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H/D Isotope effects in the conductivity of LiCl aqueous solutions in sub and supercritical state

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The electrical conductances of LiCl in H_2O and D_2O solutions were measured in the temperature range 373 - 673 K at pressures up to 37.27 MPa, using a flow type electrical conductance cell.

Keywords: electric conductance, LiCl, supercritical water, subcritical water, heavy water

Since deuterium and hydrogen differ so greatly in mass, it is expected that corresponding deuterium and hydrogen compounds will differ in their various physical properties. Among these compounds light water, H_2O, and heavy water, D_2O, received maximum attention from the scientific community. One of the most powerful, convenient and direct methods to obtain information on the properties of a solution is measurement of the electrical conductance of that solution, this is the method used to check the quality of D_2O used in nuclear reactors.[5] Electrical conductance measurements have provided a significant portion of the current knowledge about the behavior of ions in solution and have allowed the testing of theoretical equations derived for ion–ion interactions in dilute solutions. If these measurements are carried out at high temperatures and pressures, they provide us with accurate information about the degree of association of electrolyte solutions, which tend to associate at high temperature.[6] In fact there are large number of conductance studies of different electrolytes in H_2O shown in literature, but very limited data are available for the case of D_2O.[5] Therefore, in the present work, the electrical conductances of 0.01 M LiCl in H_2O and D_2O solutions were measured in the sub- and supercritical conditions. Knowledge of the properties of these solutions is important to elaborate the H/D isotope effects on the ion-solvent interactions at these severe conditions.

Experimental apparatus: The essential features of the design are shown in Fig. 1. An outer cylinder of Inconel 600 was used as a housing. The working electrode was made of Pt–Ir alloy and was electrically insulted from the rest of the cell components by means of alumina.

Conductance measurements: The electrical conductance was measured by a DS-12 conductivity meter supplied by HORIBA. The cell constant was calculated by means of the measured conductance of five solutions of KCl, with concentrations range of 0.0001–0.002 M and the equivalent values calculated from Barthel equation at 25°C,[16] and found to be equal to 0.111 cm^{-1}.

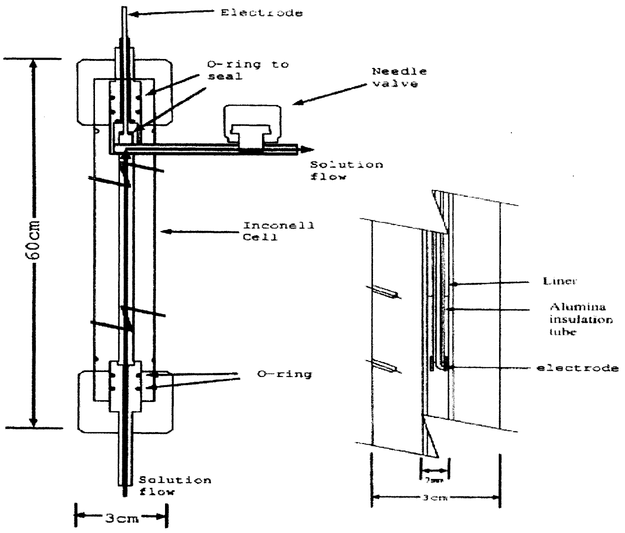

Fig. 1 The conductance cell.

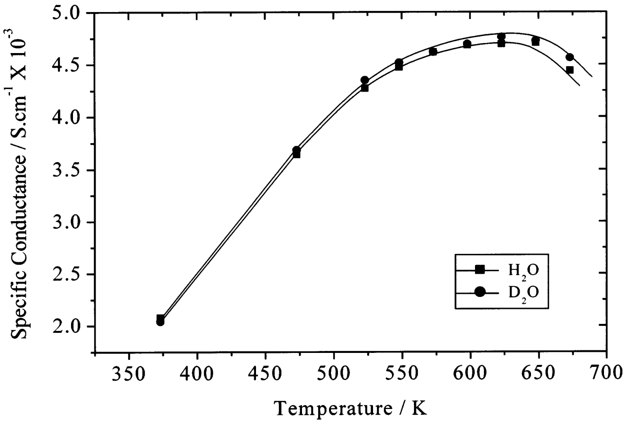

Fig. 3 Specific conductance of 0.01 M LiCl in H_2O and D_2O solutions as a function of temperature at 37.27 MPa.

Figure 3 shows the specific conductances of 0.01 M LiCl in H_2O and D_2O solutions as a function of temperature at 37.27 MPa. Although the change in the electrical conductance of LiCl with temperature in both solutions is almost similar as mentioned above, it can be easily noticed from Figure 3 that the specific conductance in case of D_2O is slightly higher than the case of H_2O. The D–O bond is known to be much stronger than the H–O bond. For example, the pH of neutral light water is 7, while in case of heavy water it is equal to 8. This stronger interaction between the D atom and the O atom in the heavy water molecules reduces the hydration effect of the Li^+ ions, which increases the mobility of these ions compared with the case of light water. This effect is slightly offset by the higher value of the heavy water viscosity compared with the light water. The viscosity ratio $\mu D_2O/\mu H_2O$ was studied by several researchers and found to be decreased by increasing the temperature at constant pressure.[19] Therefore, at higher temperature, the effect of higher viscosity of the heavy water on the

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mobility of Li^+ ions, compared with light water, is decreased and the difference in the conductivity of Li^+ ions in the two solvents is increased.

Figures: 4
Tables: 4
References: 20

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