

Deuterium Isotope Effect on the Molar Volume of Aqueous Solutions of 3-methylpyridine

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3-methylpyridine dissolved in heavy water exhibits a closed immiscibility loop between 38.5 and 117 °C at normal pressure, while it is completely miscible with water at any concentration and temperature (see e.g. Pápai and Jancsó, 2000, Almásy et al., 2002). The purpose of the present investigation is to compare the volumetric characteristics of dilute solutions of 3-methylpyridine in H₂O and D₂O. Densities of dilute solutions of 3-methylpyridine in water and heavy water were measured over the concentration range of 0.4 - 4 mole% as a function of temperature between 25 and 45 °C using a vibrating tube densitometer. The excess molar volumes for mixtures containing D₂O were found to be more negative than those with H₂O.

From the densities of the mixtures the partial molar volume of the solute at infinite dilution and the coefficients in the virial expansion of the excess molar volume ($V^E = V_{xx}m^2 + V_{xxx}m^3 + \dots$) in terms of the aquamolality (m , which is the number of moles of solute per 55.508 mol solvent) have been evaluated. The values of the partial molar volume at infinite dilution were found to be slightly higher (about 0.3%) for the solutions in H₂O than for those in D₂O. The temperature dependence of the excess volume second virial coefficient (V_{xx}) representing the contribution of solute pairs to the excess molar volume shows a characteristic difference between normal and heavy water solutions: while the V_{xx} - t curve for H₂O solution is linear in the temperature range investigated, that for D₂O solution shows a maximum at about 35 °C. The solvent isotope effects are discussed in terms of solute-solvent and solute-solute interactions.

References

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