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Volumetric properties of {*n*-butyl acetate + 1-butanol + 1,2-butanediol} at temperature between [298.15 ,303.15 and 308.15] K.

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Abstract

Densities and excess molar volume of the binary and ternary mixtures formed by *n*-butylacetate + 1-butanol + 1,2-butanediol were measured at (298.15, 303.15, and 308.15) K for the liquid region and at ambient pressure (81.5) k Pa , for the whole composition range. The excess molar volumes, V_m^E and excess partial molar volume V_i^E ,were calculated from experimental densities.The excess molar volumes are positive over the mole fraction rage for binary mixtures of *n*-butylacetate (1) + 1-butanol (2) and *n*-butylacetate (2) + 1,2-butanediol (3) and increase with increasing temperatures from (298.15 to 308.15)K. The excess molar volumes of 1-butanol (1) + 1,2-butanediol (3) are negative and decrease with increasing temperatures from (298.15 to 308.15)K..The experimental data of constitute were correlated as a function of the mole fraction by using the Redlich–Kister equation for binary and , Cibulka, Jasinski and Malanowski , Singe *et al*, Pintos *et al* , Calvo *et al*, Kohler, and Jacob - Fitzner for ternary mixture ,respectively. The experimental data of the constitute binaries are analyzed to discuss the nature and strength of intermolecular interactions in these mixtures.

Keywords: Excess molar volume; *n*-butylacetate; 1-butanol; 1,2-butanediol; Molecular interactions.

1. Introduction

This paper is a continuation of our earlier work related to the study of thermodynamic properties of binary and ternary mixtures [1–4]. Multicomponent liquid mixtures have attracted the attention of researchers in the past decades. Physical properties are very important factors in chemical and engineering processes because of their influence upon the effectiveness of the operations. Mass and heat transfer processes and flow operations are evident examples of the importance of the knowledge of these properties [5, 6]. It is well-known that the knowledge of the dependence of dynamic viscosity on both temperature and composition of the system is needed for many engineering processes and the study of fluid phenomena. There are several

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predictive equations [7] for estimating thermodynamic properties of multicomponent systems. Geometrical solution models are considered to predict excess molar volumes and deviations of the density and viscosity for the ternary mixture from binary contribution because of dependence of interactions in ternary systems on the interaction in binary systems [8–11]. Recently, new models have been developed for the prediction of densities and viscosities of mixtures. Some of them are based on the group contribution concept [12, 13] and others are based on the molecular approach that requires binary interaction parameters for each binary system present in the multicomponent mixture [14, 15]. Such methods are rarely used for viscosity because some of them cannot be immediately extensible to multicomponent mixtures or they may require moreparameters (such as three- and four-body interaction terms) for mixtures containing more than two components or require binary interaction parameters for each binary system present in the multicomponent mixture.

Here, we have measured densities (ρ), for the binary systems formed by *n*-butylacetate + 1-butanl, + 1,2-butanediol, and 1-butanol + 1,2-butanediol and ternary system *n*-butylacetate + 1-butanol + 1,2-butanediol at (298.15, 303.15, and 308.15) K for the liquid region and at ambient pressure for the whole composition range. Hence, for the later binary mixture the only densities were determined. The derived properties (excess molar volumes $V_{\mathrm{m}}^{\mathrm{E}}$, and excess molar volume $V_{\mathrm{i}}^{\mathrm{E}}$,in combination with other mixing properties, provide valuable information for qualitatively analyzing the molecular interactions between molecules. The excess molar volumes of binary mixtures have been fitted to the Redlich–Kister [16] and ternary mixture has been fitted to the Cibulka [17], Jasinski and Malanowski [17], Singe *et al*. [17], Pintos *et al*. [17], Calvo *et al*. [17], Kohler [17], and Jacob- Fitzner [17], equations to determine the coefficients.

2. Experimental

2.1. *Materials*

n-Butylacetate, 1-butanol and 1,2-butanediol were high purity grade reagents from Merck. The purity of reagents is summarized in Table 1. It was checked by comparing the measured densities and refractive indices of the compounds with those reported in the literature [18-25], showing a good agreement. Their values are also shown in Table 1. No further purification was attempted owing to their high purity grade.

Table 1
Purity grades, densities, ρ, refractive indices, n_{D} of the pure components at different temperatures and ambient pressure (81.5 mPa).

Component	Purity		ρ/g ·cm^{-3}		$n_{\mathbf{D}}$	
	(mass fraction)	T/*K*	Experimental	Literature	Experimental	Literature
n-butylacetate	99.5%	298.15	0.87636	0.87636[18]	1.3921	1.39191[19]
		303.15	0.87133	0.87134[20]		
		308.15	0.86604	0.86622[21]		
1-butanol	99.5%	298.15	0.80573	0.80575[18]	1.3976	1.3974[24]
		303.15	0.80218	0.80190[22]		
		308.15	0.79855	0.79827[22]		
1,2-butanediol	99.5%	298.15	0.99881	0.99887[23]	1.4381	1.4382[23]
		303.15	0.99526	0.99531[23]		
		308.15	0.99139	0.99143[23]		

2.2. *Apparatus and procedures*

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 uncertainties were estimated to be within $\pm 1 \cdot 10^{-5}$ 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 stopered 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. 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 $\pm 2 \cdot 10^{-4}$.

Refractive indices were measured at 298.15 K to 308.15 K using a thermostated Abbe´ refractometer. Water was circulated into the prism of the refractometer by acirculation pump connected to an external thermostated water bath. The uncertainty of the refractive index is on the order of (0.0002) units, and for the temperature, it was (0.01 K).

3. Results and discussion

The excess molar volumes, V^{E}, of the binary and ternary mixtures were calculated from the densities using the following equation:

$$V_{\mathrm{m}}^{\mathrm{E}}\ (\mathbf{cm^3 \cdot mol^{-1}}) = \sum_{i=1}^{n} \frac{x_i M_i}{\rho} - \sum_{i=1}^{n} \frac{x_i M_i}{\rho_i} \qquad \textbf{(1)}$$

where ρ is the density of the mixture and x_i, ρ_i, and M_i are the mole fraction, density and molecular weight of pure component *i*, respectively. Tables 2 shows that the densities , excess molar volumes V^{E},and excess partial molar volumes $V_{\mathrm{i}}^{\mathrm{E}}$, for the binary mixtures of *n*-butylacetate (1) + 1-butanol (2) , *n*-butylacetate (1) + 1,2-butanediol (3) and 1-butanol (2) + 1,2-butanediol (3) at (298.15, 303.15, and 308.15) K and graphically represented in Fig. 1.

Table 2

Densities, excess molar volumes, and excess partial molar volumes for the binary mixtures of *x* *n*-butylacetate + (1-*x*)1-butanol, *x* *n*-butylacetate + (1-*x*) 1,2-butanediol and *x* 1-butanol + (1-*x*) 1,2-butanediol at 298.15 K to 308.15 K and atmospheric pressure.

x_1	ρ / g cm $^{-3}$	V_m^E / cm ^{3} mol $^{-1}$	/ cm ^{3} mol $^{-1}$ V_1^E	/ cm ^{3} mol $^{-1}$ V_2^E
	x n-butylacetate +(1-*x*) 1-butanol *T*=298.15 *K*			
0.0496	0.81035	0.037	0.709	0.003
0.0994	0.81481	0.072	0.588	0.013
0.1500	0.81925	0.095	0.479	0.028
0.2003	0.82350	0.116	0.389	0.048
0.3002	0.83158	0.141	0.265	0.088
0.3501	0.83542	0.149	0.228	0.106
0.3978	0.83898	0.153	0.203	0.121
0.4980	0.84609	0.159	0.171	0.147
0.5501	0.84960	0.159	0.157	0.162
0.5993	0.85282	0.158	0.142	0.181
0.6997	0.85909	0.149	0.104	0.254
0.7984	0.86495	0.126	0.058	0.396
0.8997	0.87076	0.078	0.016	0.633
	x n-butylacetate +(1-*x*) 1-butanol *T*=303.15 *K*			
0.0496	0.80673	0.034	0.757	-0.002
0.0994	0.81107	0.072	0.708	0.000
0.1500	0.81535	0.103	0.630	0.011
0.2003	0.81945	0.132	0.533	0.032
0.3002	0.82725	0.172	0.360	0.089
0.3501	0.83100	0.181	0.299	0.118
0.3978	0.83446	0.189	0.258	0.143
0.4980	0.84142	0.195	0.204	0.187
0.5501	0.84487	0.194	0.182	0.210
0.5993	0.84803	0.192	0.160	0.240
0.6997	0.85421	0.178	0.104	0.347
0.7984	0.86005	0.140	0.043	0.529
0.8997	0.86582	0.079	0.004	0.743
	x n-butylacetate +(1-*x*) 1-butanol *T*=308.15 *K*			
0.0496	0.80290	0.045	0.941	0.001
0.0994	0.80704	0.095	0.844	0.009
0.1500	0.81120	0.129	0.709	0.028
0.2003	0.81518	0.161	0.572	0.057
0.3002	0.82284	0.196	0.362	0.126
0.3501	0.82650	0.206	0.297	0.158
0.3978	0.82990	0.212	0.256	0.181
0.4980	0.83672	0.215	0.215	0.215

Table 2 Continued

x_1	ρ / g cm $^{-3}$	V_m^E / cm ^{3} mol $^{-1}$	/ cm ^{3} mol $^{-1}$ V_1^E	/ cm ^{3} mol $^{-1}$ V_2^E
		x 1-butanol +(1-x) 1,2-butanediol T=303.15 K		
0.0496	0.98580	-0.047	-0.764	-0.007
0.1008	0.97608	-0.077	-0.554	-0.024
0.1502	0.96663	-0.097	-0.410	-0.044
0.1999	0.95708	-0.113	-0.311	-0.065
0.2965	0.93842	-0.131	-0.209	-0.097
0.3498	0.92812	-0.136	-0.184	-0.109
0.4005	0.91831	-0.139	-0.171	-0.117
0.4499	0.90876	-0.141	-0.162	-0.123
0.4996	0.89918	-0.142	-0.153	-0.132
0.5499	0.88949	-0.143	-0.140	-0.146
0.5998	0.87985	-0.140	-0.124	-0.167
0.6504	0.87010	-0.137	-0.105	-0.200
0.6994	0.86066	-0.132	-0.083	-0.245
0.7499	0.85092	-0.123	-0.060	-0.306
0.7994	0.84132	-0.108	-0.039	-0.379
0.8494	0.83162	-0.088	-0.021	-0.463
0.8999	0.82177	-0.061	-0.008	-0.551
		x 1-butanol +(1-x) 1,2-butanediol T=308.15 K		
0.0496	0.98215	-0.047	-0.727	-0.006
0.1008	0.97241	-0.077	-0.545	-0.020
0.1502	0.96296	-0.099	-0.413	-0.039
0.1999	0.95339	-0.114	-0.317	-0.059
0.2965	0.93474	-0.135	-0.208	-0.094
0.3498	0.92447	-0.143	-0.177	-0.109
0.4005	0.91467	-0.148	-0.158	-0.120
0.4499	0.90512	-0.151	-0.145	-0.130
0.4996	0.89553	-0.152	-0.135	-0.139
0.5499	0.88582	-0.151	-0.123	-0.152
0.5998	0.87618	-0.149	-0.110	-0.170
0.6504	0.86642	-0.145	-0.094	-0.196
0.6994	0.85698	-0.140	-0.077	-0.233
0.7499	0.84724	-0.131	-0.058	-0.283
0.7994	0.83764	-0.116	-0.039	-0.346
0.8494	0.82792	-0.094	-0.023	-0.424
0.230	0.200	0.214	0.84009	0.5501
0.253	0.184	0.211	0.84318	0.5993
0.352	0.132	0.197	0.84921	0.6997
0.555	0.065	0.165	0.85488	0.7984
0.849	0.013	0.096	0.86057	0.8997
		x 1-butanol +(1-x) 1,2-butanediol T=298.15 K		
-0.006	-0.727	-0.041	0.98951	0.0496
-0.020	-0.545	-0.074	0.97981	0.1008
-0.039	-0.413	-0.095	0.97036	0.1502
-0.059	-0.317	-0.111	0.96079	0.1999
-0.094	-0.208	-0.127	0.94209	0.2965
-0.109	-0.177	-0.132	0.93178	0.3498
-0.120	-0.158	-0.136	0.92196	0.4005
-0.130	-0.145	-0.138	0.91239	0.4499
-0.139	-0.135	-0.138	0.90278	0.4996
-0.152	-0.123	-0.136	0.89305	0.5499
-0.170	-0.110	-0.133	0.88339	0.5998
-0.196	-0.094	-0.128	0.87361	0.6504
-0.233	-0.077	-0.124	0.86416	0.6994

Table 2 Continued

x_1	ρ / g cm $^{-3}$	V_m^E / cm ^{3} mol $^{-1}$	/ cm ^{3} mol $^{-1}$ V_1^E	/ cm ^{3} mol $^{-1}$ V_2^E
	x n-butylacetate +(1-*x*) 1,2-butanediol *T*=298.15 *K*			
0.0496	0.98880	0.121	2.244	0.011
0.0996	0.97935	0.225	1.866	0.041
0.1513	0.97032	0.306	1.533	0.089
0.1995	0.96240	0.368	1.274	0.144
0.3000	0.94732	0.454	0.872	0.276
0.4000	0.93389	0.497	0.611	0.415
0.4917	0.92283	0.494	0.446	0.547
0.5995	0.91095	0.468	0.297	0.726
0.7000	0.90092	0.412	0.179	0.945
0.7997	0.89195	0.312	0.083	1.237
0.8978	0.88392	0.181	0.020	1.587
	x n-butylacetate +(1-*x*) 1,2-butanediol *T*=303.15 *K*			
0.0496	0.98518	0.117	2.475	0.006
0.0996	0.97530	0.252	2.194	0.029
0.1513	0.96600	0.350	1.875	0.075
0.1995	0.95790	0.422	1.584	0.136
0.3000	0.94242	0.536	1.070	0.306
0.4000	0.92885	0.581	0.711	0.498
0.4917	0.91765	0.583	0.487	0.677
0.5995	0.90575	0.544	0.300	0.901
0.7000	0.89582	0.462	0.163	1.156
0.7997	0.88694	0.336	0.060	1.465
0.8978	0.87892	0.189	0.007	1.755
	x n-butylacetate +(1-*x*) 1,2-butanediol *T*=308.15 *K*			
0.0496	0.98075	0.160	2.967	0.016
0.0996	0.97079	0.295	2.432	0.058
0.1513	0.96128	0.405	1.974	0.124
0.1995	0.95307	0.482	1.626	0.198
0.3000	0.93750	0.591	1.094	0.372
0.4000	0.92385	0.630	0.749	0.556
0.4917	0.91255	0.631	0.524	0.737
0.5995	0.90056	0.589	0.317	0.986
0.7000	0.89062	0.494	0.162	1.273
0.7997	0.88170	0.360	0.053	1.597
0.8978	0.87370	0.196	0.004	1.864

The average uncertainty in the excess molar volume is estimated to ± 6 $\cdot 10^{-3}$ cm^3 $\cdot$ mol^{-1} . Each set of results were fitted using Redlich–Kister expression for the binary mixtures as follows:

$$Y = x_i x_j \sum_{p=0}^{4} \left(\sum_{q=0}^{2} A_{pq} T^q \right) (x_i - x_j)^p \qquad (2)$$

where $Y \equiv (V_m^E)$, x_i and x_j are the mole fraction; A_{pq} are the temperature independent parameters for the binary mixtures; and T is the absolute temperature. These parameters were obtained by the unweighted least-squares method. The parameters A_{pq} for all the binary mixtures are listed in Table 3. The excess molar volumes for the ternary mixture were fittd to the temperature-dependet Cibulka equation:

$$Y_{ijk}^{E} = Y_{m,bin}^{E} + x_1x_2x_3(B_0 + B_1x_1 + B_2x_2) \quad (3)$$

Jasinski and Malonowski equation:

$$Y_{ijk}^{E} = Y_{m,bin}^{E} + x_1x_2x_3(B_0 + B_1(2x_1 - 1) + B_2(2x_1 - 1)^2) \quad (4)$$

Singe *et al* equation:

$$Y_{ijk}^{E} = Y_{m,bin}^{E} + x_1x_2x_3(B_0 + B_1x_1(x_2 - x_3) + B_2x_1^2(x_2 - x_3)^2) \quad (5)$$

Pintos *et al* equation:

$$Y_{ijk}^{E} = Y_{m,bin}^{E} + x_1x_2x_3(B_0 + B_1(x_1^2 + 2x_1x_2 - 1) + B_2(x_1^2 + 2x_1x_2 - 1)^2) \quad (6)$$

Calvo *et al* equation:

$$Y_{ijk}^{E} = Y_{m,bin}^{E} + x_1x_2x_3(B_0 + B_1(2x_1 + 2x_2 - 1) + B_2(2x_1 + 2x_2 - 1)^2) \quad (7)$$

where $Y_{m,bin}^{E}$ are the contributions of binary mixture *i,j*.

$$Y_{m,bin}^{E} = Y_{m,12}^{E} + Y_{m,13,}^{E} + Y_{m,23}^{E}$$

Every B_i ternary parameter is a function of temperature as expressed in Eq. 4-7.

$$B_i = \sum_{q=0}^{2} C_{iq}T^q \quad (8)$$

Table 3
Values of parameters A_{pq}, of Eq. (2) and standard deviations, σ, for binary Systems at T = (298.15, 303.15 and 308.15 K).

	p					$\sigma(V_m^E/\mathrm{cm^3mol^{-1}})$
q	0	1	2	3	4	
	{*n*-butylacetate (1) + 1-butanol(2) }					
0	-130.056	0.84082	-0.0013	29.6942	-0.2009	0.001
1	0.00034	426.867	-2.8349	0.0047	21.4267	
2	-0.13791	0.0002	598.642	-3.9195	0.0064	
	{*n*-butylacetate (1) + 1,2-butanediol (2) }					
0	-288.696	1.8665	-0.003	-265.684	1.7313	0.004
1	-0.0028	333.913	-2.195	0.00361101	902.753	
2	-5.9821	0.00991	972.418	-6.4119	0.0106	
	{1-butanol (1) + 1,2-butanediol(2) }					
0	77.0491	-0.5121	0.00084	-184.92	1.22026	0.0012
1	-0.00201	90.4656	-0.5992	0.00098	354.682	
2	-2.3414	0.0039	-35.6407	0.2355	-0.0004	

Table 4 shows that the densities, excess molar volumes V^E, for the ternary mixtures of *n*-butylacetate (1) + 1-butanol (2) + 1,2-butanediol (3) at (298.15, 303.15 and 308.15 K). The parameters C_{iq} for the ternary mixture are listed in Table 5a, along with the standard deviation σ.

Table 4

Densities (ρ) ,excess molar volumes ,(V_m^E), for ternary mixtures *n*-butylacetate (1) + 1-butanol (2) + 1,2-butanediol (3) at different temperatures of (298.15 to 308.15 K).

x_1	x_2	ρ(g ·cm^{-3})			V_m^E (cm^3 · mol^{-1})		
		298.15 K	**303.15** K	**308.15** K	**298.15** K	**303.15** K	**308.15** K
0.0667	0.1037	0.96689	0.96279	0.95880	0.053	0.078	0.089
0.0647	0.2075	0.94761	0.94351	0.93952	0.044	0.072	0.083
0.0687	0.3105	0.92766	0.92355	0.91955	0.039	0.070	0.081
0.0670	0.4139	0.90853	0.90450	0.90051	0.033	0.060	0.069
0.0658	0.5190	0.88909	0.88507	0.88111	0.022	0.053	0.059
0.0657	0.6221	0.86965	0.86625	0.86225	0.046	0.013	0.025
0.0672	0.7255	0.85072	0.84702	0.84312	-0.005	-0.001	0.000
0.0660	0.8304	0.83154	0.82783	0.82385	-0.019	-0.010	0.001
0.1384	0.1069	0.95499	0.95088	0.94674	0.077	0.090	0.100
0.1373	0.2151	0.93541	0.93137	0.92731	0.069	0.078	0.080
0.1375	0.3222	0.91605	0.91205	0.90789	0.044	0.052	0.064
0.1381	0.4299	0.89634	0.89240	0.88821	0.051	0.057	0.072
0.1377	0.5376	0.87712	0.87312	0.86882	0.023	0.039	0.068
0.1368	0.6464	0.85778	0.85398	0.84994	-0.001	-0.002	-0.002
0.1418	0.7508	0.83856	0.83476	0.83072	-0.005	-0.003	-0.002
0.2079	0.1226	0.94225	0.93792	0.93362	0.066	0.090	0.102
0.2141	0.2237	0.92365	0.91935	0.91505	0.047	0.070	0.082
0.2145	0.3367	0.90361	0.89952	0.89522	0.055	0.060	0.071
0.2143	0.4492	0.88401	0.87995	0.87565	0.038	0.044	0.057
0.2146	0.5607	0.86473	0.86073	0.85662	0.006	0.009	0.001
0.2150	0.6721	0.84535	0.84141	0.83722	-0.003	-0.001	0.001
0.2959	0.1186	0.93121	0.92691	0.92241	0.055	0.061	0.077
0.2985	0.2329	0.91179	0.90753	0.90311	0.005	0.010	0.017
0.2984	0.3506	0.89185	0.88760	0.88322	-0.002	0.006	0.010
0.3338	0.4282	0.87440	0.87040	0.86561	0.061	0.038	0.087
0.2981	0.5850	0.85213	0.84801	0.84351	0.008	0.013	0.036
0.3903	0.1222	0.91889	0.91440	0.90981	0.047	0.059	0.068
0.3892	0.2434	0.89891	0.89450	0.88991	0.069	0.078	0.089
0.3915	0.3643	0.87916	0.87480	0.87011	0.035	0.043	0.068
0.3895	0.4886	0.85936	0.85510	0.85061	0.001	0.003	0.006
0.4856	0.1304	0.90703	0.90250	0.89782	-0.010	-0.007	-0.005
0.4892	0.2546	0.88702	0.88252	0.87782	-0.013	-0.009	-0.003
0.4892	0.3822	0.86696	0.86250	0.85779	-0.017	-0.010	0.001
0.5806	0.1395	0.89556	0.89090	0.88605	-0.025	-0.020	-0.012
0.5989	0.2663	0.87458	0.86988	0.86499	-0.039	-0.023	-0.010
0.7178	0.1408	0.88179	0.87702	0.87202	-0.009	-0.007	-0.001

Other equations introduce ternary fitting parameters. Jocob and Fitzner suggested an equation for estimating the properties of a ternary system, base on binary data at compositions near ternary composition using the fllowing from for excess molar volumes:

$$Y_{123}^{E} = \frac{x_1 x_2 Y_{12}^{E}}{(x_1 + x_2/2)(x_2 + x_1/2)} + \frac{x_1 x_3 Y_{13}^{E}}{(x_1 + x_2/2)(x_3 + x_2/2)} + \frac{x_2 x_3 Y_{23}^{E}}{(x_2 + x_1/2)(x_3 + x_1/2)} \qquad (9)$$

So that, for binary systems at compositions x_i^-, x_j^- we have $x_i - x_j = x_i^- - x_j^-$.

Kohler proposed an equation for ternary system of the from

$$Y_{123} = (x_1 + x_2)^2 Y_{12}^{E} + (x_1 + x_2)^2 Y_{13}^{E} + (x_2 + x_3)^2 Y_{23}^{E} \quad (10)$$

Kohler, s equation is symmetrical in that all three binary systems are treated indentically.In this equation, Y_{ij}^{E} refer to the excess molar volumes at x_i^-, x_j^- in the binary mixtures with $x_i^- = 1 - x_j^-$ $= x_i/(x_i + x_j)$.

These equations give predications of V^E for a ternary system from experimental data on the binary systems alone. For composition with the experimental values for the ternary system. In each case, the optimum number of coefficients was ascertained from an examination of the variation of standard deviation $\sigma(Y)$ with

$$\sigma(Y) = \left[\sum \left(Y_{\text{mexp.,i}}^{E} - Y_{\text{m cal.,i}}^{E} \right)^2 \Big/ (n - p) \right]^{1/2} \quad (11)$$

where n and p are the number of experimental points and number of parameters retained in the respective equation. Standard deviation for equations (9), (10) in Table 5b.

Table 5a
Coeffiients C_{iq} of Eq (8) and standard deviations for the fits of the ternary excess molar volumes in the temperatures range (298.15, 303.15, and 308.15) K.

Cibulka equation		i			$\sigma(V_m^E)$	
q		0	1	2		
		n-butylacetate (1)+ 1-butanol (2) + 1,2-butanediol (3) }				{
	0	2205.52	-14.2485	0.02285	0.1261	
	1	-2585.15	16.6255	-0.0265		
	2	-5.7289	0.03903	-0.00007		
Jasinski equation					$\sigma(V_m^E)$	
		n-butylacetate (1)+ 1-butanol (2) + 1,2-butanediol (3) }				{
	0	840.587	-5.4464	0.0088	0.1172	
	1	-2901.79	19.1822	-0.0318		
	2	-2545.92	17.2028	-0.0294		
Singe equation					$\sigma(V_m^E)$	
		n-butylacetate (1)+ 1-butanol (2) + 1,2-butanediol (3) }				{
	0	1698.66	-11.0183	0.0177445	0.2013	
	1	6427.39	-42.3681	0.0695		
	2	-1356.96	8.9119	-0.01458		
Calvo equation					$\sigma(V_m^E)$	
		n-butylacetate (1)+ 1-butanol (2) + 1,2-butanediol (3) }				{
	0	1306.2	-8.41406	0.0134	0.2147	
	1	3038.72	-20.2239	0.0337		
	2	-4622.7	30.6564	-0.0509		
Pintos equation					$\sigma(V_m^E)$	
		n-butylacetate (1)+ 1-butanol (2) + 1,2-butanediol (3) }				{
	0	-399.12	2.66669	-0.0045	0.1581	
	1	-3831.74	25.1655	-0.0414		
	2	-40.8581	0.2726	-0.00046		

The excess molar volumes V_m^E, for *n*-butylacetate + 1-butanol and *n*-butylacetate + 1,2-butanediol are positive and become more positive when temperature increases. The excess molar volumes of (1-butanol + 1,2-butanediol) are negative and decrease with increasing temperatures from (298.15 to 308.15)K. The negative values of excess molar volume also mean

that the mixture is less compressible than the corresponding ideal mixture, graphically represented in Fig. 1.

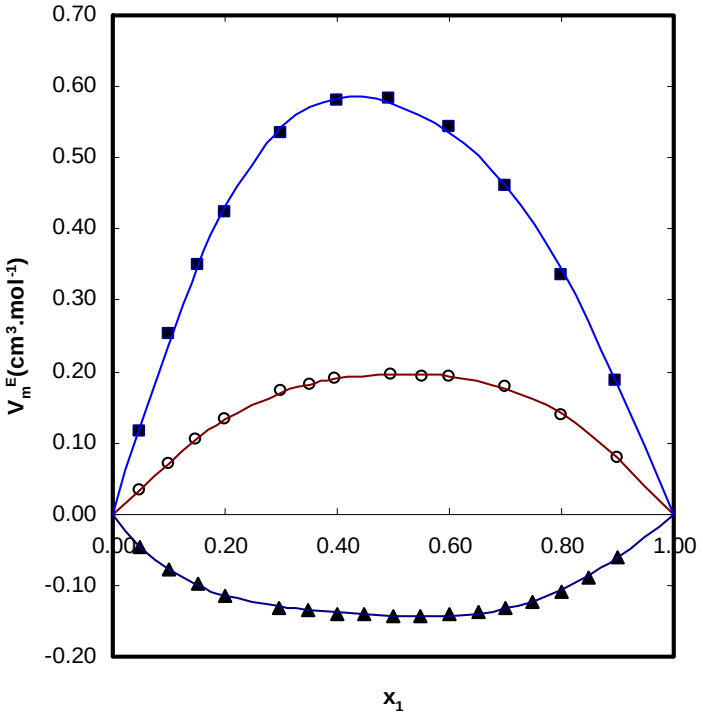

Fig. 1. Excess molar volumes (V_m^E) for {(▲) 1-butanol (1) + 1,2-butanediol (2), (■) *n*-butylacetate (1) + 1,2-butanediol (2), (○) *n*-butylacetate (1) + 1-butanol (2) }at T =303.15 K . The solid curves were calculated from parameters of Eq. (2) given in Table 2.

Table 5b
Standard deviations for the fits of the ternary excess molar volumes in the temperatures range (298.15, 303.15, and 308.15) K.

	Eq (10)	Eq (9)
$\sigma(V_m^E)$	0.2542	0.1769

The excess partial molar volumes (V_i^E) for these mixtures can be determined from excess molar volume data using [24].

$$V_i^E = V_m^E + (1 - x_i)(\frac{\partial V_m^E}{\partial x_i})_{x_j,p,T} \qquad (12)$$

$(\frac{\partial V_m^E}{\partial x_i})_{x_j,p,T}$ were calculated from Eq. (2) using the parameters in Table 3. The excess partial molar volumes (V_i^E) are given in Tables 2 and are graphically represented in Fig. 2.

4. Conclusions

The excess molar volumes are a function of molecular interactions and the size and shape of molecules. Hence, it has been pointed out in the literature that the value of excess molar volumes of multicomponent systems can constitute a reliable criterion for assessing or for excluding the presence of interactions of any kind between dissimilar molecules.

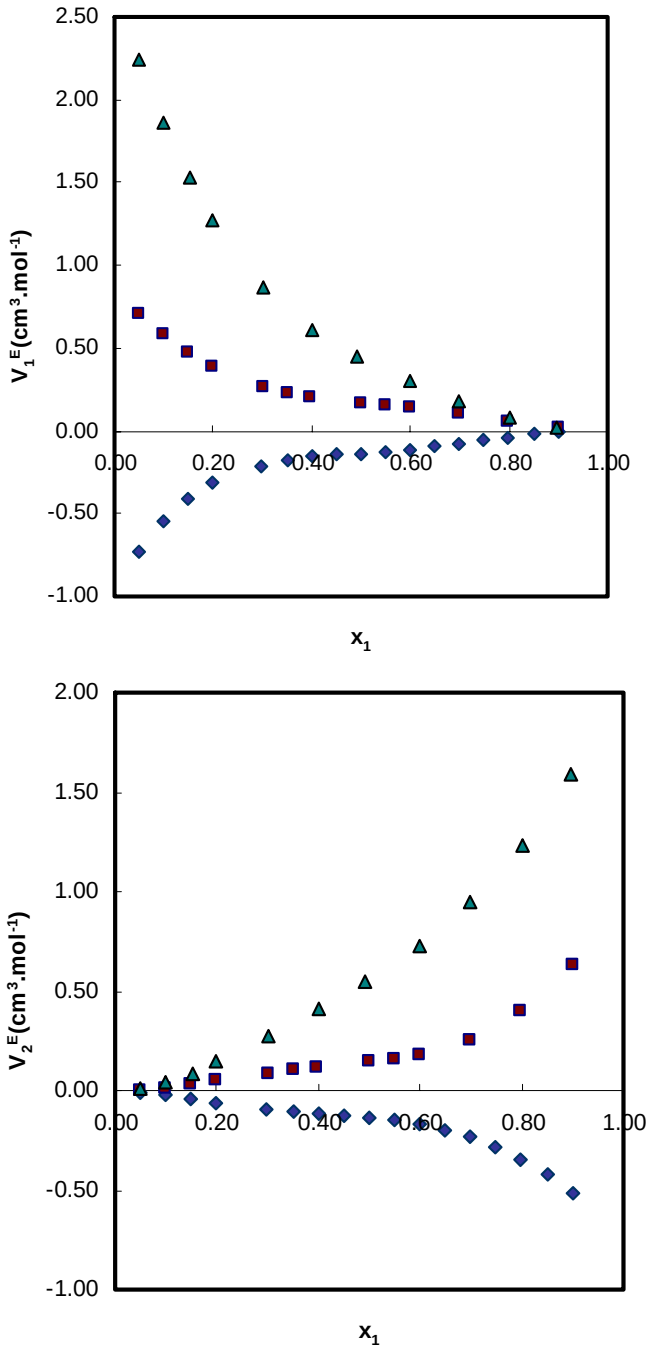

Fig. 2. Plot of :(a),(b) Excess partial molar volumes ,against mole fraction for {(▲) *n*-butylacetate (1) +1,2-butanediol (2), (■) *n*-butylacetate (1)+ 1-butanol (2), (◆)1-butanol (1)+ 1,2-butanediol (2)} at$T$ =303.15 K.Solid curevs represent the values calculated from Eq.(12) in Table (2).

Therefore, the magnitude of these deviations from ideality of the system that can be negative, positive, or zero may be explained as a balance between positive contributions (hydrogen bond rupture and dispersive interactions between unlike molecules) and negative contributions (intermolecular dipolar interactions and geometrical fitting between components) [26-28].

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