Partial molar volumes of organic solutes in water. XIII. Butanols (aq) at temperatures $T = 298$ K to 573 K and at pressures up to 30 MPa

Pavel Hynčica, Lubomír Hnědkovský, Ivan Cibulka *

Department of Physical Chemistry, Institute of Chemical Technology, Technická 5, 166 28 Prague, Czech Republic

Abstract

Density data for dilute aqueous solutions of 1-butanol, 2-butanol, 2-methyl-1-propanol (iso-butanol), and 2-methyl-2-propanol (tert-butanol) are presented together with partial molar volumes at infinite dilution calculated from the experimental data. The measurements were performed at temperatures from $T = 298.15$ K up to $T = 573.15$ K and at pressure close to the saturated vapour pressure of water, at pressures close to $p = 20$ MPa and $p = 30$ MPa. The data were obtained using a high-temperature high-pressure flow vibrating-tube densimeter.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: Density; Partial molar volume; Aqueous alcohols; 1-Butanol; 2-Butanol; 2-Methyl-1-propanol; 2-Methyl-2-propanol; High temperature; High pressure

1. Introduction

This study is a continuation of a systematic investigation of partial molar volumes of organic solutes in dilute aqueous solutions in a wide interval of temperature and pressure. Data for solutes of the aromatic series (benzene and its mono- and di-substituted derivatives) [1–11] and the intermediates between aromatic and aliphatic series (phenylmethanol, 2-phenylethanol) [12] have been already published. Recently the data for methanol, ethanol, 1-propanol, and 2-propanol [13] have been published. This paper is the second part of a systematic study of aliphatic solutes; new data for 1-butanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol are presented. The data were obtained using a high-pressure high-temperature densimeter [1,3,7].

2. Experimental

The densimeter and experimental procedure are described in more details elsewhere [1]. The period of the vibrating tube of the densimeter was measured by means of a counter with an uncertainty of about ± 0.2 ns, which corresponds to $\pm 10^{-3}$ kg · m^{-3} in density. Repeated calibrations of the densimeter at each experimental temperature and pressure were performed using water and nitrogen whose densities were taken from the literature [14,15]. The maximum systematic error of the measured density differences $\{\rho(\text{solution}) - \rho(\text{water})\}$ resulting

---

* Corresponding author. Tel.: +420 220 444 063; fax: +420 220 444 333.
  E-mail address: ivan.cibulka@vscht.cz (I. Cibulka).

from the densimeter calibration was about 0.1 per cent and the reproducibility of the measurements was within $\pm 2 \cdot 10^{-3}\,\text{kg} \cdot \text{m}^{-3}$ in most cases.

The temperature of the densimeter cell was measured using a calibrated (ITS 90) platinum resistance thermometer (BURNS Engineering), with a resistance $R_0 = 100\,\Omega$ at $T = 273.15$ K, connected to a multimeter in a four-lead configuration. The resolution of the temperature measurements was 0.1 mK. Temperature stability of the cell during one experiment (measurement of one sample) was within 1 mK. The total uncertainty of the temperature measurements was estimated to be about ± 20 mK at $T = 298$ K and ± 0.10 K at $T = 573$ K.

The pressure was measured by means of a strain gauge (DPI 280, Druck Ltd.), calibrated by the manufacturer with an accuracy of ± 0.1 per cent or $\pm 1 \cdot 10^{-2}$ MPa, whichever is greater. The pressure stability was within $\pm 1 \cdot 10^{-2}$ MPa at lower pressures and $\pm 3 \cdot 10^{-2}$ MPa at $p = 30$ MPa.

Most of measurements were performed using our manual sampling device [1], new automated sampling device [16] was employed for measurements of aqueous 2-methyl-2-propanol at temperatures greater than 408.15 K.

The organic solutes, *i.e.*, 1-butanol (Fluka, stated mass fraction purity >0.995), 2-butanol (Fluka, stated mass fraction purity >0.990), 2-methyl-1-propanol (Fluka, stated mass fraction purity $\geqslant$0.995), and 2-methyl-2-propanol (Fluka, stated mass fraction purity $\geqslant$0.997), were used without further treatment. The content of water in pure solutes was determined by the Fischer method and the concentrations (molalities) were corrected with respect to the water content. Distilled, demineralized (Millipore RQ) and degassed water was used as both a solvent and a calibration fluid for the densimeter. Nitrogen (Linde, mole fraction purity = 0.9999) was used as supplied. The solutions were prepared by weight using a Precisa 40SM-200 A balance (resolution = 10^{-2} mg, accuracy = ± 0.1 mg) to determine the mass of the solute and a Precisa 2200C SCS balance (resolution = 10 mg, estimated accuracy = $\pm 2 \cdot 10^{-2}$ per cent) to determine the total mass of a solution. The mass of each prepared solution was about 1 kg. Corrections of molality due to the evaporation were derived from actual volumes of both the vapour and liquid phases in the storage bottle and vapour–liquid equilibrium data for respective (alkanol + water) system. The uncertainty of the solute molality m_2 was estimated to be $\pm 2 \cdot 10^{-5}\,\text{mol} \cdot \text{kg}^{-1}$. Some organic solutes may decompose at high temperatures [3,5] which would always be accompanied by a distortion of the time course of the baseline–sample plateau–baseline during the measurement of the sample. No such indication of decomposition was observed up to the highest experimental temperature (573 K).

3. Results

3.1. Direct experimental data

Measured values of the density differences $\Delta\rho = \rho - \rho_1$ where ρ and ρ_1 are the densities of the solution and water, respectively, and the molalities of organic solutes m_2 at various temperatures and pressures are available as a supplementary material (258 data points in the range of molality from (0.05 to 0.61) $\text{mol} \cdot \text{kg}^{-1}$ for aqueous 1-butanol, 291 data points in the range of molality from (0.05 to 0.58) $\text{mol} \cdot \text{kg}^{-1}$ for aqueous 2-butanol, 294 data points in the range of molality from (0.03 to 0.61) $\text{mol} \cdot \text{kg}^{-1}$ for aqueous 2- methyl-1-propanol, and 401 data points in the range of molality from (0.04 to 0.57) $\text{mol} \cdot \text{kg}^{-1}$ for aqueous 2-methyl-2-propanol; total 1244 data points). The lowest experimental pressure at each temperature was chosen to be slightly above the saturated vapor pressure of water.

The dependence of $\Delta\rho/m_2$ on m_2 at constant temperature and pressure was found to be mostly a quadratic function of m_2 in the concentration ranges of measurements, in few cases a linear dependence was observed ($c = 0$). The experimental results obtained for individual temperatures and pressures were fitted with the equation

$$\Delta\rho/m_2 = (\rho - \rho_1)/m_2 = a + bm_2 + cm_2^2, \tag{1}$$

where a, b, and c are adjustable coefficients. The values of the coefficients were obtained by using a weighted least squares method, and are recorded in table 1. A relative statistical weight for each value $\Delta\rho/m_2$ was calculated from the estimated uncertainties of $\Delta\rho$ and m_2.

3.2. Partial molar volumes

The partial molar volume at infinite dilution ($m_2 \to 0$) of a solute $V_{m,2}^0$ is obtained from equation (1) as [1]

$$V_{m,2}^0 = (1/\rho_1)\{M_2 - (a/\rho_1)\}, \tag{2}$$

where M_2 is the molar mass of the solute.

The partial molar volumes at infinite dilution calculated from the experimental data and their estimated uncertainties are presented in table 1. The uncertainties in $V_{m,2}^0$ given in table 1 include random error estimates, that originate from the scatter associated with equation (1), as well as systematic errors estimated from uncertainties of temperature, pressure, and calibration constant.

There is a large amount of published experimental data on partial molar volumes at infinite dilution in water of alkanols investigated here. A comparison of our values with data found in the literature for lower temperatures and atmospheric pressure is presented in figures 1–4. Lines in the figures represent polynomial fits of partial molar volumes obtained at low pressure set