Apparent Molal Volumes and Heat Capacities of Some 1:1 Electrolytes in Anhydrous Methanol at 25°C

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A flow calorimeter and flow densimeter have been used to measure volume specific heats and densities of solutions of LiCl, LiBr, NaCl, NaBr, KF, KBr, KI, CsF, and Bu₄NBr in anhydrous methanol at 25°C. The concentrations ranged from approximately 0.01 m to close to saturation in some cases. Apparent molal heat capacities \( \Phi^o_h \) and volumes \( \Phi^o_v \) have been evaluated and extrapolated to infinite dilution to obtain \( \Phi^°_h \) and \( \Phi^°_v \). Nearly all the heat capacities in methanol are negative. However, with the exception of the lithium halides and Bu₄NBr they are more positive than heat capacities of the corresponding salts in water. The dependence of the heat capacities on ionic radii is generally opposite in methanol solutions from that observed for aqueous solutions. In agreement with others, the \( \Phi^°_h \) data indicate that electrostriction in methanol solutions is greater than in aqueous solutions.

KEY WORDS: Apparent molal heat capacity; apparent molal volume; solvent structure; alkali metal halides; tetrabutylammonium ion; electrostriction; methanol.

1. INTRODUCTION

Standard partial molal heat capacities of electrolytes, \( \bar{C}_p^o \), appear to be extremely sensitive to ion-solvent interactions, as indicated by their large dependence on temperature and solvent type.¹⁻¹² However, only a few accurate heat capacities at low concentrations have been reported for non-aqueous solutions.⁶⁻¹⁰ Nearly all these measurements were obtained by the integral heat method, and while the proper use of this technique gives reliable \( \bar{C}_p^o \) values, the method is extremely time consuming and does not easily lend itself to obtaining heat capacities at higher concentrations. On the other hand, traditional methods¹³⁻¹⁰ of measuring direct specific heats may give

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accurate heat capacities at higher concentrations, but the data are difficult to extrapolate to infinite dilution from the lower limits of measurement (ca. 0.1 m). This is especially true for nonaqueous solutions for which the theoretical limiting slopes are not known accurately.

Recently, Picker et al.\(^{14}\) have described a flow heat capacity calorimeter capable of measuring relative volumetric specific heats with a high degree of precision, enabling one to obtain useful data to concentrations as low as 0.01 m. They and others have used this instrument extensively in their investigations of aqueous solutions.

In continuation of work in this laboratory on heat capacities of electrolytes in nonaqueous solutions, we have used a Picker calorimeter to measure apparent molal heat capacities \(\phi_{oq}\) of several electrolytes in anhydrous methanol from about 0.01 m to concentrations frequently approaching saturation. Because of the volumetric characteristic of the flow calorimeter, we have also measured the densities for the corresponding electrolyte solutions using a vibrating tube densimeter\(^{15}\) and have evaluated apparent molal volumes \(\phi_v\). These measurements represent the first systematic study of the heat capacities of a series of electrolytes in a nonaqueous solution.

2. EXPERIMENTAL

2.1. Materials

Reagent grade NaCl, NaBr, KBr, and KI were dried at 110°C in a vacuum oven for 48 h. LiBr was purchased from Alpha Products and dried at 120°C under vacuum for 48 h. Gravimetric analysis with AgNO\(_3\) indicated a purity of 99.4\%. KF was prepared according to the procedure of Kilpatrick and Luborsky\(^{16}\) and dried under vacuum at 200°C for several days. It was then ground into a fine powder and heated at 200°C under vacuum for 96 h. CsF was purchased from Apache Chemical Co. The wet salt was heated above its melting point (600°C) for 24 h and cooled under vacuum. Gravimetric analysis for fluoride was carried out by precipitating PbClF as described by Belcher and Nutten,\(^{17}\) and showed a purity of 99\%. Reagent grade LiCl was recrystallized from water, partially dried at room temperature under vacuum, and finally dried at temperatures of 400°C under a stream of dry hydrogen chloride. Bu\(_4\)NBr was prepared by methods previously used in this laboratory.\(^{5}\)

Preparation of anhydrous methanol has been described previously.\(^{5,6}\) Karl Fisher titrations indicated water content of the solutions after a specific heat or density measurement to be less than 0.01\%. Water used for testing and calibration of the instruments was house-supplied distilled water which was passed through an activated charcoal filter and then an ion-exchange column.