Thermochimica Acta 502 (2010) 77–84

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

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

H. Iloukhani*, K. Khanlarzadeh

Department of Physical Chemistry, Faculty of Chemistry, University of Bu-Ali Sina, Hamedan, Iran

ARTICLE INFO

Article history:
Received 21 November 2009
Received in revised form 11 February 2010
Accepted 14 February 2010
Available online 20 February 2010

Keywords:
1-Chlorobutane
n-Butylamine
Isobutanol
Excess molar volume
PFP theory
ERAS-Model

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).

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

---

* Corresponding author. Tel.: +98 0811 8282807; fax: +98 0811 8282807.
E-mail address: iloukhani@basu.ac.ir (H. Iloukhani).

0040-6031/$ – see front matter
doi:10.1016/j.tca.2010.02.010

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] 0.88097[b] 0.88085[c] 0.88018[d]	1.3998	1.4001
n-Butylamine	0.73464	0.73460[a] 0.73225[c] 0.73300[e]	1.3980	1.3987
Isobutanol	0.79784	0.79780[a] 0.79777[b] 0.79781[c] 0.79737[d] 0.79780[f]	1.3940	1.3939

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

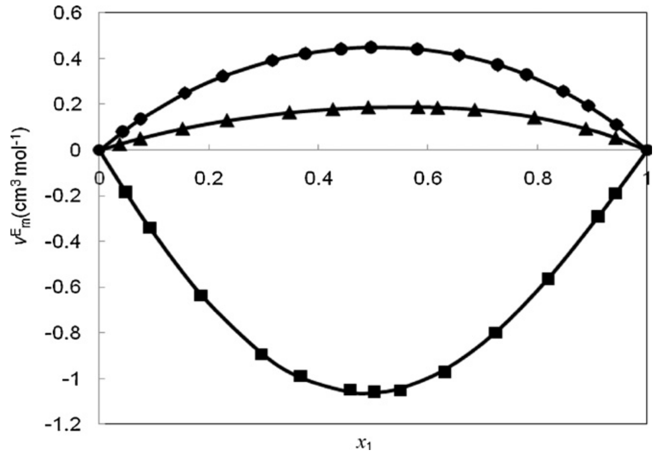

Fig. 1. Excess molar volumes at 298.15 K for the binary systems: (●) 1-chlorobutane (1) + *n*-butylamine (2), (▲) 1-chlorobutane (1) + isobutanol (3), (■) *n*-butylamine (2) + isobutanol (3). x_1 is the mole fraction of the first component in each binary. Full line calculated with Redlich–Kister equation.

were estimated to be within ±1 × 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 ±2 × 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:

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

where $V^E_{m,\exp.}$ and $V^E_{m,cal.}$ 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]:

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

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 $\overline{V}^0_{m,j}$ 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.

Table 2

Densities ρ (g cm^{-3}), excess molar volumes V_m^E (cm^3 mol^{-1}), partial molar volumes, $\bar{V}_{m,i}$ (cm^3 mol^{-1}) excess partial molar volumes, $\bar{V}_{m,i}^E$ (cm^3 mol^{-1}) and apparent molar volumes $V_{\varphi,i}$ (cm^3 mol^{-1}) for binary mixtures at 298.15 K.

x_1	ρ	V_m^E	$\bar{V}_{m,1}$	$\bar{V}_{m,2}$	$\bar{V}_{m,1}^E$	$\bar{V}_{m,2}^E$	$V_{\varphi,1}$	$V_{\varphi,2}$
1-Chlorobutane + *n*-butylamine								
0.0000	0.73465	0.0000	107.12	99.56	2.014	0.000		99.56
0.0428	0.74064	0.0809	106.93	99.56	1.824	0.004	103.21	99.47
0.0758	0.74529	0.1356	106.79	99.57	1.684	0.013	103.31	99.41
0.1564	0.75670	0.2494	106.47	99.61	1.371	0.051	103.51	99.26
0.2259	0.76661	0.3247	106.23	99.66	1.132	0.101	103.66	99.14
0.3163	0.77960	0.3924	105.96	99.74	0.859	0.187	103.86	98.98
0.3765	0.78830	0.4224	105.80	99.81	0.701	0.256	103.98	98.88
0.4412	0.79766	0.4430	105.65	99.90	0.552	0.343	104.10	98.76
0.4959	0.80559	0.4498	105.54	99.98	0.442	0.427	104.19	98.67
0.5804	0.81791	0.4420	105.40	100.14	0.298	0.581	104.34	98.50
0.6566	0.82909	0.4145	105.30	100.31	0.194	0.751	104.47	98.35
0.7272	0.83952	0.3717	105.22	100.50	0.120	0.941	104.59	98.19
0.7794	0.84726	0.3294	105.18	100.66	0.077	1.107	104.68	98.06
0.8465	0.85731	0.2568	105.14	100.92	0.036	1.358	104.80	97.89
0.8923	0.86425	0.1940	105.12	101.11	0.018	1.557	104.88	97.76
0.9437	0.87212	0.1103	105.11	101.37	0.005	1.813	104.98	97.60
1.0000	0.88086	0.0000	105.10	101.69	0.000	2.136	105.10	
1-Chlorobutane + isobutanol								
0.0000	0.79784	0.0000	105.87	92.90	0.770	0.000		92.90
0.0370	0.80107	0.0266	105.82	92.90	0.713	0.001	104.38	92.87
0.0748	0.80435	0.0517	105.76	92.91	0.656	0.004	104.41	92.84
0.1521	0.81104	0.0944	105.64	92.92	0.543	0.016	104.48	92.79
0.2331	0.81797	0.1300	105.53	92.94	0.432	0.036	104.54	92.73
0.3472	0.82762	0.1649	105.40	92.98	0.295	0.075	104.63	92.65
0.4266	0.83427	0.1780	105.32	93.01	0.215	0.113	104.68	92.59
0.4911	0.83959	0.1862	105.26	93.05	0.159	0.151	104.72	92.53
0.5817	0.84701	0.1874	105.20	93.12	0.097	0.222	104.78	92.45
0.6178	0.84995	0.1842	105.18	93.16	0.077	0.257	104.80	92.42
0.6855	0.85542	0.1761	105.15	93.24	0.046	0.335	104.84	92.34
0.7946	0.86422	0.1424	105.12	93.41	0.015	0.508	104.92	92.21
0.8885	0.87178	0.0941	105.11	93.62	0.003	0.717	105.00	92.06
0.9428	0.87618	0.0540	105.10	93.77	0.001	0.869	105.04	91.96
1.0000	0.88086	0.0000	105.10	93.96	0.000	1.060	105.10	
n-Butylamine isobutanol								
0.0000	0.79784	0.0000	95.63	92.90	−3.923	0.000		92.90
0.0482	0.79616	−0.1845	95.95	92.89	−3.610	−0.008	103.38	93.09
0.0921	0.79454	−0.3410	96.23	92.87	−3.331	−0.031	103.26	93.28
0.1855	0.79079	−0.6368	96.80	92.76	−2.761	−0.139	102.99	93.68
0.2961	0.78562	−0.8956	97.43	92.52	−2.133	−0.381	102.58	94.17
0.3674	0.78171	−0.9894	97.80	92.30	−1.759	−0.603	102.25	94.46
0.4578	0.77631	−1.0490	98.23	91.95	−1.327	−0.955	101.85	94.84
0.5021	0.77352	−1.0580	98.42	91.75	−1.133	−1.152	101.66	95.03
0.5502	0.77040	−1.0532	98.62	91.52	−0.937	−1.379	101.47	95.24
0.6313	0.76459	−0.9712	98.91	91.11	−0.644	−1.787	101.10	95.53
0.7237	0.75745	−0.8002	99.19	90.64	−0.371	−2.263	100.66	95.80
0.8191	0.74975	−0.5648	99.39	90.18	−0.163	−2.723	100.25	96.02
0.9098	0.74218	−0.2906	99.52	89.82	−0.041	−3.080	99.88	96.12
0.9418	0.73952	−0.1908	99.54	89.72	−0.017	−3.178	99.76	96.18
1.0000	0.73465	0.0000	99.56	89.60	0.000	−3.303	99.56	

3.2. Ternary system

The experimental densities and excess molar volumes from mole fraction average, of ternary system of 1-chlorobutane (1) + *n*-butylamine (2) + isobutanol (3) at 298.15 K are listed in Table 5. The derived data, V_m^E as defined in Eq. (1) for the ternary system were correlated using the Cibulka equation [21]:

$$\Delta Q_{123} = \Delta Q_{bin} + x_1 x_2 x_3 \Delta_{123} \tag{7}$$

and

$$\Delta Q_{bin} = \sum_{i=1}^{3} \sum_{j>i}^{3} \Delta Q_{ij} \tag{8}$$

where ΔQ_{123} refers to V_m^E for the ternary system and $x_3 = 1 - x_1 - x_2$. ΔQ_{ij} in Eq. (11) is the binary contribution of each $i-j$ pair to the V_m^E given by Eq. (6) with the parameters shown in Table 3. The ternary contribution term Δ_{123} was correlated using the expression

Table 3

Coefficients A_i and standard deviations σ (cm^3 mol^{-1}) of Eq. (2) for of binary systems at 298.15 K.

System	A_0	A_1	A_2	σ
1-Chlorobutane + *n*-butylamine	1.797	−0.061	0.278	0.0009
1-Chlorobutane + isobutanol	0.746	−0.136	0.160	0.0010
n-Butylamine + isobutanol	−4.257	−0.310	0.644	0.0050

Table 4

The partial molar volumes at infinite dilution $\bar{V}_{m,j}^0$, of the binary systems at 298.15 K.

System	$\bar{V}_1^0$ (cm^3 mol^{-1})	$\bar{V}_2^0$ (cm^3 mol^{-1})
1-Chlorobutane + *n*-butylamine	107.12	101.69
1-Chlorobutane + isobutanol	105.87	93.94
n-Butylamine + isobutanol	95.63	89.59

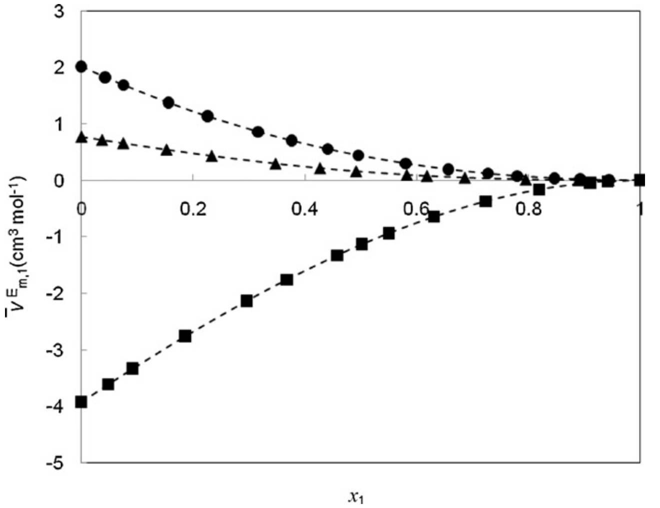

Fig. 2. Excess partial molar volumes, $\bar{V}^E_{m,1}$ at 298.15 K for the binary systems: (●) 1-chlorobutane (1) + *n*-butylamine (2), (▲) 1-chlorobutane (1) + isobutanol (3), (■) *n*-butylamine (2) + isobutanol (3). x_1 is the mole fraction of the first component in each binary system.

Table 5
Experimental V^E_m for the ternary system of 1-chlorobutane (1) + *n*-butylamine (2) + isobutanol (3) at 298.15 K.

x_1	x_2	ρ (g cm^{-3})	V^E_m (cm^3 mol^{-1})
0.0503	0.0575	0.80050	−0.2160
0.0523	0.2506	0.79337	−0.8749
0.0523	0.4516	0.78061	−0.9239
0.0570	0.6507	0.76525	−0.5287
0.0501	0.9116	0.74329	0.1806
0.0515	0.7085	0.75996	−0.3763
0.0491	0.4931	0.77752	−0.9088
0.0519	0.2995	0.78985	−0.8455
0.0526	0.1006	0.80021	−0.4963
0.1009	0.0509	0.80574	−0.2309
0.1010	0.2553	0.79797	−0.9242
0.1048	0.4544	0.78472	−0.8524
0.0990	0.6630	0.76665	−0.3050
0.0977	0.8606	0.75070	0.1919
0.2011	0.2520	0.80771	−0.9755
0.2005	0.4563	0.79160	−0.6411
0.1977	0.6566	0.77359	0.0153
0.1989	0.7610	0.76492	0.3312
0.1978	0.5590	0.78168	−0.2430
0.1990	0.3567	0.80005	−0.9038
0.4642	0.3727	0.81815	−0.4239
0.7146	0.1098	0.85398	−0.2357
0.4792	0.4020	0.81580	−0.2077
0.4210	0.4988	0.80265	0.0603
0.3626	0.5508	0.79409	0.0974
0.3029	0.6566	0.78075	0.3047
0.4481	0.0454	0.83637	−0.2123
0.4017	0.2523	0.82515	−0.9682
0.3976	0.4561	0.80568	−0.2361
0.4011	0.5559	0.79582	0.2612
0.4019	0.3529	0.81625	−0.6821
0.4145	0.1506	0.83215	−0.8720
0.5007	0.2531	0.83175	−0.7666
0.5282	0.4298	0.81482	0.2078
0.5979	0.2561	0.83672	−0.4262
0.5995	0.3540	0.82582	0.1624
0.7016	0.2526	0.84083	0.1169
0.8491	0.0493	0.86540	0.1157
0.8505	0.1010	0.86145	0.2014
0.9002	0.0512	0.86771	0.2888

Table 6
Ternary coefficients of Cibulka equation for V^E_m (cm^3 mol^{-1}) at 298.15 K.

System	B_0	B_1	B_2	σ
1-Chlorobutane + *n*-butylamine + isobutanol	−30.5214	−28.2024	63.73779	0.02

suggested by Cibulka:

$$\Delta_{123} = B_0 + B_1 x_1 + B_2 x_2 \tag{9}$$

The ternary parameters, B_0, B_1, and B_2, were determined with the optimization algorithm similar to that for the binary parameters. The fitting parameters and the corresponding standard deviations are given in Table 6. Excess molar volumes for this ternary system were also predicted using five geometrical solution models [22–26]. These models use binary contributions evaluated by Redlich–Kister equation.

1. Tsao–Smith Model [22]:

$$V^E_{123} = \frac{V^E_{12} x_2}{1 - x_1} + \frac{V^E_{13} x_3}{1 - x_1} + V^E_{23}(1 - x_1) \tag{10}$$

2. Jacob–Fitzner Model [23]:

$$V^E_{123} = \frac{V^E_{12} x_1 x_2}{[(x_1 + x_3/2)(x_2 + x_3)/2]} \frac{V^E_{13} x_1 x_3}{[(x_1 + x_2/2)(x_3 + x_2)/2]} + \frac{V^E_{23} x_1 x_3}{[(x_2 + x_1/2)(x_3 + x_1)/2]} \tag{11}$$

3. Kohler Model [24]:

$$V^E_{123} = V^E_{12}(x_1 + x_2)^2 + V^E_{13}(x_1 + x_3)^2 + V^E_{23}(x_2 + x_3)^2 \tag{12}$$

4. Rastogi Model [25]:

$$V^E_{123} = \frac{V^E_{12}(x_1 + x_2) + V^E_{13}(x_1 + x_2) + V^E_{23}(x_2 + x_3)}{2} \tag{13}$$

5. Radojkovic Model [26]:

$$V^E_{123} = V^E_{12} + V^E_{13} + V^E_{23} \tag{14}$$

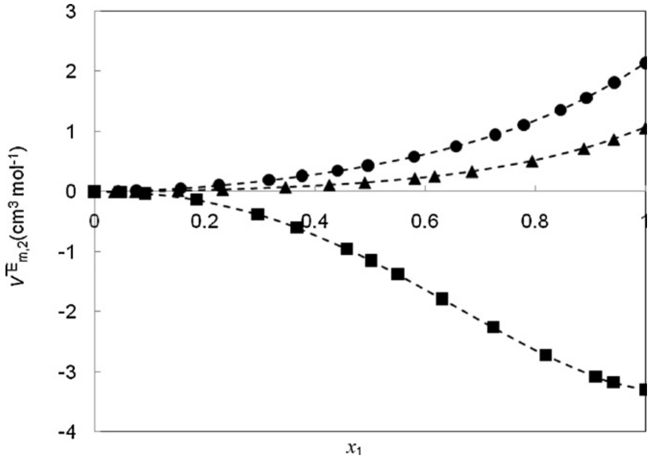

Fig. 3. Excess partial molar volumes, $\bar{V}^E_{m,2}$ at 298.15 K for the binary systems: (●) 1-chlorobutane (1) + *n*-butylamine (2), (▲) 1-chlorobutane (1) + isobutanol (3), (■) *n*-butylamine (2) + isobutanol (3). x_1 is the mole fraction of the first component in each binary system.

Table 7
Standard deviation in the prediction of V_m^E (cm^3 mol^{-1}) with different models for the ternary system at 298.15 K.

Model	$S(V_m^E)$
Tsao–Smith	0.05
Jacob–Fitzner	0.07
Kohler	0.06
Rastogi	0.06
Radojkovic	0.05

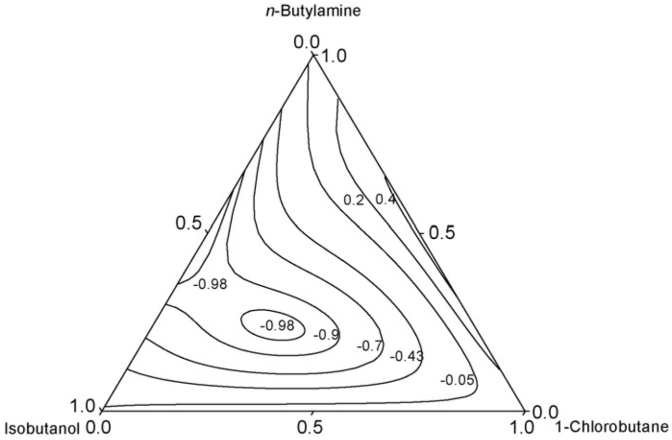

Fig. 4. Isolines at constant excess molar volume V_m^E for ternary mixtures of 1-chlorobutane (1) + *n*-butylamine (2) + isobutanol (3) correlated by Cibulka equation.

Standard deviations presented in Table 7, were determined for all models as:

$$S = \frac{1}{n}\sqrt{\sum_{i=1}^{n}(V_{123}^E(\exp)_i - V_{123}^E(cal)_i)^2} \tag{15}$$

4. Discussion

Experimental data and fitted equations for the three binary systems are depicted in Fig. 1. V_m^E is the resultant contribution from several opposing effects. These may be divided arbitrarily into three types, namely physical, chemical, and structural. Physical contributions, that is, nonspecific interactions between the real species present in the mixture, contribute a positive term to V_m^E. The chemical or specific intermolecular interactions result in a volume decrease, and these include charge-transfer type forces and other complex–forming interactions. This effect contributes negative values to V_m^E. The structural contributions are mostly negative and arise from several effects, especially from interstitial accommodation and changes of free volume.

Excess molar volumes of *n*-butylamine + isobutanol is negative but for the other binary systems containing 1-chlorobutane + *n*-butylamine and 1-chlorobutane + isobutanol are positive over the whole range of mole fractions. Positive values would indicate that molecular interactions between different molecules are weaker than interactions between molecules in the same pure liquid and that repulsive forces dominate the behavior of the solutions. For 1-chlorobutane + *n*-butylamine and 1-chlorobutane + isobutanol, attractive interactions between unlike species decrease because of breaking H-bonding and repulsive interactions predominate, leading to positive excess molar volumes.

The negative V_m^E values arise due to dominance chemical interaction between constituent molecules, such as heteromolecular association through the formation of H-bond, known as strong specific interaction.

Experimental data for V_m^E for the ternary system are shown in Fig. 4 which also present ternary fitting curve for the Cibulka equation, which is the oldest of the fitting relations used in this work and has been extensively cited by other authors.

Ternary predictions using the Tsao–Smith [22], Jacob–Fitzner [23], Kohler [24] Rastogi [25], and Radojkovic [26] models show good agreement with experimental data for this system. Although this standard deviation is beyond experimental error, these models present the advantage of using exclusively binary data, which are more easily available from the literature.

4.1. PFP theory

The Prigogine–Flory–Patterson (PFP) theory has been commonly employed to analyze excess thermodynamic function. This theory has been used to interpreting the results of measurements of the excess properties of a number of binary systems formed by molecular species which differ in size and shape. Although in the development of the theory, hydrogen bonds and interactions of strong electrostatic nature are specifically excluded, a purely empirical application of the Flory formalism can still provide an interesting correlation between the excess volumes of more complex mixtures. In fact, and despite the ionic character of the IL systems, the use of Flory-type theories has proven successful in predicting and modeling both the excess properties and fluid-phase behavior of IL-containing mixtures [27,28]. The PFP theory considered a molecule to be made of up of equal segments (isometric portions), the effective number. Each segment has intermolecular contact sites capable of interacting with neighboring sites.

According to the PFP theory, V_m^E calculations include three contributions: (i) interactional, which is proportional to the (χ_{12}) parameters; (ii) the free volume contribution which arises from the dependence of the reduced volume upon the reduced temperature as a result of the difference between the degree of expansion of the two components and (iii) the (P^*) contribution, which depends both on the differences of internal pressures and differences of reduced volumes of the components. The V_m^E was calculated by means of the PFP theory using the following equation with the three contributions:

$$\frac{V^E}{x_1V_1^* + x_2V_2^*} = \frac{(\tilde{V}^{1/3}-1)\tilde{V}^{2/3}\Psi_1\theta_2\chi_{12}}{((4/3)\tilde{V}^{-1/3}-1)/P_1^*} - \frac{(\tilde{V}_1-\tilde{V}_2)^2((14/9)\tilde{V}^{-1/3}-1)\Psi_1\Psi_2}{((4/3)\tilde{V}^{-1/3}-1)\tilde{V}} + \frac{(\tilde{V}_1-\tilde{V}_2)(P_1^*-P_2^*)\Psi_1\Psi_2}{P_1^*\Psi_2 + P*2\Psi_1} \tag{16}$$

The $\tilde{V}$ of the solution is obtained through the Flory's theory. The characteristic parameters V^* and P^* are obtained from thermal expansion coefficient (α_p) and isothermal compressibility (β_T). The thermal expansion coefficient (α_i) is used to calculate the reduced volume by equation:

$$\tilde{V}_i = \left(\frac{1+(4/3)\alpha_i T}{1+\alpha_i T}\right)^3 \tag{17}$$

Here, the molecular contact energy fraction is calculated by:

$$\Psi_1 = \frac{\varphi_1 P_1^*}{\varphi_1 P_1^*} + \varphi_2 P_2^* \tag{18}$$

with the hard-core volume fractions defined by:

$$\varphi_1 = \frac{x_1 V_1^*}{x_1 V_1^*} + x_2 V_2^* \tag{19}$$

The values of pure parameters for the pure liquid components and the mixture are obtained by Flory theory. The parameters for the pure liquid components derived using Flory theory are in Tables 8 and 9.

Table 8
Parameters of pure components used in Flory theory at 298.15 K.

Component	P^* (J cm^{-3})	V^* (cm^3 mol^{-1})	T^* (K)
1-Chlorobutane	493.651	81.6193	4749.64
n-Butylamine	586.035	77.3138	4548.75
Isobutanol	436.253	72.1443	5296.04

The values of thermal expansion coefficient and isothermal compressibility for the pure components obtained from the literature. In order to obtain V_m^E, it is necessary to find the interactional parameter (χ_{12}) which was obtained by fitting the theory to experimental values of V_m^E for each one of the binary system. Table 9 presents the calculated equimolar values of the three contributions to V_m^E according to equation, together with the interactional parameter (χ_{12}). An analysis of each of the three contributions to V_m^E shows that, the interactional contribution is always positive in all binary mixtures and seems to be the most important to explain the V_m^E behavior for system studied. The free volume effect is negative and it seems to have little significance for the system studied. Fig. 5, showed the excess molar values predicted by PFP theory for binary systems.

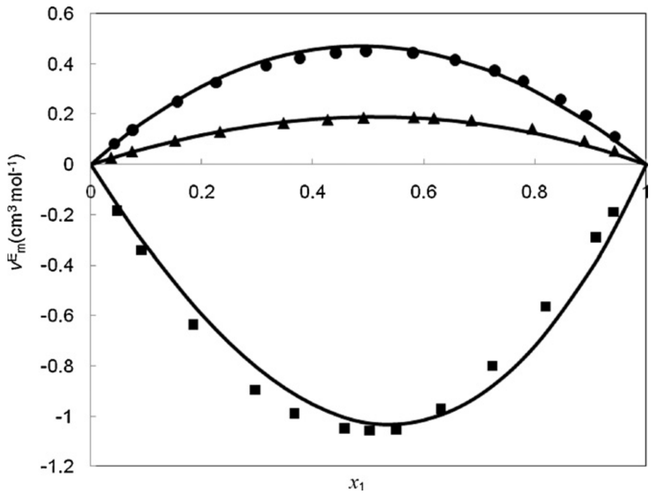

Fig. 5. Excess molar volumes at 298.15 K for the binary systems: (●) 1-chlorobutane (1) + *n*-butylamine (2), (▲) 1-chlorobutane (1) + isobutanol (3), (■) *n*-butylamine (2) + isobutanol (3). x_1 is the mole fraction of the first component in each binary. Full line calculated with PFP theory.

4.2. ERAS-Model

The ERAS-Model has been utilized to interpret quantitatively the thermodynamic properties of mixtures. ERAS-Model combines the linear-chain association model with Flory's equation of state.

We have also examined the ERAS-Model to analyze the present volumetric properties of three introduced binary systems at 298.15 K. The Extended Real Associated Solution for mixtures consisting of associating components (A, alkanol) and (B, amine), which can form cross-association complex (A_iB_j) provides a quantitative treatment which accounts for the competing effects present in the mixtures. The assumption made in frame of the ERAS-Model include the self-association of isobutanol, *n*-butylamine and polarity of chloroalkane according to the following reaction scheme:

$$A_m + A \xrightarrow{KA} A_{m+1} \tag{20}$$

$$B_n + B \xrightarrow{KB} B_{n+1} \tag{21}$$

where m or n are the degree of self-association, ranging from 1 to ∞. The cross-association between A and B molecules are represented by:

$$A_m + B_n \xrightarrow{KAB} A_mB_n \tag{22}$$

The association constants K_i ($i = A, B, AB$) are assumed to be independent of the chain length. Their temperature dependence is given by:

$$K_i = K_0 \exp\left[-\left(\frac{\Delta h_i^*}{R}\right)\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{23}$$

where K_0 is the equilibrium constant at the standard temperature T_0 (298.15 K), R the gas constant and Δh_i^* enthalpy for the reactions given by Eqs. (23)–(26), which corresponds to the hydrogen bonding energy. These reactions are also characterized by the volume change Δv_i^* related to the formation of the linear chains.

The essential property of the ERAS-Model is that the excess function V_m^E is split into a chemical and a physical contribution. The expression for V_m^E of the ERAS-Model extended to the two-block approach of cross-association are given by [29,30]:

$$V_c^E = \tilde{V}_M \left\{ x_AK_A\Delta v_A^*(\varphi_{A1} - \varphi_{A1}^0) + x_BK_B\Delta v_B^*(\varphi_{B1} - \varphi_{B1}^0) + x_AK_{AB}\Delta v_{AB}^* \times \frac{\varphi_{B1}(1 - K_A\varphi_{A1})}{(V_B/V_A)(1 - K_B\varphi_{B1}) + K_{AB}\varphi_{B1}} \right\} \tag{24}$$

$$V_p^E = (x_Av_A^* + x_Bv_B^*)(\tilde{V}_M - \varphi_A\tilde{V}_A - \varphi_B\tilde{V}_B) \tag{25}$$

$$V^E = V_p^E + V_c^E \tag{26}$$

where K_A and K_B are the equilibrium constants of chain self-association of alkanol and amine, respectively. K_{AB} and Δh_{AB}^* are the association constants and hydrogen bond energy from the cross-association. φ_{A1} and φ_{B1} are the hard-core volume fraction of the *n*-butylamine and isobutanol in the mixture, respectively. They have to be calculated numerically from the solution of the following coupled equations:

$$\varphi_A = \frac{\varphi_{A1}}{(1 - K_A\varphi_{A1})^2}\left[1 + \left(\frac{V_AK_{AB}\varphi_{B1}}{V_B(1 - K_B\varphi_{B1})}\right)\right] \tag{27}$$

$$\varphi_B = \frac{\varphi_{B1}}{(1 - K_B\varphi_{B1})^2}\left[1 + \left(\frac{K_{AB}\varphi_{A1}}{1 - K_A\varphi_{A1}}\right)\right] \tag{28}$$

Here φ_A and φ_B are the stoichiometric hard-core volume fractions of components.

The physical contribution X_p^E in ERAS-Model is derived from Flory's equation of state which is assumed to be valid not only for

Table 9
Calculated values of three contributions of the PFP theory to V_m^E for binary mixtures at 298.15 K.

System	$\chi_{1,2}$ (J cm^{-3})	Interactional	Free volume	P^*
1-Chlorobutane + *n*-butylamine	20.7	0.4104	−0.0129	538.146
1-Chlorobutane + isobutanol	8.4	0.1384	−0.0560	465.807
n-Butylamine + isobutanol	−70.2	−1.0744	−27.7956	483.734

Table 10
Properties and parameters of pure components used in the ERAS-Model.

Component	V (cm^3 mol^{-1})	$10^4 \times \beta$ (MPa^{-1})	K_A	V^* (cm^3 mol^{-1})	P^* (J cm^{-3})	Δh^* (kJ mol^{-1})	Δv^* (cm^3 mol^{-1})
1-Chlorobutane	105.11	12.038	1.20	81.62	495.39	−0.418	−2.24
n-Butylamine	99.56	11.450	5.27	76.08	591.13	−13.083	−3.68
Isobutanol	92.90	10.330	8.00	74.73	448.17	−23.250	−6.50

pure components but also for the mixture:

$$\frac{\tilde{P}_i\tilde{V}_i}{\tilde{T}_i} = \frac{\tilde{V}_i^{1/3}}{\tilde{V}_i^{1/3}-1} - \frac{1}{\tilde{V}_i\tilde{T}_i} \tag{29}$$

where $i = A, B, M$ (mixture). In Eq. (32), $\tilde{V}_i = V_i/V_i^*$; $\tilde{P}_i = P_i/P_i^*$; $\tilde{T}_i = T_i/T_i^*$; are the reduced volume, pressure, and temperature, respectively. All the reduction parameters V_i^*, P_i^*, T_i^* of pure components can be determined knowing the experimental data for molar volume V, thermal expansion coefficient α, isothermal compressibility κ_T, provided suitable association parameters K_i, Δv_i^*, Δh_i^* are known. The reduction parameters for the mixture P_M^*, T_M^* and V_M^* are calculated from mixing rules [9,31,32]:

$$P_M^* = \varphi_A P_A^* + \varphi_B P_B^* - X_{AB}\varphi_A\theta_B \tag{30}$$

$$T_M^* = \frac{P_M^*}{\varphi_A P_A^*/T_M^* + \varphi_B P_B^*/T_M^*} \tag{31}$$

$$V_M^* = x_A V_A^* + x_B V_B^* \tag{32}$$

X_{AB} is an interaction parameter characterizing the difference of dispersive intermolecular interaction between A and B. φ_i and θ_i are hard-core volume fraction and the surface fraction of the component i [33].

The mixture parameters appearing in the theoretical expression of excess molar volume are: X_{AB}, K_A, K_B, K_{AB}, Δh_A^*, Δh_B^*, Δh_{AB}^*, Δv_A^*, Δv_B^*, Δv_{AB}^*. All the parameters can be obtained by adjusting them to V_m^E of binary systems.

The properties and parameters as equilibrium constant K, thermal expansion coefficient α, isothermal compressibility κ_T, molar volume V, characteristic volume V^*, and characteristic pressure P^* for pure component are listed in Table 10 and the ERAS-Model parameters for binary mixture are listed in Table 11. The results of fitting experimental data with ERAS-Model are shown in Fig. 6.

The agreement between calculated and experimental V_m^E for all binary systems are very good.

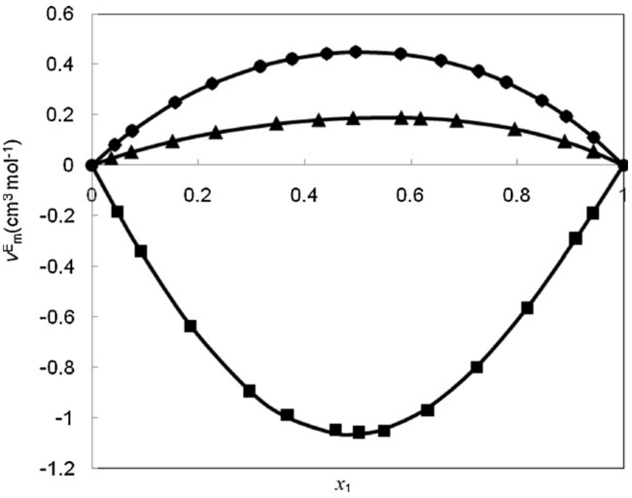

Fig. 6. Excess molar volumes at 298.15 K for the binary systems: (●) 1-chlorobutane (1) + *n*-butylamine (2), (▲) 1-chlorobutane (1) + isobutanol (3), (■) *n*-butylamine (2) + isobutanol (3). x_1 is the mole fraction of the first component in each binary. Full line calculated with ERAS-Model.

Table 11
ERAS-Model binary mixture parameters at 298.15 K.

System	$\chi_{1,2}$ (J cm^{-3})	K_{AE}	Δv^* (cm^3 mol^{-1})
1-Chlorobutane + *n*-butylamine	5.510	3.890	−0.0129
1-Chlorobutane + isobutanol	7.390	1.477	−0.0560
n-Butylamine + isobutanol	−128.699	0.079	−27.7956

5. Conclusions

Densities and excess molar volumes V_m^E of binary and ternary mixtures of 1-chlorobutane (1) + *n*-butylamine (2) + isobutanol (3) were measured at 298.15 K. The experimental V_m^E of binary systems were fitted by Redlich–Kister polynomial equation and about ternary system results were fitted by Cibulka equation and also predicted by many empirical expressions using data for the corresponding binary mixtures. The measured data and calculated values of all systems are in good accordance, and are theoretically and statistically satisfying. No data are available in the literature for the present systems for direct comparison with our results. Excess molar volumes for binary systems are described qualitatively by the PFP and ERAS-Models. The standard deviations between experiment and models are satisfactory for systems under study. The ERAS-Model parameter calculation is more complex, although suitable for the property representation, as can be observed in Fig. 3 which shows that the model is better to reproduce the experimental data.

Acknowledgment

The authors thank the University authorities for providing the necessary facilities to carry out the work.

References

[1] H. Iloukhani, B. Samiey, M.A. Moghaddasi, J. Chem. Thermodyn. 38 (2006) 190–200.
[2] H. Iloukhani, H.A. Zarei, J. Phys. Chem. Liquids 42 (2004) 75–79.
[3] H. Iloukhani, K. Khanlarzadeh, J. Chem. Eng. Data 51 (2006) 1226–1231.
[4] H. Iloukhani, M. Almasi, Thermochim. Acta 495 (2009) 139–148.
[5] J.M. Prausnitz, R.N. Lichtenthaler, E.G. Azevedo, Molecular Thermodynamic of Fluid Phase Equilib., 2nd ed., Prentice-Hall, 1986.
[6] B. Gonzalez, A. Dominguez, J. Tojo, J. Chem. Thermodyn. 35 (2003) 939–953.
[7] D. Patterson, G. Delmas, Discuss. Faraday Soc. 49 (1970) 98–105.
[8] I. Prigogine, The Molecular Theory of Solution, North Holland, Amsterdam, 1957.
[9] P.J. Flory, J. Am. Chem. Soc. 87 (1965) 1833–1838.
[10] A. Heintz, Ber. Bunsenges. Phys. Chem. 89 (1985) 172–182.
[11] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents, Physical Properties and Methods of Purification, 4th ed., John Wiley & Sons, New York, 1986.
[12] H. Artigas, J. Santafe, M.C. Lopez, F.M. Royo, J.S. Urieta, J. Chem. Thermodyn. 25 (1993) 1403–1407.
[13] M. Dominguez, S. Rodriguez, M.C. Lopez, F.M. Royo, J.S. Urieta, J. Chem. Eng. Data 41 (1996) 37–42.
[14] A. Anson, R. Garriga, S. Martinez, P. Perez, M. Gracia, J. Chem. Eng. Data 50 (2005) 677–682.
[15] F. Davolio, C.R. Schaefer, M.F. Ruitz, M. Katz, J. Solut. Chem. 19 (1990) 1085–1094.
[16] C. Lafuente, J. Pardo, J. Santafe, F.M. Royo, J.S. Urieta, J. Chem. Thermodyn. 27 (1995) 541–549.
[17] O.J. Redlich, A.T. Kister, Ind. Eng. Chem. 40 (1948) 345–348.
[18] R.C. Weast, CRC Handbook of Chemistry and Physics, 58th ed., CRC, 1978.
[19] M.I. Davis, G. Douheret, J. Chem. Soc. Rev. 22 (1983) 127–134.
[20] F. Qi, H. Wang, J. Chem. Thermodyn. 41 (2003) 265–272.
[21] Y. Cibulka, Collect Czech. Commun. 47 (1982) 1414–1419.
[22] C.C. Tsao, J.M. Smith, Chem. Eng. Progr. Symp. 7 (1953) 107–117.

[23] K.T. Jacob, K. Fitzner, Thermochim. Acta 18 (1977) 197–206.
[24] F. Kohler, Monatsh. Chem. 91 (1960) 738–740.
[25] R.P. Rastogi, J. Nath, S.S. Das, J. Chem. Eng. Data 22 (1977) 249–252.
[26] N. Radojkovic, A. Tasic, D. Grozdanic, B. Djorjevic, M. Malic, J. Chem. Thermodyn. 9 (1977) 349–355.
[27] L.P.N. Rebelo, V. Najdanovic-Visak, Z.P. Visak, M. Nunes da Ponte, J. Szydlowski, C.A. Cerdeirina, J. Troncoso, L. Romani, J.M.S.S. Esperancu, H.J.R. Guedes, H.C. de Sousa, Green Chem. 6 (2004) 369–381.
[28] J.N. Canongia Lopes, T.C. Cordeiro, J.M.S.S. Esperancu, H.J.R. Esperancu, L. Guedes, P. Rebelo, N.K.R. Seddon, J. Phys. Chem. B 109 (2005) 3519–3525.
[29] H. Funke, M. Wetzel, A. Heintz, Pure Appl. Chem. 61 (1989) 1429–1439.
[30] A. Heintz, D. Papaioannou, Thermochim. Acta 310 (1998) 69–76.
[31] P.J. Flory, R.A. Orwoll, A. Vrij, J. Am. Chem. Soc. 86 (1964) 3507–3514.
[32] J.A. Gonzalez, I. Garcia de la Fuente, J.C. Cobos, Fluid Phase Equilib. 168 (2000) 31–58.
[33] A. Bondi, Physical Properties of Molecular Crystals, Liquids, and Glasses, Wiley, New York, 1968.