $^{109}\text{Ag}$  chemical shift of this solution as a function of the Ag-concentration, given in Fig. 1, is a curve, which has nearly the same shape as the corresponding acetonitrile curve. Therefore we may assume in the pn-solution the corresponding complexes as in the an-solution:  $[\text{An pn}]^+$  and  $[\text{Ag pn}_2]^+$ . Especially at lower Ag-concentrations the  $[\text{Ag pn}_2]^+$  complex predominates, which was supposed by Pawelka<sup>21</sup> from potentiometric investigations. The extrapolation to Ag-concentration  $\rightarrow 0$  yields the chemical shift of the complex ion  $[\text{Ag pn}_2]^+$  in propionitrile:

$$\delta[\text{Ag pn}_2]^+ = (303 \pm 5) \text{ ppm}.$$

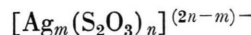
The temperature dependence of the  $^{109}\text{Ag}$  chemical shift of a 9 molal solution of  $\text{AgNO}_3$  in pn is nearly linear with the gradient

$$C = -(0.48 \pm 0.03) \text{ ppm/K}$$

(defined in the same manner as in Sect. 4.2.3 and for the same temperature interval).

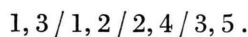
#### 4.2.5 $\text{AgCl}$ in 3 molal aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$

In aqueous solutions of thiosulphate a variety of silver complexes of the form



were pointed out. The distribution of the silver dissolved in different complexes was investigated with solubility measurements<sup>22</sup> and potentiometric measurements<sup>23</sup> by Nilsson and also by Pouradier and Rigola<sup>24</sup>. Extrapolating these results to our thio-sulphate concentration (3 molal) and to our Ag-concentrations, there are especially the mononuclear complexes  $m, n = 1, 3$  and  $1, 2$  and probably in lower abundance the polynuclear complexes  $m, n =$

2, 4 and 3, 5 in our samples. With decreasing Ag-concentration and for constant  $\text{S}_2\text{O}_3^{2-}$ -concentration, the equilibrium is shifted to the left of the following series of complexes:



For Ag-concentration  $\rightarrow 0$  and high  $\text{S}_2\text{O}_3^{2-}$ -concentration, practically the only complex to occur is  $m, n = 1, 3$ . Extrapolating the measured chemical shifts of the  $^{109}\text{Ag}$  NMR line, given in Fig. 1, to Ag-concentration  $\rightarrow 0$ , the chemical shift of the complex ion  $m, n = 1, 3$  in a 3 molal aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution is

$$\delta[\text{Ag}(\text{S}_2\text{O}_3)_3]^{5-} = (841 \pm 7) \text{ ppm}.$$

From the high negative gradient of the chemical shift curve in Fig. 1, a much lower chemical shift of the complex  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{-3}$  follows.

#### 4.2.6 Silver Halides in 70% aqueous Solution of Ethylamine

In aqueous solutions of ethylamine (=ea) and silver salts, the following complex ions are known:  $[\text{Ag ea}]^+$  and  $[\text{Ag ea}_2]^+$ , i. e. the maximum coordination number of  $\text{Ag}^+$  is also 2. The complex formation constants for these complex ions were determined by a variety of authors (p. 43 of Ref. <sup>14</sup>). The logarithms of the equilibrium constants are  $\lg K_1 \approx 3.3$  and  $\lg K_2 \approx 3.9$ , i. e. in a 70% aqueous solution of ea practically the only silver complex to occur is  $[\text{Ag ea}_2]^+$ .

The results of our measurements of the chemical shift of the  $^{109}\text{Ag}$  NMR line in solutions of the silver halides AgF, AgCl, AgBr, and AgI are plotted in Figure 2. The chemical shifts of the individual halides are spread over a range from 430 to 790 ppm. But the shift of each of the halides is only slightly depending on the Ag-concentration of the solution. The different shifts of the halides must be due to the different anions. From the behaviour of the  $^{109}\text{Ag}$  shifts of different Ag salts dissolved in water<sup>6</sup>, one would also expect a monotonous increase of the difference between the shift curves in Fig. 2 with increasing concentration of the anions. Obviously in Fig. 2 there is only a slight increase of the difference. Particularly Fig. 2 does not show a convergence of the four curves to a common shift value for Ag-concentration  $\rightarrow 0$ . Such a

convergence may occur in the concentration range 0...0.5 molal, in which Ag NMR investigations can not be easily performed up until now.

From the chemical shifts, plotted in Fig. 2, the conclusion must be drawn, that at least a fraction of the halide anions is coordinated to the  $[\text{Ag ea}_2]^+$  complex ion.

To confirm this result, solutions of mixtures of different silver halides in ea were investigated: In each sample only a single  $^{109}\text{Ag}$  NMR line was to be detected. The chemical shifts of mixtures of AgCl and AgBr, and of AgCl and AgI are plotted in Fig. 3 as a function of the mole fraction  $X_{\text{Cl}}$  of the anion  $\text{Cl}^-$ ; for each of the two curves, the total Ag-concentration was held constant (4 molal or 2 molal respectively). Within the limits of error ( $\pm 2$  ppm for the measured chemical shifts) for both mixtures the  $^{109}\text{Ag}$  chemical shifts are linear functions of the mole fraction  $X_{\text{Cl}}$ .

This result may be explained in the following way: Most of the anions are coordinated to the  $[\text{Ag ea}_2]^+$  complexes, but there is a rapid chemical exchange of the anions, i. e. the Ag nucleus records a time-averaged chemical shift. As the ratio of the lifetimes of the two complexes with different coordinated anions is the same as the ratio of the abundances of the two anions, the measured chemical shift is an average of the shifts of the two complexes weighted with the ratio of the abundances of the anions.

Assuming free anions, i. e. not coordinated to the  $[\text{Ag ea}_2]^+$  complexes, the result of Fig. 3 could only be explained, provided that the influence of the anions on the chemical shift is a linear function of their concentration. This supposition would be in striking contrast to the results of Figure 2.

## 5. Conclusion

The results about silver complexes deduced here from  $^{109}\text{Ag}$  chemical shift measurements are fragmentary in many points of view:

Most of the different solutions under investigation contain more than one complex ion, but only for those ions, which predominate for vanishing Ag-concentration, the chemical shift value was to be given. By investigating silver salts in mixtures of water and the solvents used here, more information

should be obtainable about the chemical shifts of complexes with only one organic ligand.

The ethylamine-complexes with coordinated anions, never described elsewhere up until now, should be investigated in detail; particularly measurements of the chemical shifts for Ag-concentrations  $<0.5$  molal would be of great interest. By using improved measuring techniques, such investigations should be possible.

On the other hand, no statements about the lifetimes of those complexes were made till now. From measurements of the  $^{109}\text{Ag}$  relaxation times, using new techniques<sup>2</sup>, such informations would result.

Measurements with these objects in view are presently running in our laboratory.

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