^{17}O Nuclear Magnetic Resonance Studies in Water of Different Isotopic Composition

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^{17}O and ^{2}H Fourier transform NMR studies have been made in water with varying contents of hydrogen isotopes. Chemical shifts of ^{17}O as a function of ^{2}H contents and as a function of the hydrogen ion concentration are given. The ratios of the Larmor frequencies of ^{17}O and ^{2}H in water are used for evaluation of a magnetic moment of ^{17}O in water. The deuterium isotope effect on the ^{17}O NMR line in water is (3.08 ± 0.20) ppm to lower frequency for deuterium oxide. No ^{17}O shift was found in deuterium oxide with high ^{18}O enrichment.

Introduction

Many years ago, Diehl et al.[1] have reported on the difference between the Larmor frequencies of ^{17}O in H_2O and D_2O. A change in the magnetic shielding of about 3 ppm was found. Further, solvent isotope effects in electrolyte solutions in H_2O and D_2O of mononuclear ions have been investigated for the following elements: alkalis[2,3], halides[2,4,5], II b group[6–8], III a group[9,10] and lead[11]. This effect increases from a nearly undetectable shielding difference to more than 30 ppm for lead[11] and mercury[8]. For the central nucleus in oxyanions also a solvent isotope effect was detectable in some cases: ^{53}Cr (Ref.[12]), ^{55}Mn (Ref.[13]), ^{95}Mo (Ref.[14]).

For the ^{17}O NMR line in aqueous solutions of oxyanions a negligible isotope effect was found in the oxyanions but in the water molecule an effect of about 3 ppm was evaluated[15,16]. As further approach to the understanding and explanation of these effects the "simplest" solvent isotope effect, the dependence of the Larmor frequency of ^{17}O in water was investigated by varying experimental parameters such as ^{2}H contents and hydrogen ion concentration. A further aim of this work was to establish a better magnetic moment of ^{17}O in water.

Experimental

The measurements were done with a multinuclei Bruker pulse spectrometer SXP 4 – 100 in an externally stabilized magnetic field of 2.114 T produced by a Bruker high resolution 15″ magnet system. The free induction decays of ^{17}O and ^{2}H were accumulated and Fourier transformed by a Bruker BNC 12 computer. The Larmor frequencies of ^{17}O and ^{2}H are at this field approximately 12.201 MHz, and 13.816 MHz respectively. Both signals can be observed with the spectrometer by retuning without further apparative changes.

Nonrotating cylindrical sample tubes of 10 mm outer diameter were used. The temperature was (299 ± 2) K. ^{17}O was observed always at the natural abundance of water. In D_2O signal-to-noise ratios of about 40 were achieved for ^{17}O within 7 minutes of accumulation time and of more than 300 for ^{2}H within about 1 minute accumulation time. The chemical shift is given by $\delta = \nu_{\text{sample}}/\nu_{\text{reference}} - 1$, a positive value means a shift to higher frequencies at a constant field, a D_2O sample with 99.75% ^{2}H was used as reference.

Results and Discussion

a) ^{17}O *Isotopic Effect in Water*

The dependence of the Larmor frequency of ^{17}O on the contents of deuterium in water at $p_H = 7$ has been measured. As reference D_2O was used, 99.75% enriched in ^{2}H. The results are given in Figure 1. The Larmor frequency of ^{17}O is always lower in water enriched in deuterium. The isotopic effect of ^{17}O in D_2O (99.75% ^{2}H) and H_2O (0.7% ^{2}H) is $\delta = (3.08 \pm 0.20)$ ppm. The error is two times the standard deviation.

In the region of overwhelming ^{1}H-contents the chemical shift is proportional to the proton contents. In the region where the isotopic composition is dominated by the ^{2}H contents there is found an unexplained deviation from the linearity. A linear dependence of the solvent isotope effect was found for example for ^{19}F (Ref.[4]) and ^{45}Sc (Ref.[17]).

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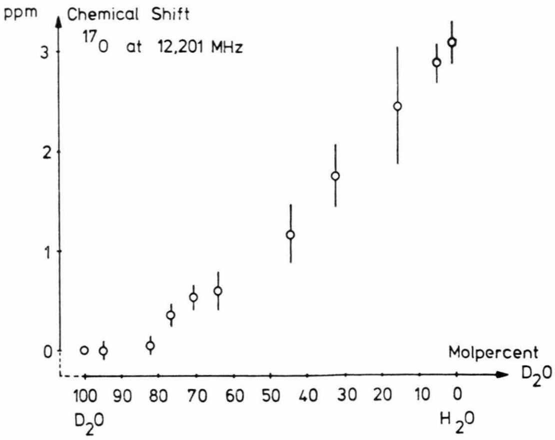

Fig. 1. Chemical shift of ^{17}O in water with different abundance of deuterium, the reference sample is D_2O with 99.75% ^{2}H.

b) Isotopic Effect and Hydrogen Ion Concentration

The line width of ^{17}O in water is dependent on the p_H-value[18]. A proof was made for the dependence of the Larmor frequency of ^{17}O in D_2O (99.75% ^{2}H) and H_2O (0.7% ^{2}H) on the concentration of the hydrogen ions. The different concentrations of hydrogen ions were produced by adding DCl (20% in D_2O) or NaOD in D_2O respectively the protonated species.

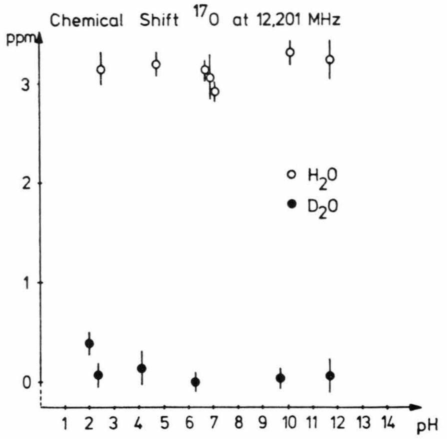

Fig. 2. Chemical shift of ^{17}O in H_2O in natural abundance and in D_2O (99.75% ^{2}H) as a function of the hydrogen ion concentration of the samples.

The results are given on Figure 2. There is no dependence of the isotope effect in the hydrogen ion concentration.

c) ^{17}O NMR Line in $D_2{}^{18}O$

As a further test the ^{17}O NMR signal was observed in a sample of $D_2{}^{18}O$, enriched to 99% in ^{18}O. The ^{17}O content was 0.037%. The Larmor frequency of ^{17}O in this sample is the same within the uncertainty of $2 \cdot 10^{-7}$ as that in the reference sample D_2O with the usual isotopic composition. For ^{133}Cs also only the usual H_2O-D_2O solvent isotopic effect of 1.18 ppm was found whereas in $H_2{}^{18}O$ also no isotopic shift was detectable[3].

d) ^{2}H Chemical Shift in H_2O and D_2O

The Larmor frequency of the ^{2}H line was studied in the same samples with different ^{2}H contents used for a). No dependence of the line position was observed with an accuracy of $2 \cdot 10^{-8}$. Further the ^{2}H NMR signal was observed in the $D_2{}^{18}O$ (99% enriched in ^{18}O). Also no chemical shift was detected for ^{2}H.

e) Nuclear Magnetic Moment of ^{17}O

The ratio of the Larmor frequencies of ^{17}O and ^{2}H was observed as a function of the deuterium contents of water at $p_H = 7$. More than 40 ratios of the Larmor frequencies were measured at four different days for each sample. The results are given in Table 1 together with earlier ones which are

Isotopic composition of water	present work	Uhl[22]	Alder and Yu[21]
99.8% D_2O	0.883 117 64 (12)	0.883 117 42 (64)	0.883 13 (4)
82.4% D_2O	0.883 117 75 (16)	—	—
64.2% D_2O	0.883 118 39 (14)	—	—
45.0% D_2O	0.883 118 57 (24)	—	—
32.0% D_2O	0.883 119 06 (28)	—	—
15.4% D_2O	0.883 119 75 (22)	—	—
5.0% D_2O	0.883 120 11 (26)	—	—
1.0% D_2O	—	0.883 120 35 (84)	—
0.7% D_2O	0.883 120 40 (32)	—	—

Table 1. Ratios of the Larmor frequencies of ^{17}O and ^{2}H for samples of different D_2O contents (mol−percent) in water. The given error is twice the standard deviation. Alder and Yu observed ^{17}O in a H_2O-sample and ^{2}H in a D_2O-sample.

within the limits of error in good agreement. They are also in very good agreement with the chemical shift measurements a) and d). For an evaluation of the magnetic moment of ^{17}O in D_2O the following data are used: $\nu(^{17}\text{O})/\nu(^{2}\text{H}) = 0.883\,117\,64(12)$ of this work, $\nu(^{2}\text{H})/\nu(^{1}\text{H}) = 0.153\,506\,083(60)$ of Smaller[19], the magnetic moment of the proton in water $\mu_\text{p} = 2.792\,7740(11)$ μ_N of Cohen and Taylor[20] and the nuclear spin $I = 5/2$ of ^{17}O. With these values the magnetic moment of ^{17}O in D_2O is derived which is not corrected for the diamagnetism $|\mu(^{17}\text{O in D}_2\text{O})| = 1.892\,997\,1(6)$ μ_N. The error results from the error of the magnetic moment of the proton in units of the nuclear magneton. It should be mentioned that the magnetic moment of ^{17}O is negative (see Ref.[21]).

Conclusions

The influence of deuterium on the ^{17}O NMR frequency is rather large compared with the solvent isotope effects observed for other nuclei also with higher atomic numbers in aqueous solutions[2–6, 23]. This fact seems to be not unreasonable since the effect for ^{17}O in water must be ascribed rather to an intramolecular isotope effect than to an intermolecular effect. But for ^{11}B, ^{13}C, ^{14}N and ^{31}P the intramolecular isotope effects in deuterated small molecules[24–26] are also usually much smaller than the effects found in this work for ^{17}O. For the origin of this effect not only the difference between the vibrational and rotational states in the electronic ground and excited states of the water molecules of different isotopic composition is suggested but also a stronger change in the hydrogen bonding in water.

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