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**INTERMOLECULAR INTERACTIONS
IN AQUEOUS BINARY MIXTURES
OF NON-ELECTROLYTES**

A thesis presented to the
University of Auckland
for the degree of
Doctor of Philosophy in Chemistry

By
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Abstract

The density and shear viscosity of mixtures of *tert*-Butyl alcohol (Bu'OH) and *tert*-Butylamine (Bu'NH₂) with water have been determined for various temperatures (288.15 K to 318.15 K for H₂O + Bu'OH and 288.15 K to 308.15 K for H₂O + Bu'NH₂) over the whole composition range. Excess molar volumes and apparent molar volumes of the components of each system were calculated from the density data. In both systems the apparent molar volume of the organic component passes through a minimum in the water-rich region. Both systems exhibit large negative excess molar volumes which are essentially independent of temperature at all compositions. The two systems show pronounced maxima in their shear viscosity isotherms.

The empirical solvent polarity parameters E_{NR} and E_T for the solvatochromic compounds Nile Red and pyridinium-N-phenoxide betaine respectively, have been determined as a function of composition for water + *tert*-Butyl alcohol and water + *tert*-Butylamine binary mixtures, over the whole composition range at 298.15 K. For both systems the two parameters vary with composition in a strongly nonlinear fashion, and the polarity of the mixture decreases with increasing proportion of the organic cosolvent. The nonlinear variation of the polarity parameters is attributed to water-cosolvent hydrophobic interactions at low cosolvent contents, and hydrogen bonding interactions at higher cosolvent contents.

Permittivity and refractive index have also been measured at 298.15 K for both systems, and both properties are strongly nonlinear functions of composition.

The self-diffusion coefficients of water and of the organic component have been measured for $\text{H}_2\text{O} + t$ -butyl alcohol and $\text{H}_2\text{O} + t$ -butylamine mixtures over the whole composition range at 301.15 K, using the NMR spin-echo technique. In the water-rich region below 20 mole % of cosolvent, the self-diffusion coefficients of both components for each binary solvent system decrease rapidly with increasing cosolvent content. In cosolvent-rich mixtures with more than 50 mole % cosolvent, motions of water are evidently strongly correlated with those of cosolvent molecules. The semiempirical equation proposed by Albright relating the shear viscosity of a mixture to the diffusion coefficients of its components successfully predicts the general shape of the viscosity curve for each binary system. For the composition region above 50 mole % cosolvent the Albright equation gives calculated viscosities which agree well with observed values, but in the water-rich region there are significant deviations between the observed and calculated viscosities.

Volume ratios have been measured with a bellows volumometer for t -Butylamine and six water + t -Butylamine mixtures at 278.15, 288.15, 298.15 and 313.15 K, at pressures up to about 200 MPa or at a lower pressure slightly below the freezing pressure at the temperature of measurement. From densities measured at 0.1 MPa together with the volume ratios at higher pressures, excess molar volumes, and isothermal compressibilities have been evaluated. The compressibility is a relatively simple function of pressure, temperature, and composition.

Hydroxyl-proton chemical shifts for water and *t*-Butyl alcohol in water + *t*-Butyl alcohol mixtures with ≥ 8 mol% *t*-Butyl alcohol, and the averaged hydroxyl and amino proton chemical shift for water + *t*-Butylamine mixtures, have been determined at 200 MHz for four temperatures (263.15, 278.15, 298.15 and 313.15 K) as a function of composition. Further measurements have been made for water + *t*-Butyl alcohol + *t*-Butylamine ternary mixtures at 310.15 K over the complete mole fraction range at 60 MHz. Variations in solvent composition have little effect on the resonance for the methyl protons of the cosolvent, but the signal for the hydroxylic protons is substantially influenced. The water proton resonance initially shifts to higher frequencies (low fields) as the cosolvent is added to water, and the shift to higher frequency in the water proton resonance induced by the hydrophobic cosolvent is strongly temperature dependent, the effect being greatly enhanced at lower temperatures. As the proportion of cosolvent increases the hydroxyl proton signals in the water + *t*-Butyl alcohol system and the averaged proton signal in water + *t*-Butylamine mixtures shift to lower frequency (high field).

Raman and FT-IR absorption spectra of aqueous *t*-Butyl alcohol and *t*-Butylamine in the region of O-H and NH₂ stretching and bending modes have been measured at 298.15 K as a function of organic cosolvent concentration in the whole cosolvent mole fraction region. Vibrational intensities of some bands show definite trends with varying concentrations of the solutions. In the concentration dependence study unusual linewidth changes of certain bands were observed.

Conductivities, densities and viscosity B-coefficients from the Jones-Dole equation were determined for NaI, KI, Bu₄NI, LiCl and KCl at 298.15 K in various mixtures of water with *t*-Butyl alcohol and *t*-Butylamine. The limiting molar conductances and the corresponding Walden products have been computed. Values of the partial molar volumes of the electrolytes at infinite dilution in the various solvent mixtures were obtained from the density measurements.

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