Nuclear Magnetic Resonance Studies of $^{35}$Cl, $^{37}$Cl, $^{79}$Br, and $^{81}$Br in Aqueous Solution

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The NMR signals of the nuclei $^1$H, $^{35}$Cl, $^{37}$Cl, $^{79}$Br, and $^{81}$Br have been investigated in aqueous solutions. The concentration dependence of the NMR signals of $^{35}$Cl and $^{81}$Br has been determined in solutions of alkali halides and alkali perchlorates in $H_2O$ and $D_2O$ and the large solvent isotope effect on the chemical shift has been established. The ratios of the Larmor frequencies of the halide nuclei relative to $^1$H have been measured with high accuracy. Using the concentration dependence, the ratios of the Larmor frequencies of the halide nuclei for infinite dilution relative to $^1$H in pure $D_2O$ are given. From these ratios, magnetic moments for the halide nuclei have been derived.

Introduction

Alkali metal and halide nuclei in aqueous alkali halide solutions show chemical shifts which vary with concentration. In dilute solutions, interaction of the alkali metal or halide ion with surrounding water molecules gives rise to a chemical shift between the free ion and the hydrated ion. This chemical shift will be denoted as the nuclear magnetic shielding constant $\sigma(X^\pm)$ or absolute chemical shift of the alkali metal and halide nuclei in aqueous solution of vanishing concentration. A determination of this quantity would yield an absolute scale for the relative chemical shifts of these nuclei.

Recently, Deverell has used various methods for calculating the nuclear shielding constants of alkali metal and halide ions in aqueous solutions. To proof the usefulness of Deverell's methods, experimental values for the shielding constants would be desirable.

A value for $\sigma(F^-)$ has been given by Ramsey. By comparing the nuclear magnetic moment of the free atom derived from atomic beam magnetic resonance or optical pumping techniques, with NMR measurements of the nuclear magnetic moment of the atom in solution, the nuclear magnetic shielding constants of $^{23}$Na (see 7), $^{85}$Rb (see 8), $^{87}$Rb (see 9, 10), $^{133}$Cs (see 2) and $^{207}$Pb (see 11) have been determined experimentally. An application of this method to chlorine, bromine and iodine fails, because the nuclear magnetic moments of these halides have not been measured with sufficient accuracy by either of these methods.

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We describe in the following the determination of the nuclear magnetic moments of $^{35}$Cl, $^{37}$Cl, $^{79}$Br and $^{81}$Br in the ions for vanishing concentration of aqueous solutions by the nuclear magnetic resonance method.

Experimental

Our frequency-swept spectrometer, which was described elsewhere, was used with some modifications. The frequency range is extended to 6 MHz...32 MHz. The rotation of spherical and cylindrical samples with diameters up to 10 mm is now possible. The magnetic field of 18.07 kOe is held constant by the aid of a $^7$Li NMR probe 12. The Larmor frequencies of the investigated nuclei are given in the Table 1.

Table 1. Larmor frequencies of the nuclei studied at a magnetic field of 18.07 kOe.

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>$^2$H</th>
<th>$^{35}$Cl</th>
<th>$^{37}$Cl</th>
<th>$^{79}$Br</th>
<th>$^{81}$Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>Larmor frequency (MHz)</td>
<td>11.810</td>
<td>5.378</td>
<td>6.275</td>
<td>19.276</td>
<td>20.778</td>
</tr>
</tbody>
</table>

The line width due to the inhomogeneity of the magnet was e.g. for the $^2$H resonance in $D_2O$ in a 10 mm rotating sample about 2 Hz. The range of the line width goes from some Hertz of the deuterium and chlorine resonances to some hundred Hertz of the bromine resonances; therefore appropriate conditions of modulation, radiofrequency field and sweep rates were employed to prevent distortion of the signals.

The chemical shifts were measured relative to an external standard by the probe exchange method. The chemical shift is given by $\delta = \nu_{\text{probe}} - \nu_0$; a positive value means a shift to higher frequency at constant field. Concentrations are given as moles salt per kg solvent or as the mole fraction, i.e. moles salt per moles solvent.

The temperature was $(28 \pm 2) ^\circ \text{C}$.
The Ratios of the Larmor Frequencies

In defined solutions of alkali halides in D$_2$O (99.75% isotopic purity), the ratios of the Larmor frequencies

\[ \nu(\text{halide}) / \nu(\text{H}) \]

were determined. The Larmor frequency of a halide nucleus and the Larmor frequency of $^2$H were measured alternately in the same probe at constant field only by varying the radio frequency. The radio frequency was controlled by a frequency counter during the registration of the resonance lines. For each halide nucleus about 30...50 frequency ratios were determined at different runs. The results are given in Table 2.

Table 2. Ratios of the Larmor frequencies $\nu(\text{halide}) / \nu(\text{H})$

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Salt</th>
<th>Concentration ( c ) (moles salt/moles D$_2$O)</th>
<th>$\nu(\text{halide}) / \nu(\text{H})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{35}$Cl</td>
<td>NaCl</td>
<td>0.090</td>
<td>0.638 272 39 (4)*</td>
</tr>
<tr>
<td>$^{37}$Cl</td>
<td>NaCl</td>
<td>0.090</td>
<td>0.531 294 35 (4)*</td>
</tr>
<tr>
<td>$^{79}$Br</td>
<td>KBr</td>
<td>0.080</td>
<td>1.632 131 (2)**</td>
</tr>
<tr>
<td>$^{81}$Br</td>
<td>KBr</td>
<td>0.080</td>
<td>1.759 331 (2)**</td>
</tr>
</tbody>
</table>

* Three times the rms error.
** Three times the rms error and a systematic error due to unsymmetric lines.

From this table, the ratios

\[ \frac{\nu(35\text{Cl})}{\nu(37\text{Cl})} = 0.832 394 43 (8) \]

and \[ \frac{\nu(81\text{Br})}{\nu(79\text{Br})} = 1.077 934 9 (18) \]
can be calculated. These are in excellent agreement with the directly measured ratios of LUTZ, which were used for calculating the hyperfine structure anomalies.

No directly measured values for $\nu(37\text{Cl}) / \nu(2\text{H})$, $\nu(79\text{Br}) / \nu(2\text{H})$ and $\nu(81\text{Br}) / \nu(2\text{H})$ are known. The value $\nu(35\text{Cl}) / \nu(2\text{H})$ of PROCTOR and YU is in good agreement within the limits of error of their value, the ratio of WALCHLI was measured in RbCl-solution and lies therefore higher than ours.

NaCl and KBr solutions were chosen because of their small concentration dependence and the small line widths. The other halide solutions showed larger line widths. Only for NH$_4$Cl and NH$_4$Br solutions the line widths are smaller for chlorine and bromine resonances respectively. Because of the isotopic exchange of hydrogen and deuterium, the ammonium halide solutions could not be used for measuring the frequency ratios.

For a determination of the Larmor frequencies for vanishing concentration, the concentration dependence of the deuterium and halide resonances had to be studied.

Concentration Dependence

a) $^{35}$Cl and $^{81}$Br in Chlorine and Bromine Solutions

DEVERELL and RICHARDS have presented the concentration dependence of $^{35}$Cl in solutions of the chlorides of Li, Na, K, Rb and Cs in H$_2$O and of $^{81}$Br in solutions of the bromides of Na, K, Rb and Cs in H$_2$O.

For an accurate extrapolation to vanishing concentration, proceeding from our values of Table 2, we had to remeasure the concentration dependence for some alkali metal chloride and bromide solutions in H$_2$O and D$_2$O.

These chemical shifts of $^{35}$Cl and $^{81}$Br resonances in aqueous solutions of ammonium and alkali chlorides and bromides are shown in Figures 1 and 2. The shifts are referred to the resonance frequency of the Cl$^-$ and Br$^-$ at infinite dilution in H$_2$O respectively. The values for NH$_4^+$, and its Goldschmidt ionic radius as well, are situated between Rb$^+$ and Cs$^+$. The large solvent isotope effect is discussed later in this paper. A comparison with the results of DEVERELL and RICHARDS shows good agreement.

The concentration dependence had to be measured only for one isotope. For the second isotope, the chemical shift can be calculated by

\[ \delta(35\text{Cl}) = \delta(35\text{Cl}) \cdot \left[ \frac{\nu(37\text{Cl})}{\nu(35\text{Cl})} \right], \]

correspondingly for $^{79}$Br and $^{81}$Br.

That this relation holds very well has been ensured for example by measuring $\nu(35\text{Cl}) / \nu(37\text{Cl})$ in NH$_4$Cl and NaClO$_4$ solutions. This ratio is the same within 1.10$^{-7}$, although the chemical shift of these solutions is about 1000 ppm. Further, $\sigma_p(85\text{Rb}^+)$ and $\sigma_p(87\text{Rb}^+)$ have been measured independently. The results are

\[ \sigma(87\text{Rb}^+) = -2.116 (12) \cdot 10^{-4}, \]

\[ \sigma(85\text{Rb}^+) = -2.11 (2) \cdot 10^{-4}. \]

There is no difference within the limits of the errors. The error for the extrapolation to infinite dilution was assumed to be ±0.4 ppm for $^{35}$Cl and ±0.5 ppm for $^{81}$Br.

b) $^{35}$Cl in Perchlorate Solutions

The $^{35}$Cl resonance line of the perchlorate ion in HClO$_4$ is situated about 946 ppm to higher frequency than that of the Cl$^-$ ion in HCl. The con-
Fig. 1. $^{35}\text{Cl}$ chemical shifts in solutions of chlorides. Positive values are to higher frequencies. The measured shifts are adjusted so that they refer to the chloride ion at infinite dilution as standard. Rotating cylindrical probes (9 mm inner diameter) were used; no bulk susceptibility correction was made. The errors are smaller than the given circles. The line widths are $15 \ldots 25$ Hz.

Fig. 2. $^{81}\text{Br}$ chemical shifts in solutions of bromides. Positive values are to higher frequencies. The measured shifts are adjusted so that they refer to the bromide ion at infinite dilution in H$_2$O as standard. Cylindrical probes (9 mm inner diameter) were used; no bulk susceptibility correction was made. The line widths are $350 \ldots 750$ Hz.
concentration dependence of alkali perchlorates has not been studied before. Our measured shifts are shown in Figure 3. They are very small and to increasingly lower frequency with increasing concentration. Similar shifts to lower frequency have also been found for the $^{55}\text{Mn}$ resonance line of alkali permanganates in aqueous solution. Nearly the same shift for NaClO$_4$ and LiClO$_4$ in H$_2$O and of LiClO$_4$ in D$_2$O has been found. This reveals the small influence of the surrounding on the Perchlorate ion. The chemical shift of $^{35}\text{Cl}$ in the Cl$^-\text{ion}$ and in the

\[ \nu_{\text{ClO}_4^-} - \nu_{\text{Cl}^-} = (7563.4 \pm 3) \text{ Hz} \]

to the Larmor frequency of the hydrated Cl$^-\text{ion}$:

\[ \sigma = (1003.3 \pm 0.4) \text{ ppm} \]

c) $^2\text{H}$ in Alkali Halide Solutions

For the extrapolation of the ratio of the Larmor frequencies, the influence of the alkali metal halides on the $^2\text{H}$ resonance line in D$_2$O had to be measured also. The $^2\text{H}$ resonance is shifted to lower frequency for NaCl and KBr in D$_2$O. The shift is small; (-3.3 $\pm$ 1.0) Hz for the KBr and (-2.2 $\pm$ 0.5) Hz for the NaCl solutions quoted in Table 2, referred to pure D$_2$O.

### Ratios of the Larmor Frequencies for Infinite Dilution

The ratios of the Larmor frequencies, which have been measured in somewhat arbitrary solutions (Table 2), are now transferred to a general base by using the dependence on concentration. As the common base, the ratio of the Larmor frequency of the halide nucleus at vanishing concentration to the Larmor frequency of $^2\text{H}$ in pure D$_2$O is chosen:

\[ \nu_{(\text{halide})}/\nu_{(^2\text{H})} \text{extrapol.} \]

Table 3 shows these ratios resulting from the values of Table 2 and the concentration dependence. The errors arise from the extrapolation to zero concentration.

### The Magnetic Moments

From the ratios of the Larmor frequencies of Table 3, nuclear magnetic moments can be derived, using $\nu_{(^2\text{H})}/\nu_{(^1\text{H})} = 0.153 506 083 (60)$ of Small-er and the uncorrected magnetic moment of the proton in water $\mu_p = 2.792 709 (17)$ $\mu_S$ of Taylor et al. The so calculated nuclear magnetic moments are listed in Table 4. All moments are affected by the uncertainty of the magnetic moment of the proton and are not corrected for the ionic diamagnetism. Because a crossed-coil type spectrometer was used, the sign of the magnetic moments is also given.

These values of the magnetic moments are influenced only by the electrons of the ion itself and by the surrounding water molecules, which interact
with the ion. If such magnetic moments could be compared with magnetic moments of free ions, the effect of the water molecules could be evaluated, the shielding constant calculated and compared with the results of Deverell. Further, an absolute scale for the relative chemical shifts could be established and e.g. the arbitrary zero of Fig. 1 of the paper of Hall could be replaced.

### Solvent Isotope Effect

The Larmor frequencies of nuclei of ions in aqueous solutions depend on the isotopic composition of the solvent. Solvent isotopic shifts in water have been found for several nuclei, the size of the shift ranges up to 31 ppm in the case of $^{207}\text{Pb}$ (see 11) and is always to lower frequencies, going from $\text{H}_2\text{O}$ to $\text{D}_2\text{O}$.

Solvent isotope shifts of $^{35}\text{Cl}$ and $^{81}\text{Br}$ as a function of concentration are shown in Figs. 1 and 2 for $\text{NaCl}$ and $\text{KBr}$. The shift of $^{81}\text{Br}$ in $\text{KBr}$ was different from that of Loewenstein et al. for Br in RbBr. We have therefore measured the difference in the Larmor frequencies i.e. the solvent isotope effect in solutions of the alkali bromides and chlorides with a constant mole ratio of $c = 0.009$ in H$_2$O and D$_2$O. We use this assignment for the concentration because the ratio of the number of ions to the number of solvent molecules is a constant also for the isotopic change. The results are given in Table 5. Within the limits of error, no cation dependence of the solvent isotope effect for the anionic nuclei was established. The value of Loewenstein et al. for $^{81}\text{Br}$ is not in agreement with ours. Recently, the first absolute shielding of the chloride and bromide ions by water was measured more accurately by A. Uhl in this laboratory with our new Fourier transform NMR spectrometer. The result was 9.4 ± 0.3 ppm.

With increasing concentration, the solvent isotope effect decreases, a fact which Halliday et al. have also found for $^{133}\text{Cs}$. For $^{133}\text{Cs}$ and $^{87}\text{Rb}$, the solvent isotope effect is 0.3% and 0.14% of the total absolute shielding of the nuclei of the ions by water. If a similar fraction for the halides is assumed, the absolute shielding of the chloride and bromide ion by water would be about some 10$^{-4}$ to some 10$^{-3}$, which is larger than the calculated value of Ikenberry and Das. But for Rb and Cs, the calculated shielding constants are also in disagreement with the experimental ones.

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8. O. Lutz and A. Nolle, to be published.