^{14}N Quadrupole Relaxation of DMF and DMF-d_7 in DMSO at Infinite Dilution

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The ^{14}N quadrupole relaxation time in pure DMF is by 9% longer than in pure DMF-d_7, showing the dependence of the reorientational molecular motion on the square root of the moment of inertia. But for traces of DMF and DMF-d_7 in DMSO, the ^{14}N quadrupole relaxation time tends to obey the "square-root-of-the-reduced-mass law", as expected from the kinetic theory of dense fluids. The vanishing of the moment-of-inertia effect on the intramolecular nuclear quadrupole relaxation is discussed in terms of molecular translation-rotation coupling.

1. Introduction

In molecular diffusion studies, isotope-substituted trace-substances, neglecting isotope effects, were often used to obtain self-diffusion data [1]. Many of the self-diffusion coefficients of pure liquids have this way been measured. For example, the self-diffusion of water was studied with traces of HDO, HTO and $H_2{}^{18}O$ in H_2O [2, 3]. A recent study [4] of isotope effects on transport coefficients of methanol, using the NMR spin-echo method for the diffusion-measurements, showed that the self-diffusion coefficient of CD_3OD ($0.211 \cdot 10^{-9}$ m^2 s^{-1}) is indeed very close to the diffusion coefficient of trace CH_3OD in CD_3OD ($0.215 \cdot 10^{-9}$ m^2 s^{-1}). They differ by only 2%.

Recently we found that the nuclear quadrupole relaxation time of ^{14}N of trace DMF (N,N-dimethylformamide) in DMSO (dimethyl sulfoxide) was close to that of trace DMF-d_7 in the same solvent, showing only a small difference within 2%. However, for pure liquids, ^{14}N relaxes faster in DMF-d_7 than in DMF, a 9% isotope effect being found, which can be related to the difference of the moments of inertia. For the trace-substances, the inertia effect is obviously lost.

This communication reports for the first time the dependence on the composition of a liquid mixture of the dynamic isotope effect on the intramolecular nuclear quadrupole relaxation. The results could be helpful in understanding the translation-rotation coupling of molecular motions in liquids.

2. Experimental

The samples studied were mixtures of DMF (or DMF-d_7) and DMSO, which were prepared by accurately weighing the substances. Spin-lattice relaxation experiments were carried out on a Bruker AM-400 spectrometer at the University of Karlsruhe with a broad band probe tuned to the ^{14}N resonance frequency of 28.903 MHz, and the temperature was controlled within 25 ± 0.5 °C. The relaxation times T_1 of ^{14}N were measured using inversion-recovery technique by averaging over at least three independent measurements. Sufficient transients were accumulated to achieve a good signal-to-noise ratio. The T_1 data were obtained by a 3-parameter fit with standard deviations smaller than 5×10^{-4}, which ensured that the T_1 error did not exceed 2% according to an empirical criterion established recently [5].

3. Results and Discussions

Figure 1 shows a plot of the relaxation times T_1 of ^{14}N in DMF and DMF-d_7 versus the mole fraction of DMSO. When extrapolated to infinite dilution, the ^{14}N relaxation times of DMF and DMF-d_7 tend to converge to almost the same value. The ratio of the ^{14}N relaxation time of pure DMF to that of DMF-d_7 is $T_1^H/T_1^D = 1.85/1.70 = 1.088$, i.e. the dynamic isotope effect amounts to 9%. But at infinite dilution the relaxation times of the two species show an isotope effect of only ca. 2%.

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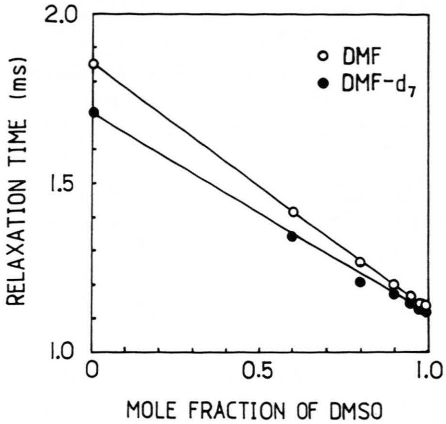

Fig. 1. Plot of the ^{14}N quadrupole relaxation time of DMF and DMF-d$_7$ in DMSO versus the mole fraction of DMSO. In the pure liquids, the relaxation time of ^{14}N shows a 9% isotope effect between DMF and DMF-d$_7$, while at infinite dilution the isotope effect amounts to only 2%.

It is well known that ^{14}N in organic compounds relaxes dominantly by the quadrupole mechanism [6]:

$$(1/T_1)_{QF} = (3\pi^2/10)\{(2I+3)/[I^2(2I-1)]\}\, C_{QF}^2(1+\eta^2/3)\,\tau_c\,, \tag{1}$$

where τ_c is the correlation time of the molecular reorientation, η is the asymmetry parameter and C_{QF} is the quadrupole coupling constant (in Hz), which is related to the nuclear quadrupole moment eQ and the electric field gradient eq_{zz} by

$$C_{QF} = e^2 q_{zz} Q/h\,. \tag{2}$$

Although the quadrupole coupling constant of ^{14}N in gaseous DMF was reported recently [7], that for DMF-d$_7$ is not yet available. Thus the isotope effects on the quadrupole coupling constants is not exactly known. But it can be shown that C_{QF} cannot change much by deuterium substitution. For example, the molecular beam maser experiment [8] showed that in the gaseous state, the quadrupole coupling constant of ^{14}N in acetonitrile is $C_{QF} = -4224.4$ kHz for CH_3CN and $C_{QF} = -4229.7$ kHz for CD_3CN, the change being only about 1‰. Another example [9] is the ^{2}D quadrupole coupling constant in deuterated monochloromethane: $C_{QF} = 74.687$ kHz for CH_2DCl and $C_{QF} = 74.573$ kHz for CHD_2Cl, the change being smaller than 2‰. The relaxation rate being proportional to the square of C_{QF}, see (1), such small changes in C_{QF} can be completely ignored. The asymmetry parameter η, which depends on the geometrical structure of the molecule, cannot change much either, since H and D are isotopes of the same element. So it can be concluded that the isotope effect on $(1/T_1)_{QF}$ depends exclusively on the reorientation correlation time τ_c.

In the pure fluids of DMF and DMF-d$_7$ the dynamic behavior of the two species is different, since they possess different molecular weights and moments of inertia, and the two fluids have different macroscopic viscosities. Thus, the reorientational correlation time τ_c of DMF and DMF-d$_7$ in pure liquids must be different. The larger molecular moment of inertia of DMF-d$_7$ slows down the rotational diffusion, and therefore the reorientational correlation time τ_c of DMF-d$_7$ is longer. Therefore ^{14}N relaxes faster in pure DMF-d$_7$ than in DMF according to (1). Through calculations we obtained the following data for the moments of inertia I: $(I_D/I_H)_a^{1/2} = 1.160$, $(I_D/I_H)_b^{1/2} = 1.075$, $(I_D/I_H)_c^{1/2} = 1.089$, where the subscripts D and H denote the deuterated and protonated species, respectively, and a, b, and c label the three principle axes of the molecular inertia tensor. The averaged ratio of the square root is found to be $(I_D/I_H)^{1/2} = 1.097$. This quantitative calculation supports the inertia dependence of the isotope effect found in the quadrupole relaxation.

The 9% dynamic isotope effect observed in the ^{14}N quadrupole relaxation time for pure liquids is in good agreement with the dynamic isotope effects found in the translational diffusion coefficients (11%) and in the viscosities (10.9%) reported in [10], where the square root of the moment of inertia dependence was predicted. These results for the isotope effects could serve as evidence for translation-rotation coupling of the molecular motion in liquids.

The fact that the ^{14}N relaxation times of DMF and DMF-d$_7$ in infinitely diluted DMSO solutions differ only by 2% shows that their reorientation correlation times do not differ much. This means that, although DMF-d$_7$ has a larger moment of inertia than DMF, it rotates nearly as fast as DMF at infinite dilution in the same solvent. For a proper interpretation of this experimental phenomenon, the concept of translation-rotation coupling should also be applied here. In liquids, the molecules undergo rapid random tumbling, which is associated with molecular collisions. Under the condition of infinite dilution, a single trace solute molecule collides only with the solvent molecules. In other words, the rotation of the trace DMF or DMF-

d_7 molecules is strongly coupled to the same "translational environment" of DMSO molecules, and the translational DMSO motion is in turn coupled to the DMSO rotation. Because of the molecular collisions and the translation-rotation coupling, the rotation of the tracer cannot be determined by its own moment of inertia but by the motion of the solvent molecules. Therefore the $I^{1/2}$ law breaks down for the tracer relaxation time.

The remaining isotope effect (about 2%) on the ^{14}N quadrupole relaxation of tracer DMF and DMF-d_7 in DMSO solutions could be interpreted by the square root of reduced mass law as obtained from the kinetic theory of dense fluids [11]. The reduced mass is defined by

$$\mu_i = m_i m_0/(m_i + m_0)\,, \tag{3}$$

where the subscripts i and 0 denote the solute and the solvent, respectively. We have in our case: $\mu_D = 39.54$, and $\mu_H = 37.77$. The square root of their ratio $(\mu_D/\mu_H)^{1/2} = 1.023$ is in excellent agreement with the 2% dynamic isotope effect on the relaxation times of the trace substances.

The molecular collisions and the translation-rotation coupling explain also the almost negligible isotope effect on the translational diffusion mentioned in the introduction. In water for example, the collision frequency of trace HDO, HTO or $H_2{}^{18}O$ is completely controlled by the huge number of common water molecules. In other words, the tracer and the solvent molecules have the same collision frequency. The collision causes the reorientation of the molecule(s), and the rotational motion is coupled to the translational motion. Due to the same chemical structure of the solvent (H_2O) and the tracer solute molecules (HDO, HTO and $H_2{}^{18}O$), only a single average translational velocity and a single average free path [12] in the solution can be claimed. Therefore, the translational diffusion coefficient of the trace substance does not differ much from that of solvent with the same chemical structure.

Full interpretation of the translation-rotation coupling needs a fairly developed theory which is not yet available. However, the discussions above can lead to the point that the dynamic (both translational and rotational) behavior of the trace solute may be very similar to that of the solvent. This suggests that just like the transport properties, the rotational properties of the solvent can also be studied by tracer-substance methods, provided that the small $\mu^{1/2}$ effect can be neglected or can be taken into account. Detailed investigation is undergoing.

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