The Conductance of Tetraethylammonium Salts in Water–Methanol Mixtures

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Conductance measurements are reported for tetraethylammonium halide and perchlorate salts in water–methanol mixtures over the complete composition range at 25°C. Limiting conductances and association constants are evaluated together with the distance parameters. The maxima in the limiting ionic Walden products are considered in some detail. Ionic association is generally weak, and the lack of reliable correlation between $K_A$ and the solvent dielectric properties supports the assumption of specific ion–solvent interaction.

KEY WORDS: Conductance; ionic associations; methanol–water mixtures; tetraethylammonium salts.

1. INTRODUCTION

Previous studies of ion–solvent interactions in aqueous–organic solvent mixtures have shown the great dependence on the nature of the organic component, particularly in investigations involving the hydrogen ion. In order to explain the results, it has been assumed by some that in the water-rich region of some binary systems an enhanced structure occurs that is related to the phenomenon of hydrophobic hydration, whereas in other mixed aqueous solvents, such as water–acetonitrile mixtures, a continuous disruption of the water lattice appears to take place upon the addition of the aprotic organic component.

This study of the symmetrical tetraethylammonium salts in aqueous methanol mixtures logically follows our previous investigations of aqueous acetonitrile systems where the organic solvent composition is a nonassociated polar liquid. Methanol is capable of forming two hydrogen bonds per...
molecule and is known to be an associated liquid. Also, conductances in methanol–water mixtures have not been studied in any detail.

2. EXPERIMENTAL

$\text{Et}_4\text{NCl}$ was recrystallized several times from acetone, $\text{Et}_4\text{NBr}$ from a 1:1 $n$-butanol–ether mixture, whereas $\text{Et}_4\text{NI}$, puriss. p.a. grade, was used without any further purification. $\text{Et}_4\text{NClO}_4$ was prepared from perchloric acid by adding $\text{Et}_4\text{NBr}$, the isolated product being recrystallized from water. All salts were thoroughly dried and stored at moderate temperature under reduced pressure. Their water content was determined by Karl Fischer analysis and was found to be less than 0.1%, except for $\text{Et}_4\text{NCl}$ (0.5%). Corresponding corrections have then been made when evaluating molal and molar concentrations.

Methanol was refluxed over picric acid for several hours and then twice distilled. It was stored under purified dry nitrogen. The final product had a conductivity less than $1.0 \times 10^{-7} \Omega^{-1}\text{-cm}^{-1}$, a density of 0.7866 g-ml$^{-1}$ at $25^\circ\text{C}$, and a water content of less than 0.02%.

Water was purified by means of a demineralizer. Its conductivity was less than $1 \times 10^{-6} \Omega^{-1}\text{-cm}^{-1}$. It was stored in the same way as methanol.

The mixed solvents were prepared by weight and vacuum corrected and were kept in a closed system under nitrogen.

Physical properties of the water–methanol mixtures were taken from the literature. Densities and dielectric constants have been reported by Bates, whereas viscosities are those used by Kay and Shedlovsky.

The conductivity cell has been designed so that disturbing effects are minimized. The cell constant was determined by conductivity measurements on potassium chloride solutions in water at 25$^\circ\text{C}$ at concentrations between $10^{-2}$ and $5 \times 10^{-4}$ mole-liter$^{-1}$. It was found that a systematic decrease of the cell constant (0.25% per log $R$ unit) occurred when solutions of increasing electrical resistances $R$ were studied. In order to obtain a better accuracy, the cell constant used was interpolated on the graph of cell constant vs. log $R$ for each measurement. For each set of measurements, the original solution (volume: 50 ml) was diluted directly in the conductivity cell. The successive additions of appropriate amounts of solvent were made by means of an automatic buret SOLEA “Electroburex,” with digital display, whose 50-ml syringe had been previously calibrated with water. After each addition, the solution was stirred and introduced into the electrode compartment under nitrogen. Approximately 400 ml of solvent was required to cover the whole range of electrolyte concentration.

Resistances were measured with a Beckman RC-18 A bridge at 1000 Hz. Suitable corrections were made for the bridge resistors (using a Jones bridge.