



# Experimental study of the density and derived volumetric (excess, apparent, and partial molar volumes) properties of aqueous 1-propanol mixtures at temperatures from 298 K to 582 K and pressures up to 40 MPa



I.M. Abdulagatov<sup>a,\*</sup>, N.D. Azizov<sup>b</sup>

<sup>a</sup> Geothermal Research Institute of the Dagestan Scientific Center of the Russian Academy of Sciences, Makhachkala, Dagestan, Russia

<sup>b</sup> Azerbaijan State Oil Academy, Baku 370601, Azerbaijan

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## ABSTRACT

Densities of (water + 1-propanol) mixtures have been measured over the temperature range from 298 K to 582 K and at pressures up to 40 MPa using the constant-volume piezometer immersed in a precision liquid thermostat. The measurements were made for six compositions of (0.869, 2.465, 2.531, 7.407, 14.377, and 56.348) mol · kg<sup>-1</sup> of 1-propanol. The expanded uncertainty of the density, pressure, temperature, and concentration measurements at the 95% confidence level with a coverage factor of  $k = 2$  is estimated to be 0.06%, 0.05%, 15 mK, and 0.015%, respectively. The derived volumetric properties such as excess ( $V_m^E$ ), apparent ( $V_\Phi$ ), and partial ( $\bar{V}_2^\infty$ ) molar volumes were calculated using the measured values of density for the mixture and for pure components (water and 1-propanol). The concentration dependences of the apparent molar volumes were extrapolated to zero concentration to yield the partial molar volumes of 1-propanol at infinite dilution ( $\bar{V}_2^\infty$ ). The temperature, pressure, and concentration dependence of density and derived properties of the mixture were studied. All experimental and derived properties (excess, apparent, and partial molar volumes) were compared with the reported data by other authors. The small and negative values of excess molar volume for the mixtures were found at all experimental temperatures, pressures, and over the entire concentration range. The excess molar volume minimum is found at concentration about 0.4 mole fraction of 1-propanol. The concentration minimum of the derived apparent molar volumes  $V_\Phi$  near the 2.5 mol · kg<sup>-1</sup> (dilute mixture) was observed.

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## 1. Introduction

Accurate volumetric (density, excess, apparent, and partial molar volumes) data of aqueous solutions are crucial for understanding industrial and natural processes. In many applications, these processes occur at high temperatures and high pressures. To use (water + 1-propanol) mixtures effectively, it is necessary to know their fundamental  $pVTx$  relationships and other derived volumetric properties such as excess ( $V_m^E$ ), apparent ( $V_\Phi$ ), and partial ( $\bar{V}_2^\infty$ ) molar volumes at high temperatures and high pressures. The values of the excess, apparent and partial molar volumes are very useful tools for understanding the interactions between the solute and solvent molecules occurring in the mixtures. Alcohol is the standard example of associated fluids. Alcohol molecules strongly affect water structure which leads to anomaly of the

thermodynamic properties of the (water + alcohol) mixtures. Due to specific interaction between the water and alcohol molecules, alcohol molecules rebuild water's structure, therefore considerable changes the thermodynamic properties of the aqueous alcohol mixture. Studies of the apparent and partial molar volumes of aqueous mixtures are used to examine solute–solvent, solute–solvent, and solvent–solvent (structural) interactions, *i.e.*, provide useful information on the nature of interaction between solute (1-propanol) and solvent (water) molecules. The excess properties, like  $V_m^E$ , reflect of the origin of the non-ideality in the mixture, especially in the mixtures that show strong interactions between the unlike molecules. The prediction of the properties changes and understanding of fundamental mechanism at the molecular level by applying statistical mechanics is very difficult due to complexity of the interactions between the unlike complex molecules of the mixture. For a deep understanding of the nature, physical and chemical mechanism of the properties of aqueous alcohol mixture anomalies, accurate experimental studies of the volumetric properties are needed.

\* Corresponding author. Present address: Applied Chemicals and Materials Division, National Institute of Standards and Technology, 325 Broadway, Boulder, CO 80305, USA.

E-mail address: [ilmutdin@boulder.nist.gov](mailto:ilmutdin@boulder.nist.gov) (I.M. Abdulagatov).

The thermodynamics of dilute binary mixtures are subject of wide-ranging scientific interest because of the dominant role played the interaction between solvent–solute molecules (solute–solute molecules can be neglected due to small concentration of solute). Dilute mixtures also very important for engineering applications such as impurity effect on the thermodynamic properties of the mixture [1]. For dilute mixtures the impurity effects are proportional to the compressibility of the pure solvent [2–4]. For example, the relative deviation between the dilute mixture and pure solvent molar volumes can be expressed as  $\delta V = K_T \left(\frac{\partial V}{\partial x}\right)_{T,x=0}$ , where  $\delta V = [V_m(P, T) - V_0(P, T)]/V_0(P, T)$  is the relative deviation,  $V_m(P, T)$  molar volume of the dilute mixture,  $V_0(P, T)$  is the molar volume of pure solvent,  $K_T$  is the isothermal compressibility of the pure solvent, and  $\left(\frac{\partial V}{\partial x}\right)_{T,x=0}$  concentration derivative of pressure at  $x = 0$  [2–4]. Some cases even very small impurity (0.1% impurity, for example) can cause a considerably changes (by a several percent) in a density at given  $p$  and  $T$  depending on compressibility of the pure solvent [1–4]. However,  $pVTx$  data for the (water + 1-propanol) mixture under high pressures and high temperatures are scarce. The main objective of this paper is to provide reliable experimental volumetric (density) and derived (excess, apparent, and partial molar volumes) properties for aqueous 1-propanol mixtures at high temperatures and high pressures. All available density and apparent and partial molar volumes data sources of the (water + 1-propanol) mixture were comprehensively evaluated and critically assessed for internal consistency and for mutual agreement.

### 1.1. Brief review of the reported density data for (water + 1-propanol) mixture

A literature survey revealed that the number of measurements reported for the density of aqueous 1-propanol mixture under pressure and at high temperature is rather limited. Table 1 summarizes experimental measurements of the density [5–12] of aqueous 1-propanol mixtures reported in the literature. The literature search was based on the TRC/NIST archive [13] and the author's own literature search. In table 1, the first author is given together with the method employed, uncertainty of the measurements, and the temperature, pressure, and concentration ranges. Only five data sources [5–8,10] for the density of the mixture under pressure are available in the literature. The quoted uncertainties of the reported density data are within  $(1 \text{ to } 5) \times 10^{-5} \text{ g} \cdot \text{cm}^{-3}$  for VTD technique [5,8,9],  $10^{-4} \text{ g} \cdot \text{cm}^{-3}$  for pycnometric method, and 0.09% [6] (for specific volume) and 0.16% [3]. The reported data sets cover temperature range from 278 K to 573 K and pressures up to 209 MPa, and molal concentration from 0.03 to 166. Most previous high-pressure density measurements were performed using VTD

technique [5,8,9] with typical uncertainty of about  $10^{-5} \text{ g} \cdot \text{cm}^{-3}$  and cover very limited concentration range (basically dilute mixtures) and pressures up to 30 MPa. Criss and Wood [5] reported density measurements for (water + 1-propanol) mixtures along the one selected isobar of 28 MPa at temperatures from 373 K to 523 K for concentration of  $0.1199 \text{ mol} \cdot \text{kg}^{-1}$  using the VTD technique. Shakhverdiev *et al.* [6] used constant-volume technique to measure  $pVTx$  properties of (water + 1-propanol) mixtures in the temperature range from 373 K to 573 K and at pressures up to 5 MPa. These measurements cover only vapour phase. Kitajima *et al.* [7] measured simultaneously isochoric heat capacity and  $pVTx$  relationship of (water + 1-propanol) mixtures in the liquid phase at temperatures between 285 K and 430 K and pressures up to 30 MPa. The authors employed constant-volume adiabatic calorimeter technique. Uncertainty of the measured densities is 0.16%. Measurements were made along the quasi-isochores. Kubota *et al.* [10] reported high pressure (up to 209 MPa) measurements for (water + 1-propanol) mixtures (for three concentrations 0.07, 0.25, 0.50, and 0.75 mole fraction) in the temperature range from 283 K to 348 K. The uncertainty of the measured densities is 0.09%. Measurements were made using Adam's piezometer. The measured mixture densities were used to calculate the excess and partial molar volumes as a function of temperature, pressure, and concentration. Measurements by Hynčica *et al.* [8] are covering the temperature range from 298 K to 573 K and at pressures up to 30 MPa for concentrations from  $(0.094 \text{ to } 0.847) \text{ mol} \cdot \text{kg}^{-1}$ . The uncertainty of the measured density differences  $(\rho_{\text{mix}} - \rho_w)$  between the mixture and pure water is 0.1%. Measurements were performed with a VTD. The densities of (water + 1-propanol) mixtures were measured by Høiland *et al.* [9] at atmospheric pressure within the limited temperature range from 278 K to 313 K for concentrations  $(0.03 \text{ to } 0.50) \text{ mol} \cdot \text{kg}^{-1}$  using VTD. The uncertainty of the density measurements was  $0.005 \text{ kg} \cdot \text{m}^{-3}$ . These data were used to evaluate the apparent molar volumes. All of these density data, which overlap the present experimental range, were used to compare with the present results (see below).

The excess molar volumes of (water + 1-propanol) mixtures have been studied by several authors [14–16]. Miyamoto *et al.* [14] used compression measurements for (water + 1-propanol) at  $T = 298.15 \text{ K}$  and at pressures up to 200 MPa to calculate the values of excess molar volumes. Benson and Kiyohara [15] reported excess molar volume data for (water + 1-propanol) mixtures for five isotherms between 288 K and 308 K at atmospheric pressure. These data were obtained from measured densities for the mixture and pure components data. Density was measured with a flow type oscillating tube densimeter. Uncertainty in density measurements was  $2 \times 10^{-5} \text{ g} \cdot \text{cm}^{-3}$ . Zielkiewicz [16] used dilution dilatometer to measure excess molar volumes for (water + 1-propanol)

**TABLE 1**  
Summary of the density measurements of the aqueous 1-propanol mixture.

First author	Year	Method <sup>a</sup>	Density uncertainty (% or $\text{g} \cdot \text{cm}^{-3}$ )	Temperature/K	Pressure/MPa	Concentration (mole fraction or $\text{mol} \cdot \text{kg}^{-1}$ )
Chu [12]	1962	PYC	$10^{-4} \text{ g} \cdot \text{cm}^{-3}$	298	0.101	0–1 m.f.
Mikhail [11]	1963	PYC	$10^{-4} \text{ g} \cdot \text{cm}^{-3}$	298–323	0.101	0–1 m.f.
Høiland [9]	1980	VTD	$5 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$	278–313	0.101	0.03–0.50
Kubota [10]	1987	AP <sup>b</sup>	0.09%	283–348	Up to 209	4.18–166.5
Criss [5]	1996	VTD	NA	373–523	28	0.1199
Shakhverdiev [6]	2002	CVP	0.03%	373–573 (Vapour phase)	Up to 5	18.5–166.5
Kitajima [7]	2003	PYC	0.16%	285–430	Up to 30	0.255–0.738 m.f.
Hynčica [8]	2004	VTD <sup>c</sup>	0.10%	298–573	Up to 30	0.094–0.847
This work	2013	CVP	0.06%	298–582	Up to 40	0.869–56.348
This work	2013	PYC	0.05%	292–352	0.101	0.869–56.348

<sup>a</sup> VTD – vibrating tube densimeter; CVP – constant volume piezometer; PYC – pycnometer; AP – Adam's piezometer.

<sup>b</sup> Uncertainty for the specific volume.

<sup>c</sup> Uncertainty 0.1% is for the density differences  $(\rho_{\text{mix}} - \rho_w)$ .

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