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The study of excess molar volumes and related properties for binary mixtures containing benzyl alcohol and 1,3-dichloro-2-propanol with vinyl acetate, ethyl acetate and t-butyl acetate at T = 293.15 to 313.15 K and P = 0.087 MPa

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ABSTRACT

The density data for binary mixtures of benzyl alcohol or 1,3-dichloro-2-propanol with vinyl acetate, ethyl acetate and t-butyl acetate were measured at T = (293.15–313.15) K and P = 0.087 MPa. From these data, the excess molar volumes, partial molar volumes, excess partial molar volumes, partial molar volumes at infinite dilution, apparent molar volumes, thermal expansion coefficients and their excess values are calculated for studied binary systems. The Redlich- Kister equations were fitted to excess molar volumes data. The results show that excess molar volumes for all considered systems are negative and decrease with increasing temperature. The same behavior was observed for excess thermal expansion coefficients. The interactions between molecules in mixtures are discussed and explained based on these experimental data.

1. Introduction

The study of thermophysical properties of liquid mixtures is growing day by day since this type of considerations gives us a better understanding about interactions between molecules in mixtures. The studies on volumetric and thermodynamic properties of alcohols and esters binary mixtures are increasing [1–10]. Alcohols are identified as polar associated liquids with ability of hydrogen-bond formation while esters are known as compounds including both carbonyl and alkyl groups so that recognizing the interactions between these components in solutions are helpful to develop theories concerning our knowledge about liquid mixtures.

Benzyl alcohol is used as a general solvent for inks, paints, lacquers, and epoxy resin coatings. It is also a precursor to a variety of esters, used in the soap, perfume, and flavor industries. It is also used as a photographic developer and as a bacteriostatic preservative at low concentration in intravenous medications, cosmetics and topical drugs. 1,3-dichloro-2-propanol has several applications in glycerol, celluloid and plastics production and also in pharmacy. Ethyl acetate is a solvent which is used in glues, nail polish removers, decaffeinating tea and coffee, and cigarettes. Vinyl acetate is an organic compound which is the precursor to polyvinyl acetate, an important polymer in industry. *Tert*-butyl acetate is used as a solvent in the production of enamels, inks, adhesives, thinners and industrial cleaners.

In our previous work we reported volumetric properties for binary mixtures of 1-propanol and i-butanol with vinyl, ethyl and t-butyl acetate [11].

There are rare experimental data for volumetric properties of binary mixtures including benzyl alcohol or 1,3-dichloro-2-propanol with vinyl, ethyl and t-butyl acetate in the literature. So we were interesting to do this study on volumetric properties of these systems.

2. Experimental

2.1. Materials

Table 1 includes the properties of used materials. All solutions were prepared afresh by mass using an analytical balance (Sartorius, CP224S, Germany) with a standard uncertainty of 10^{-4} g. The average uncertainty in the mole fraction of the mixtures was estimated to be less than ±0.003. Caution was taken to prevent

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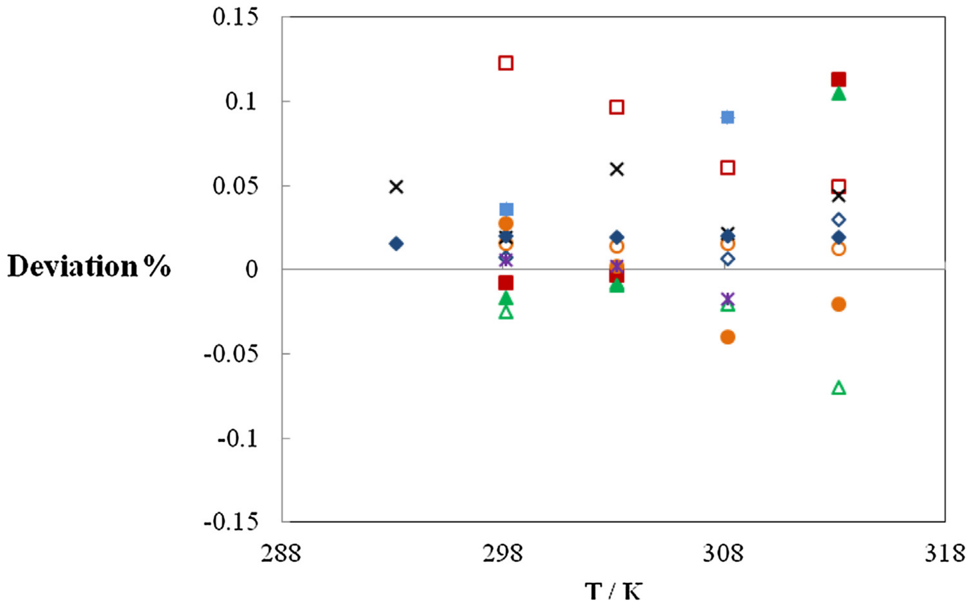

Fig. 1. Deviation plot for comparison of density of pure components. Benzyl alcohol comparison with: ◊ , Ref. [11], □ Ref. [12], △ , Ref. [13], ○ , Ref. [14]. Vinyl acetate comparison with: ◆ , Ref. [18]. Ethyl acetate comparison with: ■ , Ref. [21], ▲ , Ref. [3], ● , Ref. [22], ×, Ref. [23], ✻ , Ref. [6]. T-butyl acetate comparison with + , Ref. [24]. Deviations are calculated as: $[(\rho_{exp.} - \rho_{reported})/\rho_{exp.}] \times 100$.

Table 1
Provenance and mass fraction purity of the compounds studied.[a]

compound	CAS number	supplier	Mass fraction purity (purification analysis method)	Molar mass (g.mol^{-1})
Benzyl alcohol	100-51-6	Merck	>99% (GC)	108.14
1,3-Dichloro-2-propanol	96-23-1	Merck	>99% (GC)	128.99
Vinyl Acetate	108-05-4	Merck	>99% (GC)	86.09
Ethyl Acetate	141-78-6	Merck	>99% (GC)	88.10
t-Butyl Acetate	540-88-5	Merck	>99% (GC)	116.16

[a] All materials are used without further purifications.

evaporation of the sample after preparation. Measurements were performed immediately after preparation of solutions.

2.2. Apparatus

Densities were measured using a U-tube vibrating densitometer (Anton Paar DMA 4500).

The apparatus was calibrated with double distilled deionized and degassed water, and dry air at ambient pressure (0.087 MPa). All injections to densimeter were done by using micro syringe for afresh prepared solutions. Temperature was automatically kept constant within ±0.05 K by instrument with its built-in thermostat. All measurements were performed three times, and the reported results are the relevant averages. The apparatus is precise within 1×10^{-5} g cm^{-3}, its repeatability is within 3×10^{-5} g cm^{-3} and the uncertainty of density measurements was estimated to be better than $\pm 1 \times 10^{-3}$ g cm^{-3}.

3. Results and discussion

Table 2 lists the values of measured and reported densities [1–8,12–25] for pure materials. Fig. 1 shows deviation graph which compares our values with literature for density at different temperatures. Deviations are calculated using following equation:

$$\mathrm{Dev}\% = [(\rho_{exp} - \rho_{exp})/\rho_{report}] \times 100 \quad (1)$$

where ρ_{exp} and ρ_{report} stand for measured and reported densities, respectively.

Table 2 and Fig. 1 confirm that agreement between our data and literature values within experimental uncertainty are excellent. The values of density for six binary mixtures at studied temperatures are tabulated in Tables 3–8. Densities for the pure esters are those reported in our previous work [11]. As can be seen from these tables, densities are increased with mole fraction of benzyl alcohol and/or 1,3—dichloro -2-propanol in their binary mixtures and decreased with raising temperature. This is happened because in these mixtures the mentioned alcohols are the component with larger density. Also due to increasing of volume with temperature, it is reasonable that density show decreasing with enhancing temperature. Also excess molar volumes are computed using the following equation:

$$V_m^E = \Sigma_i \left(\frac{1}{\rho} - \frac{1}{\rho_i}\right) x_i M_i \quad (2)$$

where ρ denotes density of solution, and x_i,ρ_i and M_i are the mole fraction, density and molar mass of component i. The excess molar volumes are included in Tables 3–8. The values for excess molar volumes are negative (and relatively small) for all considered mixtures over the whole range of composition and at all temperatures. This behavior is illustrated graphically in Figs. 2 and 3. Negative excess volumes usually arise from predominance of specific and attractive interactions factor to possible differences in size and shape of components in mixture (which in turn led to inadequate accommodation of molecules between each other). Interstitial accommodation that comes from changing of free volumes and formation of new polymers of ester-alcohol will lead to negative excess volumes and under these conditions contraction