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Self-Diffusion of Neon in Water by ^{21}Ne NMR

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We are currently examining the use of NMR pulsed field-gradient spin-echo (PFGSE) experiments with less-common nuclei for determining self-diffusion coefficients of sparingly soluble gases in liquids which at the conditions of interest coincide with the interdiffusion coefficients defined by Fick's law. Such applications could provide a powerful tool for studying a large spectrum of problems in physical, pure, and applied chemistry. Continuing previous work on xenon diffusion,[1] we describe here the use of ^{21}Ne NMR, reporting on what we believe to be the first reliable set of data for neon diffusion in water. ^{21}Ne NMR in solution is a relatively new field, opened by a previous magnetic relaxation study.[2]

One major impetus of this work has come from the wide interest in the properties of noble gases in water, related to their prototypical hydrophobic character, and their potential use as hydrophobic test particles in biochemical systems. In this context, a comparison between data for Ne and Xe allows one to obtain unique information on the effect of solute size upon the solution properties of these chemically inert test particles. Over the years, a quite detailed picture of these hydrophobic effects has evolved from thermodynamic and spectroscopic work, while accurate transport coefficient data are lacking. This is particularly unfortunate, when it is noted that the self-diffusion coefficient is a key quantity when the results of computer simulations and transport theories are compared with experiment.

The use of the spin-$^3/_2$ nucleus ^{21}Ne in PFGSE experiments is made possible by its comparatively long relaxation times in solution ($T_1 \sim 1$ s), and by the availability of highly enriched ^{21}Ne for overcoming problems with its low NMR sensitivity, low gas solubility (<0.05 mol dm^{-3} at 5 MPa pressure), and low natural abundance (0.26%). We have conducted PFGSE experiments of ^{21}Ne at a resonance frequency of 23.68 MHz (magnetic field of 7.05 T) with a sample of Ne in heavy water (96.7 atom % ^{21}Ne, delivered by I. C. Chemikalien, Munich; sample volume, 1.4 cm^3; pressure, 4 MPa; T_1(^{21}Ne), 1 s at 298 K) using an experimental setup described elsewhere.[1] The use of D_2O enables calibration of the magnetic field gradient by use of the ^{2}D resonance,[3] so that calibration and actual measurements were done without changing the sample. Typically, a signal-to-noise ratio of the Fourier-transformed spin-echo signal without field gradient of 6:1 has been reached after 500 accumulations.

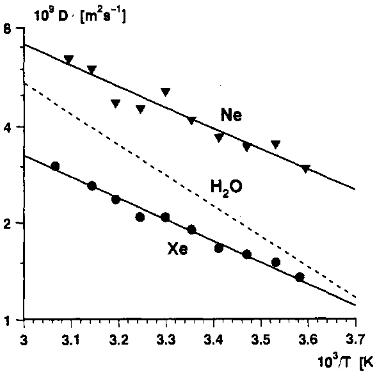

Figure 1. Temperature dependence of the self-diffusion coefficient of neon in water (▼) compared with data for xenon in water (●) and for the self-diffusion coefficient of water (dashed line). For details, see text.

Figure 1 shows the temperature dependence of the self-diffusion coefficient of Ne in water from 278 to 323 K. For easier comparison the results have been converted from D_2O to H_2O by equating the solvent isotope effect with that upon the viscosity.[4] The smoothed value at 298.15 K is D(Ne) = (4.18 ± 0.20) × 10^{-9} m^2 s^{-1}. Within the error limits the plot of log D vs the inverse temperature $1/T$ is linear with an activation energy E_A(Ne) = (11.6 ± 1.5) kJ mol^{-1}. Older data for neon diffusion (D(Ne) = 1.82 × 10^{-9} m^2 s^{-1} at 298 K and E_A(Ne) = 10.3 kJ mol^{-1} in ref 5; D(Ne) = 3.63 × 10^{-9} m^2 s^{-1} at 298 K and E_A(Ne) = 17.4 kJ mol^{-1} in ref 6) appear to be in error, if we presume that the PFGSE technique is more reliable than the quite indirect experimental techniques applied in refs 5 and 6. In Figure 1 the data are compared with results for the diffusion of xenon in water and for the self-diffusion of water itself.[1] The two major features are the fast diffusion of Ne as compared with Xe and water and the low activation energies of Ne (11.6 kJ mol^{-1}) and Xe diffusion (12.9 kJ mol^{-1}), as compared with those for the self-diffusion and viscosity of water (18.5 kJ mol^{-1} near 298 K).

Diffusion theories are still too rudimentary for interpretation, which at present can only come from computer simulations. Nevertheless, it is worthwhile to note that the ratio of the self-diffusion coefficients of Xe and Ne corresponds almost to the inverse square root of their masses, as is predicted by many simple theories.[7,8] However, mass and size effects cannot be disentangled experimentally, and comparison with the self-diffusion coefficient of methane ($D(CH_4) \sim 2 \times 10^{-9}$ m^2 s^{-1}) extracted from ref 9 would indicate that this agreement is incidental.

The current picture of noble gas hydration evolving from computer simulations presumes the existence of a first hydration sphere with 15 (Ne) to 21 (Xe) water molecules,[10,11] the translational and rotational motions of which are perceptibly slower than those of bulk water.[10] This appears to reflect some residues of the clathrate-I structure of the corresponding solid noble gas hydrates.[10,11] At least for the larger homologues there is no marked difference between the self-diffusion coefficients of the solute and solvent,[12] as we could prove experimentally for Xe in water.[1] The latter observation distinguishes the behavior of the larger homologues sharply from that of Ne, which obviously very easily escapes the cage of the surrounding water molecules. In fact, with a Lennard-Jones diameter of 279 pm[13] Ne is much closer to He (258 pm) than to argon (342 pm), methane (382 pm), and Xe (406 pm), and in contrast to the latter, He and Ne do not form solid clathrates. It has, however, been suggested that Ne could enter a host lattice of the ice-II type, as found for

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solid He hydrates at high pressure.[14] It may therefore be well worth examining the structure of the first hydration sphere of Ne, which appears to contain 15 water molecules,[10,11] with respect to a transition from the clathrate-I structure with 23 water molecules to the ice-II structure with 12 water molecules.

Finally, we draw attention to the low activation energies of Ne and Xe diffusion as compared with that of the solvent viscosity η. Simple hydrodynamic theories like the Stokes–Einstein equation and its descendents predict the group $D\eta/T$ to be constant. Relations of this type are widely used for temperature extrapolation of diffusion data, but fail in the present cases. While these findings still await a detailed explanation, they indicate that much of the picture of dynamical processes near apolar solutes in water is bound to conditions near room temperature. It is therefore hoped that the present results will stimulate the investigation of noble gas plus water systems by molecular dynamics simulations over a wider range of temperatures. Also, extension to smaller sizes of Lennard-Jones solutes appears to be fruitful, as there is the possibility that the hydration of He and Ne is quite different from that of the heavier noble gases.

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