^{55}Mn NMR Studies in Aqueous Permanganate Solutions

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The NMR signals of the nuclei ^{55}Mn and ^{2}H have been investigated in aqueous solutions of permanganates. The concentration dependence of the NMR signals of ^{55}Mn has been determined in potassium permanganate solutions in H_2O and D_2O and a large solvent isotope effect on the chemical shift of ^{55}Mn has been established. The ratio of the Larmor frequencies of ^{55}Mn relative to ^{2}H has been measured with high accuracy. Using the concentration dependence, the ratio of the Larmor frequencies of ^{55}Mn for infinite dilution relative to ^{2}H in pure D_2O is given. From this ratio a magnetic moment for ^{55}Mn in the permanganate ion has been derived.

I. Introduction

A useful choice of the reference compound for chemical shifts and Knight-shifts is always a problem in NMR spectroscopy, especially in the case of the transition elements. The best reference would be the bare nucleus or the free atom or ion. Unfortunately the magnetic moment of the bare nucleus is hardly to be measured, but for the free atom or ion there are some techniques to measure the magnetic moment with high accuracy[1, 2]. Comparing these magnetic moments with those measured by the NMR method in a definite compound, the nuclear magnetic shielding constant can be evaluated[3]. With the shielding constant an atomic reference scale for all measured chemical shifts and Knight-shifts can be established[3]. An application of this method to manganese fails, because the nuclear magnetic moment of ^{55}Mn has not been measured with sufficient accuracy by either of these methods by now. In the following we describe the determination of the nuclear magnetic moment of ^{55}Mn for vanishing concentration of aqueous permanganate solutions by the NMR method[4]. Further, an investigation of the dependence of the Larmor frequency of ^{55}Mn on the concentration of different permanganates in H_2O and D_2O was made, since the few given[5, 6] chemical shifts of ^{55}Mn are referred to aqueous permanganate solutions and the Knight-shift is referred[7] to one of the compounds given in Reference[5].

II. Experimental

A frequency swept spectrometer which was described elsewhere[8] was used. At the externally stabilized field[9] of 1.807 Tesla the ^{55}Mn has a Larmor frequency of approximately 19.087 MHz, and ^{2}H of about 11.81 MHz. The chemical shifts were measured relative to an external standard by the sample exchange method. The chemical shift is given by $\delta = \nu_{\text{sample}} - \nu_{\text{refer.}}$, a positive value means a shift to higher frequency at constant field. Concentrations are given as the mole fraction, i. e. moles salt per moles solvent. Rotating spherical samples of 5 mm diameter have been used, the linewidths due to the inhomogeneity of the magnetic field are about 1 Hz. Appropriate conditions of modulation, radio frequency field and sweep rates are employed to prevent distortions of the signals of ^{55}Mn and ^{2}H which showed linewidths of some Hertz. The temperature was (298 ± 2) K.

As reference sample a solution of potassium permanganate in D_2O (mole fraction $f = 0.00516$) has been used. The signal-to-noise ratio for ^{55}Mn is high enough for measuring solutions with low concentrations (down to mole fractions of 0.0004).

III. The Ratio of the Larmor Frequencies of ^{55}Mn and ^{2}H

The ratio of the Larmor frequencies $\nu(^{55}\text{Mn})/\nu(^{2}\text{H})$ was measured in a solution of $KMnO_4$ and D_2O (99,75% deuterium) with a concentration of $f = 0.0051$. The Larmor frequencies were measured alternately in the same probe and sample at constant field only by varying the excitation frequency. 41 measurements of the ratio were carried out on different days. The result is $\nu(^{55}\text{Mn})/\nu(^{2}\text{H}) = 1.61486483(9)$ at (298 ± 2) K. The error is three times the rms error. The linewidths were 4 Hz for ^{55}Mn and 2 Hz for ^{2}H.

There are only two earlier measurements[10, 11] of ratios of Larmor frequencies which can not be compared with this work, since the Larmor frequencies

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of ^{55}Mn are referred to ^{23}Na (Ref. [10]) and to ^{45}Sc (Reference [11]).

Since there is a dependence of the Larmor frequency on the concentration of the solution for both ^{55}Mn and ^{2}H, this dependence had to be studied for an extrapolation to vanishing concentration.

IV. Chemical Shifts

a) ^{55}Mn in Aqueous Solutions of Permanganates

Solutions of potassium and lithium permanganate have been used as reference samples [5, 6]. For the ^{35}Cl-resonance a concentration dependent shift to lower frequency was found in aqueous perchlorate solutions [8], whereas for the ^{33}S-resonance in sulfate solutions no shift was observable [12]. Therefore the dependence of the Larmor frequency on the concentration of some permanganates has been investigated. The results are given in Figure 1. The shifts are referred to the Larmor frequency of ^{55}Mn at infinite dilution of MnO_4^- in H_2O. With increasing concentration, the shifts go to lower frequency. The shifts are relatively large compared with that of ^{35}Cl in perchlorate solutions [8]. The shifts increase with increasing atomic number for alkalis and earth alkalis.

b) Solvent Isotope Effect

The Larmor frequency of a nucleus in aqueous solution usually depends on the isotopic composition of the water [13]. The size of the solvent isotope effect ranges up to 31 ppm in the case of ^{207}Pb and the shift goes usually to lower frequency [14]. Two exceptions have recently been found [3, 13]. In Fig. 2 the results of the solvent isotope effect of ^{55}Mn in potassium permanganate solutions in H_2O and D_2O are given. A surprisingly large effect is found for the permanganate ion, contrary to the case of ^{35}Cl in perchlorate [8]. The difference of the shielding of

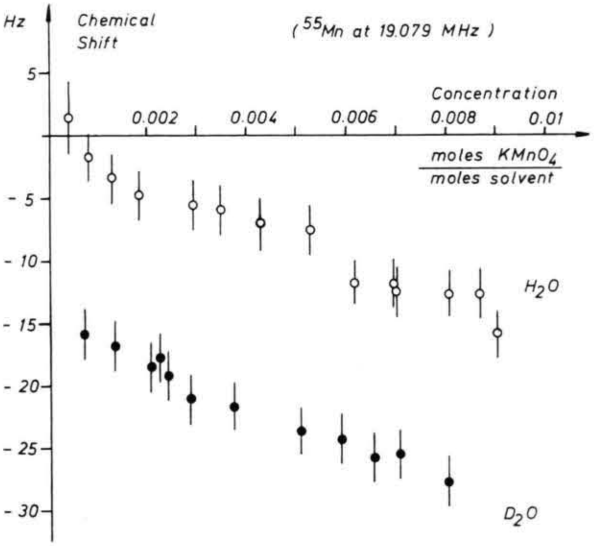

Fig. 2. ^{55}Mn chemical shifts in potassium permanganate solutions in H_2O and D_2O. Rotating spherical samples were used.

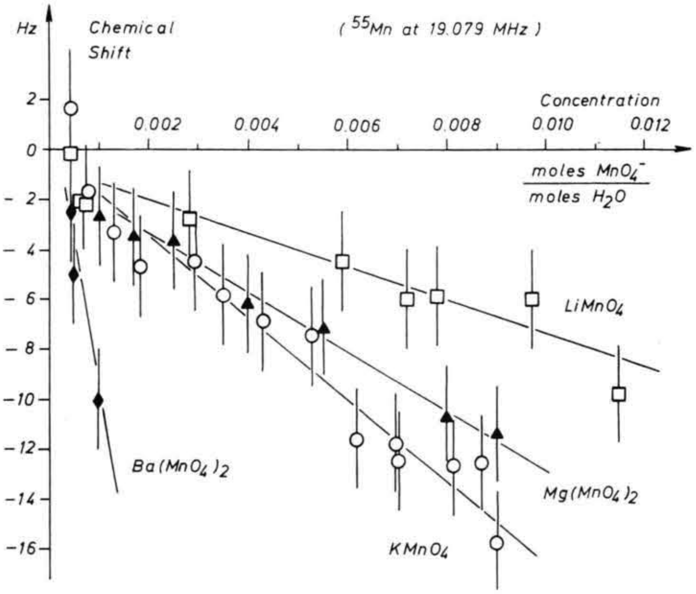

Fig. 1. ^{55}Mn chemical shifts in aqueous solutions of diverse permanganates. Positive values are to higher frequencies. The measured shifts were adjusted so that they refer to the MnO_4^- ion at infinite dilution as standard. Rotating spherical samples (5 mm diameter) were used. Linewidths of about 2 to 5 Hz were observed.

the ^{55}Mn between MnO_4^- in H_2O and D_2O is:

$$\sigma(H_2O) - \sigma(D_2O) = -(0.76 \pm 0.05) \text{ ppm}$$

c) ^{2}H-Resonance Shift

The Larmor frequency of ^{2}H is nearly linearly dependent on the concentration of the solutions of $KMnO_4$ in D_2O. The ^{2}H resonance shows a shift of $-(1.4 \pm 1.0)$ Hz for the $KMnO_4$-solution used for the measurement of the ratio of the Larmor frequencies $(f = 0.0051)$.

d) Temperature Dependence of ^{55}Mn-Resonance Line

Preliminary studies on the temperature dependence of the ^{55}Mn resonance lines were made. For increasing temperature a shift to higher frequencies of about 0.3 Hz/K has been found for a $KMnO_4$-solution.

V. Ratio of the Larmor Frequencies for Infinite Dilution

Using the dependence of the Larmor frequencies on concentration, the ratio of the Larmor frequencies was transferred to the ratio of the Larmor frequencies of ^{55}Mn at vanishing concentration and of ^{2}H in pure D_2O: The result is:

$$\left.\frac{\nu(^{55}\text{Mn in } MnO_4^-)}{\nu(^2\text{H in } D_2O)}\right|_{\text{Extrapol.}} = 1.614\,8654(4)\ .$$

The additional error is due to the uncertainty of the extrapolation to zero concentration.

VI. Magnetic Moment of ^{55}Mn

From the ratio of the Larmor frequencies given in the last section, a nuclear magnetic moment can be derived, using $\nu(^2H)/\nu(^1H) = 0.153506083(60)$ of Smaller [15] and the uncorrected magnetic moment of the proton in water $\mu_p = 2.792709(17)\ \mu_N$ of Taylor et alias [16].

The result is:

$$\mu(^{55}\text{Mn in } MnO_4^- \text{ hydrated by } D_2O) = +3.461\,4464(22)\ \mu_N\ .$$

The moment is affected by the uncertainty of the magnetic moment of the proton and is not corrected for the diamagnetic shielding due to the electrons.

A comparison of this magnetic moment with magnetic moments measured by the atomic beam magnetic resonance method or optical pumping technique on free manganese atoms or ions would yield the shielding constant for ^{55}Mn in the MnO_4^- ion. Such a shielding constant seems to be rather large since the chemical shift range for ^{55}Mn is about 3000 ppm [5, 6]. But at the moment no magnetic moment measured by the mentioned methods on free Mn atoms or ions is known.

From ENDOR measurements on Mn^{2+}: $CaWO_4$, Mn^{2+}: ZnS and Mn^{2+}: CaO, Mims et al. [17] derived a weighted magnetic moment for ^{55}Mn of

$$\mu(^{55}\text{Mn}) = 3.4438(20)\ \mu_N\ .$$

The difference between this value and the value given above is very large and is certainly partly due to the chemical shift of MnO_4^-.

But it is uncertain, if the ENDOR value can be used for the calculation of the shielding constant with the same reliability as the magnetic moments derived from free atoms or ions. In the case of ^{153}Eu and ^{155}Gd, the magnetic moments measured by the atomic beam [18, 19] and the ENDOR [20, 21] method are also different. Therefore the measurement of $\mu(^{55}\text{Mn})$ on free atoms would also by very interesting for the decision wether the ENDOR method yields the "right" magnetic moment or not.

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