The Effect of Pressure and Temperature on Self-Diffusion Coefficients in Several Concentrated Deuterium Oxide Diamagnetic Electrolyte Solutions

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The pressure dependences of the self-diffusion coefficients of deuterium oxide in 4.5 m solutions of LiCl–D\(_2\)O and CsCl–D\(_2\)O (also 7 m) and 3.06 m CaCl\(_2–D\(_2\)O have been measured by the NMR spin-echo method at 30°C, 60°C, and 90°C. Shear viscosities and densities of these solutions have also been determined over the same range of experimental conditions. The experimental data show that the diffusion constant D decreases with the increasing structure-making ability of the electrolyte cation Ca\(^{2+}\) > Li\(^+\). In contrast, the diffusion coefficient for D\(_2\)O in the 4.5 and 7 m CsCl solutions is equal to that for pure D\(_2\)O at 30°C but lower at 60°C and 90°C. It has been found that the Stokes–Einstein equation relates well the diffusion coefficients to shear viscosity in these concentrated electrolyte solutions.

**KEY WORDS:** Self-diffusion; concentrated electrolyte solutions; high pressure; NMR.

1. INTRODUCTION

As a part of our systematic studies\(^1\) of the effects of density and temperature on the dynamic structure of dense liquids, the behavior of water and deuterium oxide under high compression has recently been investigated.\(^2,3\)

Lee and Jonas\(^4\) studied the pressure dependence of the proton spin-lattice relaxation time \(T_1\) in several concentrated H\(_2\)O–diamagnetic electrolyte solutions. A large difference was found in the proton \(T_1\) for the classes of electrolytes generally known as “structure makers” and “structure breakers.”

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In solutions containing the former ions the mobility of water molecules is reduced due to an increase in the structure of the solution. In the solutions containing the latter ions the mobility of water molecules is increased due to a decrease in the solution structure.

Continuing the study of the effects of electrolytes on the structure of water, Lee, Campbell, and Jonas (5) measured the deuteron $T_1$'s along with macroscopic viscosities as functions of pressure for several concentrated D$_2$O--diamagnetic electrolyte solutions. The behavior of the reorientational correlation time $\tau_\theta$ was of main interest. The data showed $\tau_\theta$ increases with an increasing degree of structure-making ability of the electrolyte cation \( \text{La}^{+3} > \text{Ca}^{+2} > \text{Li}^+ \). In addition, in solutions of the structure-breaking electrolyte cations, $\tau_\theta$ (for D$_2$O) for Rb$^+$ $\sim$ Cs$^+$ $\sim$ K$^+$; in all three solutions $\tau_\theta$'s are slightly smaller than the $\tau_\theta$ of pure D$_2$O. At atmospheric pressure, $\tau_\theta$ calculated from the NMR measurements and $\tau_\theta$ calculated from the viscosities using the Debye equation are nearly equal for the structure-breaking electrolytes, but are quite different for the structure-making electrolytes. The difference between $\tau_\theta^\text{NMR}$ and $\tau_\theta^\text{Debye}$ comes from changes in either the quadrupole coupling constant and/or changes in the coupling between the rotational and translational motions of the water molecules.

There are several goals of the present study. First, since our earlier study of the reorientational correlation times showed that the $\tau_\theta$ for D$_2$O is nearly the same for all structure breakers (Cs$^+$, Rb$^+$, K$^+$), it is of interest to find what is the behavior of the diffusion constant for D$_2$O in CsCl solutions. Our second goal is to determine the effect of density and temperature on the self-diffusion of D$_2$O in these concentrated electrolyte solutions and compare them with the results obtained for pure D$_2$O. Our third goal is to find whether the Stokes–Einstein relation between the diffusion coefficient and shear viscosity is valid for these systems.

The deuteron $D$ was measured at 30°, 60°, and 90°C over the pressure range from 1 to 4500 bar for the electrolytes LiCl at 4.5 m concentration, CsCl at concentrations of 4.5 m and 7.0 m, and CaCl$_2$ at a concentration of 3.06 m. Since viscosities and densities for most of these solutions under the above experimental conditions were not available in the literature, they were also measured in our laboratory.

The experimental data show that $D$ decreases with the increasing structure-making ability of the electrolyte cation \( \text{Ca}^{+2} > \text{Li}^+ > \text{D}_2\text{O (pure)} \), while $D$ for solutions containing Cs$^+$ is approximately equal to $D$ for pure D$_2$O at 30°C, and $D_{\text{Cs}^+} < D_{\text{D}_2\text{O (pure)}}$ at the other temperatures. The diffusion coefficients of D$_2$O in electrolytic solutions were compared to $D$'s for pure D$_2$O under the same experimental conditions. Using the hydration theory (6–10) and the procedure introduced by Hertz, (11) we attempted to estimate the diffusion coefficient $D^+$ for D$_2$O in the first hydration sphere of