Volumetric properties for binary and ternary systems consist of 1-chlorobutane, *n*-butylamine and isobutanol at 298.15 K with application of the Prigogine–Flory–Patterson theory and ERAS-Model

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ABSTRACT

Densities of the ternary system consist of 1-chlorobutane (1) + *n*-butylamine (2) + isobutanol (3) and related binary systems were measured at 298.15 K for the liquid region. Excess molar volumes, V_m^E, for the mixtures were derived and correlated as a function of the mole fraction by using the Redlich–Kister and the Cibulka equations. From the experimental data, partial molar volumes, $\bar{V}_{m,i}$, excess partial molar volumes, $\bar{V}_{m,i}^E$, partial molar volumes at infinite dilution, $\bar{V}_{m,j}^0$, and apparent molar volumes, $V_{\varphi,i}$ were also calculated. For mixtures of 1-chlorobutane (1) + *n*-butylamine (2) and 1-chlorobutane (1) + isobutanol (3), V_m^E is positive over the entire range of mole fractions, while for *n*-butylamine (2) + isobutanol (3), V_m^E are negative. The experimental results of the constitute binary and ternary mixtures have been used to test the applicability of the Prigogine–Flory–Paterson (PFP) theory and Extended Real Associated Solution (ERAS-Model).

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1. Introduction

This paper is a part of an ongoing research effort to measure and characterize the properties of mixtures containing organic solvents [1–4]. It reports the densities, ρ, excess molar volume, V_m^E, partial molar volumes, $\bar{V}_{m,i}$, and apparent molar volumes, $V_{\varphi,i}$, for the mixtures of 1-chlorobutane, *n*-butylamine, and isobutanol at 298.15 K.

In recent years, measurements of thermodynamic properties have been adequately employed in understanding the nature of molecular systems and physico-chemical behavior in liquid mixtures [5,6]. The nonrectilinear behavior of above mentioned properties of liquid mixtures with changing mole fractions is attributed to the difference in size of the molecules and strength of interactions.

The derived properties provide valuable information for qualitatively analyzing the molecular interactions between molecules. In fact the excess functions of binary and ternary 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 accommodations so these are very important from theoretical points of view, to understand liquid theory. Amines, alkanols, and their binary mixtures

find applications as solvent in chemistry and modern technology. The excess quantities of binary mixtures have been fitted to the Redlich–Kister equation to determine the coefficients. For correlating the ternary data, the Cibulka equation was used. No reported mixing properties of these studied systems at this temperature have been found. The Prigogine–Flory–Patterson theory [7–9] and extended real associated solution (ERAS-Model) developed by Heintz [10] have been applied for correlating excess molar volumes of binary mixtures.

2. Experimental

2.1. Materials

The mass fraction purity of the components from Merck were as follows: 1-chlorobutane (≥99.5%), *n*-butylamine (>99.5%) and isobutanol (≥99%) and used without further purification. Densities and refractive indices were measured and their values were in good agreement with values found in the literature [11–16], reported in Table 1. Compounds were stored in brown glass bottles and fractionally distilled immediately before use.

2.2. Apparatus and procedure

The density of the compounds and their binary and ternary mixtures were measured with Anton Paar DMA 4500 oscillating U-tube densitometer, operated in the static mode and the uncertaintities

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Table 1
Experimental and literature values of densities ρ, and refractive indices n_D, of pure components at 298.15 K.

Compound	ρ (g cm^{-3})		n_D	
	Experimental	Literature	Experimental	Literature[a]
1-Chlorobutane	0.88086	0.88090[a]	1.3998	1.4001
		0.88097[b]		
		0.88085[c]		
		0.88018[d]		
n-Butylamine	0.73464	0.73460[a]	1.3980	1.3987
		0.73225[c]		
		0.73300[e]		
Isobutanol	0.79784	0.79780[a]	1.3940	1.3939
		0.79777[b]		
		0.79781[c]		
		0.79737[d]		
		0.79780[f]		

[a] Ref. [11].
[b] Ref. [12].
[c] Ref. [13].
[d] Ref. [14].
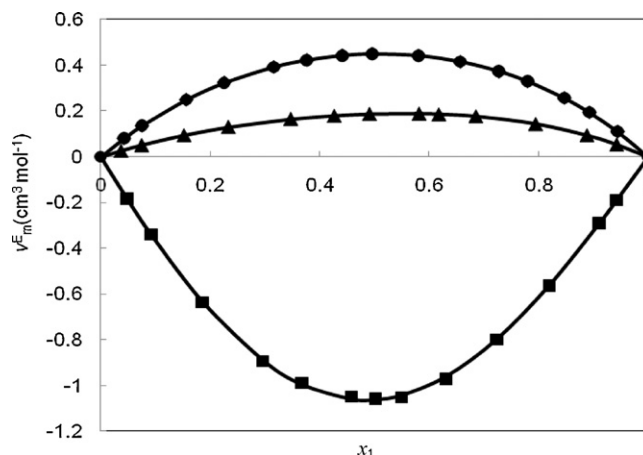[e] Ref. [15].
[f] Ref. [16].

Fig. 1. Excess molar volumes at 298.15 K for the binary systems: (●) 1-chlorobutane (1) + n-butylamine (2), (▲) 1-chlorobutane (1) + isobutanol (3), (■) n-butylamine (2) + isobutanol (3). x_1 is the mole fraction of the first component in each binary. Full line calculated with Redlich–Kister equation.

were estimated to be within $\pm 1 \times 10^{-5}$ g cm^{-3}. The temperature in the cell was regulated to ± 0.01 K with solid-state thermostat. The apparatus was calibrated once a day with dry air and double-distilled freshly degassed water. Airtight stoppered bottles were used for the preparation of the mixtures. The mass of the dry bottle was first determined. The less volatile component of the mixture was introduced in the bottle, and the total mass was recorded. Subsequently, the other component was introduced, and the mass of bottle along with the two components was determined. Ternary mixtures were prepared by mixing of three components. A total of 40 compositions was measured at 298.15 K for the ternary system of 1-chlorobutane (1) + n-butylamine (2) + isobutanol (3). Each mixtures was immediately used after it was well-mixed by shaking. All the weightings were performed on an electronic balance (AB 204-N Mettler) accurate to 0.1 mg. The uncertainty in the mole fraction is estimated to be lower than $\pm 2 \times 10^{-4}$.

3. Results

3.1. Binary systems

The excess molar volumes, V_m^E, for three binary systems and the corresponding ternary system were evaluated using the equation:

$$V_m^E = \sum_{i=1}^{N} x_i M_i (\rho^{-1} - \rho_i^{-1}) \tag{1}$$

where ρ is the density of the mixture, ρ_i is the density of pure component i, x_i is the mole fraction, M_i is the molar mass of component i, and N stands for the number of components in the mixture.

The corresponding V_m^E values of three binary systems of 1-chlorobutane (1) + n-butylamine (2), 1-chlorobutane (1) + isobutanol (3), and n-butylamine (2) + isobutanol (3) were measured at 298.15 K and presented in Table 2 and plotted against mole fraction in Fig. 1. The values of presently investigated binary mixtures have been fitted to the Redlich–Kister polynomial equation of the form [17]:

$$V_m^E = x_1(1 - x_1) \sum_{i=0}^{N} A_i (1 - 2x_1)^i \tag{2}$$

where x_1 is the mole fraction of solvent, A_i are adjustable parameters obtained by least-squares method, and i is the degree of the

polynomials. In each case, the optimum number of coefficients was ascertained from an examination of the variation of standard deviation σ with:

$$\sigma = \sum \frac{(V_{m,\exp.}^E - V_{m,cal.}^E)^2}{(n - p)^{1/2}} \tag{3}$$

where $V_{m,\exp.}^E$ and $V_{m,cal.}^E$ are the experimental and calculated values of the excess molar volumes, and n and p are the number of experimental points and number of parameters retained in the respective equations. The coefficients A_i of Eq. (2), obtained by the method of least squares are given in Table 3 together with corresponding standard deviations.

The partial molar volumes, $\bar{V}_{m,i}$, in these mixtures were calculated over the whole composition range using Eq. (4) [18,19]:

$$\overline{V}_{m,i} = V_m^E + V_{m,i}^* + (1 - x_i)\left(\frac{\partial V_m^E}{\partial x_i}\right)_{T,P} \tag{4}$$

where $V_{m,i}^*$ is pure molar volumes of component i, respectively. The excess partial molar volumes $\overline{V}_1^E = (\overline{V}_1 - \overline{V}_1^0)$ and $\overline{V}_2^E = (\overline{V}_2 - \overline{V}_2^0)$ from V_m^E and the molar volumes of the pure components are also calculated. The values of partial molar volumes and the excess partial molar volumes are presented in Table 2 and latter was plotted against mole fraction in Figs. 2 and 3.

The partial molar volumes at infinite dilution $\overline{V}_{m,j}^0$ appear to be of particular interest. In the limit of infinite dilution, the solute–solute interactions disappear. Thus the values of the partial molar volume at infinite dilution provide insight into solute–solvent interactions. Setting $x = 0$ and $x = 1$, respectively, in Eq. (4) leads to

$$\overline{V}_j^0 = V_j^* + \sum_{i=0} A_i(\mp 1)^i \tag{5}$$

{+1 for $j = 1$ and -1 for $j = 2$}.

All partial molar volumes at infinite dilution were calculated using the Redlich–Kister coefficients, A_i in Eq. (5) listed in Table 4.

Apparent molar volume $V_{\varphi,i}$ which may be more convenient and accurate could be calculated as followings [20]:

$$V_{\varphi,i} = \frac{V_i^0 - V_m^E}{x_i} \tag{6}$$

The values of apparent molar volumes are also reported in Table 2.