Volumetric properties of binary mixtures of (water + organic solvents) at temperatures between $T = 288.15$ K and $T = 303.15$ K at $p = 0.1$ MPa

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Abstract

In this work, densities of binary mixtures of {water + formamide (FM), or + N,N-dimethylformamide (DMF), or + dimethyl-sulfoxide (DMSO), or + N,N-dimethylacetamide (DMA), or + 1,4-dioxane}, have been determined under atmospheric pressure as a function of composition and temperature using a vibrating-tube densimeter. The temperatures studied were $T = (288.15, 293.15, 298.15,$ and $303.15)$ K. The excess molar volumes (V_m^E), calculated from density data, are negative over the whole mole fraction range for the temperature range studied. The V_m^E values have been fitted to Redlich–Kister polynomial equation and others volumetric properties were calculated. The partial molar volumes at infinite dilution of each component ($\bar{V}_i^\infty$) have been determined using three different methods.
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1. Introduction

Volumetric properties of binary mixtures are complex properties because they depend not only on solute–solute, solvent–solvent and solute–solvent interactions, but also of the structural effects arising from interstitial accommodation due to the difference in molar volume and free volume between components present in the solution. Knowledge of several properties, including densities at different temperatures, is required for engineering design and for subsequent operations [1]. Moreover, there is interest in using volumetric data to test molecular theories or models of solution to extend our understanding about molecular interactions between components.

Organic solvents whose miscibility with water is unlimited usually form hydrogen bonds in aqueous solutions. Some solvents also present auto-association by hydrogen bonds in pure state but other not. The functional group of organic solvent can form hydrogen bonds with water due to the hydrophilic effects, while the hydrocarbon part of the organic solvents is responsible for hydrophobic effects.

The present work, which is a continuation of our study of volumetric properties of liquid binary mixtures [2–8], involves binary liquid mixtures of {water + formamide (FM), or + 1,4-dioxane, or + dimethylsulfoxide (DMSO), or + N,N-dimethylformamide (DMF), or

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+ *N,N*-dimethylacetamide (DMA)}, as a function of composition, at temperatures between $T = 288.15$ K and $T = 303.15$ K at $p = 0.1$ MPa.

The application of formamide in industrial processes involves its use as a synthetic intermediate in preparation of various pharmaceuticals and fungicides [9]. 1, 4-Dioxane is reported to be valuable in polymer manufacture and as a solvent for natural and synthetic resins [10]. DMSO is a low-cost solvent with excellent properties for the extraction of light aromatics from gasoline-type fractions [11]. The most important use of DMF as a solvent for polymer is in the preparation of polyacrylonitrile solutions for the manufacture of fibrous polyacrylonitrile [12]. DMA is a very good polymer solvent, dissolving polyacrylates and polyesters [13].

Thermodynamic and physicochemical properties of binary liquid mixtures of water with organic solvents studied in this work have been studied by Scharlin *et al.* [14] (H₂O or D₂O + *N,N*-dimethylformamide), Deshwal and Singh [15] (H₂O + 1,4-dioxane), Zaichikov [16] (H₂O + formamide, or + dimethylacetamide), Jelinska-Kazimierczuk and Szydlowski [17] (H₂O or D₂O + formamide, or + dimethylformamide, or + dimethylacetamide), Lin *et al.* [18] (H₂O + dimethylformamide), Sacco and Matteoli [19] (H₂O or D₂O + dimethylsulfoxide), Miyai *et al.* [20] (H₂O or D₂O + dimethylsulfoxide, or + *N,N*-dimethylformamide), and Singh and Raj [21] (H₂O + 1,4-dioxane).

We also draw attention to studies of volumetric properties which include experimental results or method of analysis that are related to our work performed by Hynčica *et al.* [22] (partial molar volumes of H₂O + *o*- or *p*-aminobenzoic acids, or + *o*-diaminobenzene), Maham *et al.* [23], Lebrett *et al.* [24], Chan *et al.* [25], Zhang *et al.* [26] and Maham *et al.* [27] (volumetric properties of H₂O + ethanolamine alkyl derivatives), Iloukhani *et al.* [28] (volumetric properties of acetonitrile + 1,2-alkanediols), Amalendu and Kumar [29] (volumetric properties of *n*-alkanol + polyether), and Davis [30] (thermodynamic studies of H₂O + amphiphile).

2. Experimental

Formamide (Merck, 0.995 mole fraction), *N,N*-dimethylformamide (Merck, 0.995 mole fraction), dimethylsulfoxide (Merck, 0.995 mole fraction), *N,N*-dimethylacetamide (Sigma, purity >0.99 mole fraction), and 1,4-dioxane (Merck, 0.995 mole fraction), were stored over molecular sieves 3A (1/8-in., 4–8 mesh, Aldrich). They were used without further purification. Deionized water was distilled and purified by passage through a Milli-Q Plus osmosis membrane. The conductance was 18.2 mW · cm⁻³. The purity of each substance was evaluated from measurements of density (ρ) (table 1).

TABLE 1

Comparison of measured values of density with those in the literature at $T = 293.15$ K and $p = 0.1$ MPa

Component	$\rho^{293.15}/(\text{g} \cdot \text{cm}^{-3})$	
	Literature [33]	Experimental
Water	0.99823	0.99820
N,N-Dimethylacetamide	0.9372[a]	0.93654
N,N-Dimethylformamide	0.9445	0.94917
1,4-Dioxane	1.0337	1.03380
Dimethylsulfoxide	1.1010[a]	1.10040
Formamide	1.1334	1.13410

[a] At $T = 298.15$ K.

Density measurements of pure liquids and mixtures were performed at atmospheric pressure at $T = (288.15, 293.15, 298.15,$ and $303.15)$ K by means of vibrating-tube densimeter (Anton Paar, DMA 4500). Before each series of measurements, the densimeter was calibrated with distilled water and air. The mixtures were prepared by mass in 10 cm³ bottles and then they were taken to the densimeter immediately. The uncertainty in the excess molar volume is estimated to be less than ±1.0% of V_m^E values for the central composition range.

3. Results and discussion

The excess molar volume is defined by

$$V_m^E = V_m - x_1 V_1^\circ - x_2 V_2^\circ, \tag{1}$$

in which V_m represents the volume of a mixture containing one mole of (water + organic solvent), x_1 and x_2 are the mole fractions of components 1 (water) and 2 (organic solvent), respectively, and V_1° and V_2° are the molar volumes of pure components.

The V_m^E can be expressed by the following equation:

$$V_m^E = x_1 M_1(1/\rho - 1/\rho_1) + x_2 M_2(1/\rho - 1/\rho_2), \tag{2}$$

in which M_1, M_2, ρ_1, ρ_2 represent the molar masses and densities of the pure components, respectively, and ρ is the density of liquid solution.

Experimental results for the mole fractions, densities of the mixtures and the volumetric properties are listed in table 2.

The experimental results were fitted with the Redlich–Kister type equation

$$V_m^E = x_1(1 - x_1) \sum_{j=0}^{j=n} A_j(1 - 2x_1)^j. \tag{3}$$

The parameters A_j, obtained using the method of least squares, are given in table 3 along with the standard deviations determined from

$$\sigma = \left[\sum \left\{ V_{(\text{expt})}^E - V_{(\text{cal})}^E \right\}^2 \middle/ (N - n) \right]^{1/2}, \tag{4}$$