Volumetric Properties of Aqueous Electrolytes at High Temperature. III.
B(OH)₃–NaBₓ(OH)₃ₓ+₁–NaOH Mixtures Up to 523 K

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The densities of aqueous solutions resulting from the partial neutralization of boric acid with sodium hydroxide were measured as a function of concentration, between 375 K and 523 K at pressures close to saturation. The speciation in this system is complex, di- and triborate ions are present in addition to the monoborate ion. The concentration dependence of the apparent partial molar volume of the mixture can be described using the Pitzer equation only if the formation of the polyborate species in the concentrated solutions is taken into account. The partial molar volumes at infinite dilution for the diborate and triborate anions, obtained by assuming ideal mixing, are reported in the range of temperature studied.

KEY WORDS: Densities; boric acid–sodium borate mixtures; partial molar volumes; high temperature; polyborates.

1. INTRODUCTION

In this work we study the volumetric properties of boric acid solutions partially neutralized with sodium hydroxide. Stoichiometrically, the final system is a ternary electrolyte solution containing B(OH)₃, NaB(OH)₄ and NaOH, but the real situation is more complex due to the formation of polyborate anions.

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In order to analyze such a system it is necessary to know the partial molar volume of the pure components. In a previous work\(^1\) we studied the volumetric properties of boric acid and sodium hydroxide–sodium borate mixtures in aqueous solutions at high temperature. Due to the borate ion hydrolysis, the mixture contains small quantities of boric acid. Nevertheless, using appropriate corrections we could obtain the volumetric parameters of the sodium borate. Due to the high pH of the mixtures [NaOH:B(OH)\(_3\) mole ratios between 1 and 2], the contribution of polyborate species to the speciation was negligible.

The partial molar volumes of NaOH aqueous solutions have been measured in a previous work\(^2\) up to 523 K, while the partial molar volumes of aqueous solutions of boric acid have been studied by several authors at high temperature.\(^{1,3-6}\) It was found that, as expected for a non-electrolyte, the partial molal volumes are independent of the concentration. On the other hand, the effect of pressure seems to be very small, except for the work by Alekhin \textit{et al.}\(^5\)

We report here the densities of these mixtures at different compositions in aqueous solutions at 375, 423, 473, and 523 K, at molalities between 0.05 and 0.6 mol-kg\(^{-1}\) (\(m\)). The compositions correspond roughly to NaOH:B(OH)\(_3\) mole ratios close to 0.33, 0.50, and 0.66.

The aim of this study is to determine the volumetric properties of the different borate anions based on the reported values of the polyborate species, which will allow us to calculate the speciation in solution at each temperature and composition.

\section*{2. EXPERIMENTAL}

Stock solutions of B(OH)\(_3\) and NaOH were prepared with carbonate-free AR grade reagents and demineralized water of conductivity less than 0.1 \(\mu\)S-cm\(^{-1}\). The NaOH solutions were standardized with potassium hydrogen phthalate and stored in plastic bottles under nitrogen until they were used.

The B(OH)\(_3\)–NaB(OH)\(_4\) mixtures were prepared by weight neutralization of the stock solution of boric acid with the stock NaOH solution. Weights were corrected for buoyancy in air. The total molalities were known to 0.01%.

A vibrating tube densimeter was used to measure the density of the boric acid solutions and its mixtures. Its operation and calibration has been described in detail elsewhere.\(^2\)

Water and deuterium oxide were used as reference fluids all over the temperature range. The densities of both pure liquids were calculated from the equations of state of Hill\(^{7,8}\) and their values at the pressures and temperatures studied in this work were already reported in Table I of the preceding work.\(^1\)