The Temperature Coefficient of Conductance for the Alkali Metal, Halide, Tetraalkylammonium, Halate, and Perhalate Ions in D₂O

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Precise limiting ionic conductance data are reported for the first time for the alkali metal and tetraalkylammonium ions in D₂O at 10°C as well as similar data for the halate and perhalate ions in D₂O and H₂O at 10 and 25°C. Precise transference numbers by the moving-boundary method are also reported for KBr in D₂O at 10°C and, as a check on earlier work, for KCl in D₂O at 25°C. In general, the structural properties of the ions, as reflected in the temperature coefficient of the limiting ionic conductances, are enhanced in D₂O compared to H₂O, although the differences are often small.

KEY WORDS: KCl; KBr; KClO₃; KBrO₃; KIO₃; KClO₄; KIO₄; D₂O; conductance; transference numbers; aqueous solutions; structural effects; solvent isotope effects.

1. INTRODUCTION

In previous investigations of ionic structural effects (¹,²) in aqueous solutions, the temperature coefficients of limiting ionic conductances as well as the comparison of limiting ionic conductances in H₂O and D₂O (³) were effective in distinguishing between three types of cosphere effects. In general, the conductances of highly solvated ions were relatively independent of temperature, whereas structure breakers and structure makers had negative and positive temperature coefficients, respectively, after a suitable correction for viscosity changes. Similarly, the conductance of structure makers was shown to decrease on going from H₂O to D₂O, whereas for structure breakers there

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was an increase, again after a suitable viscosity correction. This work was undertaken to determine whether the temperature coefficient of ionic conductances would give as consistent a pattern of behavior for D$_2$O as it did for H$_2$O solutions.

The salts of the oxyanions were included in this investigation for several reasons. Little is known concerning the temperature dependence of the limiting conductances of those ions, and no conductance information is available for solutions of these ions in D$_2$O. Furthermore, data for these ions are a convenient means of providing a complete $\lambda_0\eta$ plot for anions that fall between the I$^-$ and Ph$_4$B$^-$ ions in size.

2. EXPERIMENTAL

Cation transference numbers were measured by the autogenic moving-boundary method using the potentiometric probe detector developed in this laboratory. In this apparatus, the boundary is formed initially at a cadmium anode in a solution containing the cation under investigation by passing a constant current through the cell. As the boundary moves through the solution in a narrow calibrated tube (4 mm ID), its velocity is determined by measuring its time of passage by platinum microprobe electrodes, sealed onto the tube, by noting the sudden change in potential on an electrometer connected across adjacent probes. The cathode in all experiments was the appropriate silver–silver halide electrode. Details of cell construction, the recording electrometer, and the power supply have already been adequately described. The current was maintained constant during a run to 0.02% for the current range used here. The boundary events were timed to 0.01 min with a line-operated ac precision timer which was repeatedly calibrated against known time signals. The volumes between microprobes were determined indirectly by accepting Longsworth's value of $T^+(0.02\ M$ aqueous KCl, 25°C) = 0.4901 and making six runs on 0.02 M aqueous KCl. The calculated volumes had a standard deviation of better than 0.04%.

The conductance measurements were carried out using a 500-ml Kraus type, Erlenmeyer cell (cell constant 0.85 cm$^{-1}$) containing platinum electrodes and a Hawes–Kay salt cup dispensing device. The cell resistance was determined using a calibrated Dike–Jones bridge. All manipulations of the solvents and solutions were carried out in closed systems under nitrogen or argon. The solutions were stirred continuously. Temperature regulation was ±0.001°C as determined by Beckman thermometers calibrated with a platinum resistance thermometer. Further details of the description of the apparatus have been published.

The alkali metal and tetraalkylammonium halide salts were the same as those used in previous investigations. The halates and perhalates were