Thermochimica Acta 496 (2009) 71–86

Contents lists available at ScienceDirect

Thermochimica Acta

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

Experimental determination and modelling of densities and excess molar volumes of ternary system (1-butanol + cyclohexylamine + n-heptane) and corresponding binaries from 288.15 to 323.15 K

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ARTICLE INFO

Article history:
Received 23 April 2009
Received in revised form 7 July 2009
Accepted 8 July 2009
Available online 16 July 2009

Keywords:
Excess molar volume
Ternary system
1-Butanol
Cyclohexylamine
Modelling

ABSTRACT

Experimental densities ρ and excess molar volumes V^E of one ternary and three binary systems containing 1-butanol, cyclohexylamine and n-heptane at temperatures from 283.15 to 323.15 K are reported. Density measurements were performed by an Anton Paar DMA 5000 vibrating tube densimeter. The obtained V^E of binary systems were fitted to the Redlich–Kister equation, and to the Nagata–Tamura equation for the ternary system. For the correlation of V^E data of binary systems van der Waals (vdW1) and Twu–Coon–Bluck–Tilton (TCBT) mixing rules coupled with the Peng–Robinson–Stryjek–Vera (PRSV) equation of state were applied. The same models were applied for the prediction and correlation of V^E data of the ternary system. In addition, several empirical relationships were applied for the prediction of V^E data of the ternary system from the corresponding binary data. The obtained results have been analysed in terms of specific molecular interactions present in the investigated mixtures taking into considerations the effect of temperature increasing on present interactions.

1. Introduction

Thermodynamic investigation of alcohols with amine or alkane, alone or in mixtures is of a great interest due to complex molecular interactions present in these mixtures (for example mixtures of alcohols and amine exhibit very high values of excess volumes, indicating strong interactions present in those mixtures), as well as their diverse industrial application.

For example, 1-butanol is primarily used as a solvent, an intermediate in chemical synthesis, and a fuel [1–3]. Cyclohexylamine is used in the production of pharmaceuticals and other chemicals including insecticides, pesticides, plasticizers, emulsifying agents, dyes, dry cleaning agents and corrosion inhibitors [4]. n-Heptane is widely applied in laboratories as a totally non-polar solvent. It is ideal as a transport and a storage fluid. Also, n-heptane is a component of a fuel, but is undesirable in petrol, because it burns explosively, causing engine knocking.

In the present work the binary experimental density ρ data of the 1-butanol + cyclohexylamine, 1-butanol + n-heptane and cyclohexylamine + n-heptane, as well as the ternary 1-butanol + cyclohexylamine + n-heptane at temperatures (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15) K and atmospheric pressure have been measured.

On the other side, volumetric properties have an important role in the examination and development of thermodynamic models. With an improvement of CEOS and CEOS/G^E models, equations of state have become a leading tool for the calculation of thermodynamic properties of very non-ideal mixtures. This article presents the continuity of our previous works dealing with experimental volumetric determination [1–3,5,6] and testing of thermodynamic models based on CEOS and CEOS/G^E mixing rules in correlation and prediction of thermodynamic properties, which have been widely used, due to their simplicity and accuracy. For the correlation of binary V^E, the Peng–Robinson–Stryjek–Vera cubic equation of state (PRSV CEOS) [7] coupled with the van der Waals (vdW1) [8] and CEOS/G^E mixing rule introduced by Twu et al. (TCBT) [9] were chosen. Prediction of V^E of ternary system was performed by the same vdW1 and TCBT models. For the correlation of the V^E of ternary data only TCBT mixing rules were used.

Also, the aim of this paper was to involve the ternary data reduction approach, based on symmetric [10–14] and asymmetric [15–17] polynomial expressions. In addition the intention was to provide a comparison between CEOS approach and use of polynomial equations in ternary V^E prediction.

Literature data of V^E values for the system 1-butanol + n-heptane are available on several considered temperatures [18–22] in the range of 298.15–308.15 K, while for the other binary systems,

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doi:10.1016/j.tca.2009.07.002

Table 1
Comparison of the measured densities of pure components with the literature values.

Component	T (K)	ρ (g cm^{-3})	
		Exptl.	Lit.
1-Butanol	298.15	0.805762	0.80575[26]
Cyclohexylamine	303.15	0.857671	0.85777[26]
n-Heptane	298.15	0.679494	0.67951[26], 0.67949[19]

literature data are very scarce, covering a single temperature 303.15 K [23–25], and in the currently published articles no values of V^E have been found for the entire temperature range for the binary mixtures studied here. Also, data for the investigated ternary system are not available in the literature.

2. Experimental

2.1. Materials

1-Butanol and cyclohexylamine were supplied by Merck with a purity >99.5% and >99%, respectively, while n-heptane was a product of Fluka with a purity >99.5%. Chemicals were kept in brown bottles under inert nitrogen atmosphere and ultrasonically degassed just before a sample preparation. Table 1 lists the densities of the liquids measured in this work together with the values found in the literature. Since the agreement was very good further purifications of reagents was not performed. All mixtures were prepared by mass using the mixing cell and the procedure described previously [27,28]; presently, a Mettler AG 204 balance with a precision of 1×10^{-4} g was used. Error in mole fraction was estimated to be less than $\pm 1 \times 10^{-4}$.

2.2. Apparatus and procedure

Densities ρ of the investigated binary and ternary systems and corresponding pure substances were measured by means of an Anton Paar DMA 5000 digital vibrating U-tube densimeter (with automatic viscosity correction) having a stated accuracy of $\pm 5 \times 10^{-6}$ g cm^{-3}. Detailed explanation of the experimental procedure has been given previously [1–3]. The temperature in the cell was regulated to ±0.001 K with a built-in solid-state thermostat. Temperature in the cell was measured by means of two integrated Pt 100 platinum thermometers; temperature stability was better than ±0.002 K and its accuracy was ±0.01 K. All molar quantities were based on the IUPAC relative atomic mass table. Calibration of the apparatus was performed periodically using ambient air and ultrapure water. The experimental uncertainty in the density is about $\pm 1 \times 10^{-5}$ g cm^{-3}, while the average uncertainty in excess molar volume is estimated to be $\pm 3 \times 10^{-3}$ cm^{-3} mol^{-1}.

3. Results and discussion

The excess molar volumes V^E, were calculated from the equation:

$$V^E = \sum_{i=1}^{n} x_i M_i \left[\left(\frac{1}{\rho} \right) - \left(\frac{1}{\rho_i} \right) \right] \quad (1)$$

where n is the number of components, x_i is the mole fraction of component i in the mixture, M_i its molecular weight, and ρ and ρ_i are the measured densities of the mixture, and the pure component, respectively.

Tables 2 and 3 list the measured densities ρ, and the corresponding values of V^E in the temperature range 288.15–323.15 K for the binaries 1-butanol + n-heptane, 1-butanol + cyclohexylamine and cyclohexylamine + n-heptane and for the ternary 1-butanol + cyclohexylamine + n-heptane systems, respectively.

Data for the binary mixtures were fitted to a Redlich–Kister polynomial [29]:

$$V^E_{ij} = x_i x_j \sum_{p=0}^{k} A_p (2x_i - 1)^p \quad (2)$$

where A_p is the adjustable parameters, and k is the number of adjustable parameters determined by means of the F-test [30].

The ternary excess molar volumes were correlated by the expression proposed by Nagata and Tamura [31]:

$$V^E_{123} = V^E_{12} + V^E_{13} + V^E_{23} + x_1 x_2 x_3 RT(B_0 - B_1 x_1 - B_2 x_2 - B_3 x_1^2 - B_4 x_2^2 - B_5 x_1 x_2 - B_6 x_1^3 - B_7 x_2^3 - B_8 x_1^2 x_2) \quad (3)$$

where V^E_{12}, V^E_{13} and V^E_{23} represent the binary excess molar volumes, with x_1, x_2 and x_3 mole fractions in the ternary system. The adjustable parameters of ternary contribution B_0, B_1, …, B_8 were obtained from ternary experimental V^E data.

The results of the V^E calculation performed by Eqs. (2) and (3) were assessed by the root-mean-square deviation σ:

$$\sigma = \left(\sum_{i=1}^{N} \frac{(V^E_{\mathrm{exp},i} - V^E_{cal,i})^2}{N} \right)^{1/2} \quad (4)$$

and by the percentage average absolute deviation PD(V^E):

$$\mathrm{PD}(V^E) = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{V^E_{\mathrm{exp}} - V^E_{cal}}{(V^E_{\mathrm{exp}})_{\max}} \right|_i \quad (5)$$

In Eqs. (4) and (5) N denotes the number of experimental data points, while $(V^E_{\mathrm{exp}})_{\max}$ is the maximum value of experimental V^E.

Adjustable parameters of the Redlich–Kister and of the Nagata–Tamura equations at each temperature separately along with the corresponding values for σ and PD(V^E) are summarized in Table 4 for binary systems and in Table 5 for ternary system.

For the systems of 1-butanol with cyclohexylamine the agreement between the present and literature values [23] is very good, having the error below 1%. The excess molar volume data for the system 1-butanol + n-heptane have been previously experimentally determined using several different measuring techniques: (i) bicapillary pycnometer [21], (ii) dilatometer [18,20] and (iii) vibrating tube densimeter [19] and [22]. Treszczanowicz and Benson [18] and Berro and Péneloux [19] experimentally determined V^E of 1-butanol + n-heptane at 298.15 K, Nath and Pandey [20] at 288.15 and 298.15 K, Sastry and Valand [21] at 298.15 and 308.15 K, while Vijande et al. [22] reported V^E data at five temperatures: 288.15, 298.15, 298.15, 303.15 and 308.15 K. The $V^E - x$ curves of the literature data at each measured temperature have the same shape as those obtained in this work. Comparison of our data and those achieved by Vijande et al. [22] has shown an excellent agreement at each temperature. The results of Nath and Pandey [20] at 298.15 K are in a very good agreement with the results from this work, but at lower temperature 288.15 K are rather higher. The disagreement between data of this work and literature data at 298.15 K for the area of minima is below 2.15%. However, the results of Sastry and Valand [21] are not included in this analyses showing the largest discrepancy, especially in the range of maximal V^E values. Comparison of our experimental results of V^E at 303.15 K with data reported previously [24,25] for the system cyclohexylamine + n-heptane has shown that our V^E data are in excellent agreement with the values obtained by Grenner et al. [24], while maximum discrepancy between data reported by Raju et al. [25] and our results is 0.011 cm^3 mol^{-1}.

Table 2
Densities ρ and excess molar volumes V^E for binary systems from T = (288.15 to 323.15 K) and atmospheric pressure.

x_1	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	x_1	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	x_1	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})
				1-Butanol (1) + cyclohexylamine (2)				
				T = 288.15 K				
0.0000	0.871290	0.0000	0.4000	0.860506	−1.1407	0.7984	0.834505	−0.8309
0.0499	0.870402	−0.1876	0.4994	0.855958	−1.2435	0.8500	0.829604	−0.6575
0.1019	0.869284	−0.3614	0.6006	0.850147	−1.2368	0.8993	0.824498	−0.4553
0.1499	0.868221	−0.5209	0.6977	0.843134	−1.0952	0.9508	0.819064	−0.2449
0.1997	0.867037	−0.6795	0.7497	0.838964	−0.9862	1.0000	0.813373	0.0000
0.2995	0.864139	−0.9436						
				T = 293.15 K				
0.0000	0.866747	0.0000	0.4000	0.856206	−1.1494	0.7984	0.830511	−0.8364
0.0499	0.865907	−0.1918	0.4994	0.851708	−1.2506	0.8500	0.825664	−0.6626
0.1019	0.864828	−0.3681	0.6006	0.845964	−1.2427	0.8993	0.820606	−0.4591
0.1499	0.863800	−0.5297	0.6977	0.839036	−1.1007	0.9508	0.815223	−0.2475
0.1997	0.862648	−0.6898	0.7497	0.834921	−0.9922	1.0000	0.809573	0.0000
0.2995	0.859800	−0.9542						
				T = 298.15 K				
0.0000	0.862207	0.0000	0.4000	0.851899	−1.1577	0.7984	0.826498	−0.8407
0.0499	0.861409	−0.1953	0.4994	0.847444	−1.2565	0.8500	0.821703	−0.6664
0.1019	0.860372	−0.3746	0.6006	0.841767	−1.2476	0.8993	0.816697	−0.4622
0.1499	0.859375	−0.5380	0.6977	0.834924	−1.1054	0.9508	0.811359	−0.2487
0.1997	0.858251	−0.6992	0.7497	0.830861	−0.9971	1.0000	0.805762	0.0000
0.2995	0.855453	−0.9642						
				T = 303.15 K				
0.0000	0.857671	0.0000	0.4000	0.847581	−1.1657	0.7984	0.822464	−0.8451
0.0499	0.856914	−0.1989	0.4994	0.843167	−1.2622	0.8500	0.817720	−0.6703
0.1019	0.855914	−0.3809	0.6006	0.837554	−1.2523	0.8993	0.812762	−0.4651
0.1499	0.854945	−0.5458	0.6977	0.830791	−1.1098	0.9508	0.807471	−0.2501
0.1997	0.853850	−0.7084	0.7497	0.826780	−1.0019	1.0000	0.801923	0.0000
0.2995	0.851095	−0.9735						
				T = 308.15 K				
0.0000	0.853138	0.0000	0.4000	0.843244	−1.1726	0.7984	0.818404	−0.8493
0.0499	0.852415	−0.2019	0.4994	0.838874	−1.2676	0.8500	0.813708	−0.6739
0.1019	0.851450	−0.3866	0.6006	0.833322	−1.2568	0.8993	0.808799	−0.4680
0.1499	0.850509	−0.5532	0.6977	0.826637	−1.1141	0.9508	0.803552	−0.2514
0.1997	0.849438	−0.7168	0.7497	0.822671	−1.0061	1.0000	0.798053	0.0000
0.2995	0.846722	−0.9819						
				T = 313.15 K				
0.0000	0.848607	0.0000	0.4000	0.838892	−1.1793	0.7984	0.814315	−0.8534
0.0499	0.847912	−0.2043	0.4994	0.834561	−1.2725	0.8500	0.809660	−0.6768
0.1019	0.846979	−0.3915	0.6006	0.829067	−1.2610	0.8993	0.804804	−0.4709
0.1499	0.846063	−0.5598	0.6977	0.822458	−1.1183	0.9508	0.799601	−0.2529
0.1997	0.845013	−0.7242	0.7497	0.818541	−1.0108	1.0000	0.794147	0.0000
0.2995	0.842337	−0.9899						
				T = 318.15 K				
0.0000	0.844073	0.0000	0.4000	0.834521	−1.1843	0.7984	0.810191	−0.8543
0.0499	0.843406	−0.2068	0.4994	0.830229	−1.2759	0.8500	0.805587	−0.6778
0.1019	0.842499	−0.3958	0.6006	0.824783	−1.2624	0.8993	0.800769	−0.4702
0.1499	0.841605	−0.5654	0.6977	0.818247	−1.1196	0.9508	0.795606	−0.2503
0.1997	0.840578	−0.7310	0.7497	0.814376	−1.0124	1.0000	0.790231	0.0000
0.2995	0.837935	−0.9964						
				T = 323.15 K				
0.0000	0.839547	0.0000	0.4000	0.830136	−1.1906	0.7984	0.806034	−0.8584
0.0499	0.838847	−0.2014	0.4994	0.825872	−1.2802	0.8500	0.801472	−0.6813
0.1019	0.838018	−0.4000	0.6006	0.820478	−1.2663	0.8993	0.796696	−0.4731
0.1499	0.837144	−0.5711	0.6977	0.814010	−1.1238	0.9508	0.791569	−0.2514
0.1997	0.836136	−0.7378	0.7497	0.810181	−1.0170	1.0000	0.786238	0.0000
0.2995	0.833516	−1.0028						
				1-Butanol (1) + n-heptane (2)				
				T = 288.15 K				
0.0000	0.687954	0.0000	0.2507	0.708652	0.1882	0.6497	0.754667	0.0950
0.0691	0.692997	0.1071	0.2999	0.713405	0.1915	0.6999	0.761833	0.0759
0.0999	0.695430	0.1345	0.3501	0.718522	0.1843	0.7502	0.769372	0.0593
0.1495	0.699575	0.1582	0.3998	0.723818	0.1759	0.7999	0.777249	0.0393
0.1701	0.701352	0.1666	0.4497	0.729369	0.1684	0.8498	0.785510	0.0298
0.2000	0.703971	0.1811	0.4999	0.735288	0.1484	0.9006	0.794437	0.0155
0.2497	0.708550	0.1895	0.5516	0.741637	0.1344	1.0000	0.813373	0.0000
				T = 293.15 K				
0.0000	0.683733	0.0000	0.2507	0.704392	0.2066	0.6497	0.750570	0.1044
0.0691	0.688732	0.1198	0.2999	0.709158	0.2093	0.6999	0.757773	0.0830
0.0999	0.691164	0.1486	0.3501	0.714283	0.2024	0.7502	0.765348	0.0649

Table 2 (*Continued*)

x_1	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	x_1	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	x_1	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})
0.1495	0.695309	0.1741	0.3998	0.719595	0.1931	0.7999	0.773267	0.0429
0.1701	0.697089	0.1826	0.4497	0.725163	0.1848	0.8498	0.781573	0.0317
0.2000	0.699708	0.1983	0.4999	0.731110	0.1623	0.9006	0.790548	0.0160
0.2497	0.704296	0.2068	0.5516	0.737484	0.1468	1.0000	0.809573	0.0000
				T = 298.15 K				
0.0000	0.679494	0.0000	0.2507	0.700109	0.2264	0.6497	0.746442	0.1162
0.0691	0.684439	0.1349	0.2999	0.704880	0.2299	0.6999	0.753681	0.0927
0.0999	0.686867	0.1658	0.3501	0.710016	0.2228	0.7502	0.761298	0.0721
0.1495	0.691013	0.1929	0.3998	0.715341	0.2132	0.7999	0.769263	0.0476
0.1701	0.692795	0.2017	0.4497	0.720925	0.2041	0.8498	0.777613	0.0348
0.2000	0.695420	0.2173	0.4999	0.726892	0.1805	0.9006	0.786635	0.0178
0.2497	0.700016	0.2260	0.5516	0.733291	0.1634	1.0000	0.805762	0.0000
				T = 303.15 K				
0.0000	0.675229	0.0000	0.2507	0.695793	0.2480	0.6497	0.742276	0.1298
0.0691	0.680112	0.1520	0.2999	0.700571	0.2519	0.6999	0.749559	0.1029
0.0999	0.682541	0.1840	0.3501	0.705715	0.2450	0.7502	0.757214	0.0803
0.1495	0.686688	0.2126	0.3998	0.711055	0.2345	0.7999	0.765220	0.0539
0.1701	0.688469	0.2224	0.4497	0.716653	0.2251	0.8498	0.773620	0.0387
0.2000	0.691091	0.2397	0.4999	0.722640	0.2001	0.9006	0.782692	0.0199
0.2497	0.695692	0.2490	0.5516	0.729062	0.1817	1.0000	0.801923	0.0000
				T = 308.15 K				
0.0000	0.670941	0.0000	0.2507	0.691434	0.2736	0.6497	0.738070	0.1456
0.0691	0.675754	0.1713	0.2999	0.696222	0.2771	0.6999	0.745390	0.1160
0.0999	0.678179	0.2053	0.3501	0.701373	0.2706	0.7502	0.753090	0.0903
0.1495	0.682323	0.2362	0.3998	0.706726	0.2594	0.7999	0.761140	0.0614
0.1701	0.684105	0.2464	0.4497	0.712340	0.2491	0.8498	0.769591	0.0434
0.2000	0.686729	0.2643	0.4999	0.718343	0.2232	0.9006	0.778716	0.0224
0.2497	0.691331	0.2750	0.5516	0.724793	0.2024	1.0000	0.798053	0.0000
				T = 313.15 K				
0.0000	0.666621	0.0000	0.2507	0.687035	0.3012	0.6497	0.733819	0.1632
0.0691	0.671356	0.1927	0.2999	0.691828	0.3053	0.6999	0.741178	0.1306
0.0999	0.673778	0.2285	0.3501	0.696989	0.2984	0.7502	0.748919	0.1022
0.1495	0.677919	0.2616	0.3998	0.702355	0.2865	0.7999	0.757016	0.0702
0.1701	0.679699	0.2729	0.4497	0.707984	0.2752	0.8498	0.765519	0.0492
0.2000	0.682324	0.2916	0.4999	0.714006	0.2479	0.9006	0.774698	0.0257
0.2497	0.686930	0.3031	0.5516	0.720478	0.2256	1.0000	0.794147	0.0000
				T = 318.15 K				
0.0000	0.662273	0.0000	0.2507	0.682589	0.3338	0.6497	0.729516	0.1862
0.0691	0.666921	0.2167	0.2999	0.687391	0.3376	0.6999	0.736918	0.1499
0.0999	0.669334	0.2558	0.3501	0.692557	0.3313	0.7502	0.744697	0.1191
0.1495	0.673469	0.2918	0.3998	0.697935	0.3187	0.7999	0.752839	0.0842
0.1701	0.675246	0.3044	0.4497	0.703577	0.3069	0.8498	0.761397	0.0599
0.2000	0.677872	0.3239	0.4999	0.709618	0.2780	0.9006	0.770631	0.0337
0.2497	0.682482	0.3360	0.5516	0.716114	0.2538	1.0000	0.790231	0.0000
				T = 323.15 K				
0.0000	0.657896	0.0000	0.2507	0.678099	0.3687	0.6497	0.725167	0.2086
0.0691	0.662457	0.2410	0.2999	0.682909	0.3721	0.6999	0.732609	0.1685
0.0999	0.664851	0.2853	0.3501	0.688076	0.3667	0.7502	0.740419	0.1359
0.1495	0.668978	0.3244	0.3998	0.693471	0.3521	0.7999	0.748617	0.0961
0.1701	0.670749	0.3388	0.4497	0.699118	0.3408	0.8498	0.757222	0.0690
0.2000	0.673376	0.3589	0.4999	0.705176	0.3102	0.9006	0.766522	0.0383
0.2497	0.677987	0.3720	0.5516	0.711695	0.2838	1.0000	0.786238	0.0000
				Cyclohexylamine (1) + n-heptane (2)				
				T = 288.15 K				
0.0000	0.687954	0.0000	0.3004	0.732296	0.3198	0.6498	0.794839	0.2548
0.0501	0.694788	0.0878	0.4010	0.749067	0.3294	0.6994	0.804717	0.2330
0.1002	0.701818	0.1651	0.4497	0.757546	0.3223	0.7999	0.825611	0.1779
0.1501	0.709079	0.2204	0.5597	0.777524	0.2949	0.8992	0.847523	0.1059
0.2305	0.721227	0.2882	0.6001	0.785155	0.2825	1.0000	0.871290	0.0000
				T = 293.15 K				
0.0000	0.683733	0.0000	0.3004	0.728038	0.3093	0.6498	0.790479	0.2429
0.0501	0.690573	0.0836	0.4010	0.744783	0.3179	0.6994	0.800344	0.2209
0.1002	0.697601	0.1584	0.4497	0.753244	0.3111	0.7999	0.821199	0.1675
0.1501	0.704855	0.2122	0.5597	0.773195	0.2825	0.8992	0.843061	0.0988
0.2305	0.716988	0.2782	0.6001	0.780814	0.2701	1.0000	0.866747	0.0000
				T = 298.15 K				
0.0000	0.679494	0.0000	0.3004	0.723765	0.2987	0.6498	0.786113	0.2306
0.0501	0.686334	0.0806	0.4010	0.740484	0.3065	0.6994	0.795962	0.2090
0.1002	0.693360	0.1530	0.4497	0.748933	0.2993	0.7999	0.816783	0.1569
0.1501	0.700609	0.2049	0.5597	0.768854	0.2702	0.8992	0.838598	0.0916
0.2305	0.712729	0.2690	0.6001	0.776463	0.2576	1.0000	0.862207	0.0000

Table 2 (*Continued*)

x_1	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	x_1	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	x_1	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})
				T = 303.15 K				
0.0000	0.675229	0.0000	0.3004	0.719477	0.2869	0.6498	0.781744	0.2167
0.0501	0.682072	0.0772	0.4010	0.736173	0.2938	0.6994	0.791575	0.1962
0.1002	0.689097	0.1471	0.4497	0.744614	0.2856	0.7999	0.812360	0.1464
0.1501	0.696341	0.1972	0.5597	0.764509	0.2561	0.8992	0.834132	0.0845
0.2305	0.708452	0.2587	0.6001	0.772102	0.2445	1.0000	0.857671	0.0000
				T = 308.15 K				
0.0000	0.670941	0.0000	0.3004	0.715170	0.2750	0.6498	0.777362	0.2031
0.0501	0.677784	0.0745	0.4010	0.731847	0.2806	0.6994	0.787181	0.1829
0.1002	0.684805	0.1426	0.4497	0.740280	0.2716	0.7999	0.807934	0.1353
0.1501	0.692046	0.1907	0.5597	0.760149	0.2421	0.8992	0.829662	0.0777
0.2305	0.704150	0.2494	0.6001	0.767732	0.2307	1.0000	0.853138	0.0000
				T = 313.15 K				
0.0000	0.666621	0.0000	0.3004	0.710839	0.2625	0.6498	0.772968	0.1887
0.0501	0.673467	0.0712	0.4010	0.727504	0.2659	0.6994	0.782776	0.1691
0.1002	0.680490	0.1364	0.4497	0.735927	0.2568	0.7999	0.803499	0.1241
0.1501	0.687730	0.1822	0.5597	0.755773	0.2274	0.8992	0.825189	0.0707
0.2305	0.699827	0.2385	0.6001	0.763352	0.2154	1.0000	0.848607	0.0000
				T = 318.15 K				
0.0000	0.662273	0.0000	0.3004	0.706489	0.2488	0.6498	0.768563	0.1732
0.0501	0.669120	0.0684	0.4010	0.723139	0.2510	0.6994	0.778360	0.1544
0.1002	0.676146	0.1306	0.4497	0.731554	0.2416	0.7999	0.799055	0.1124
0.1501	0.683386	0.1740	0.5597	0.751384	0.2115	0.8992	0.820710	0.0633
0.2305	0.695479	0.2275	0.6001	0.758953	0.2002	1.0000	0.844073	0.0000
				T = 323.15 K				
0.0000	0.657896	0.0000	0.3004	0.702117	0.2347	0.6498	0.764139	0.1589
0.0501	0.664739	0.0670	0.4010	0.718756	0.2356	0.6994	0.773935	0.1396
0.1002	0.671776	0.1244	0.4497	0.727160	0.2267	0.7999	0.794605	0.1008
0.1501	0.679015	0.1658	0.5597	0.746981	0.1953	0.8992	0.816229	0.0564
0.2305	0.691106	0.2164	0.6001	0.754544	0.1843	1.0000	0.839547	0.0000

In the 1-butanol + cyclohexylamine system dominates the chemical contribution according to the complexes formed between unlike molecules, exhibiting large negative V^E, as can be observed in Fig. 1a, with small influence of temperature on V^E [32]. Influence of the disruption of the self-associated 1-butanol molecules is smaller compared to the effect of H-bonding formation between alcohol and amine molecules, causing approximately symmetrical position with respect to mole fraction. Non-associating molecule n-heptane acts as an inert component, in the mixture with 1-butanol or cyclohexylamine as associating components.

As can be seen from Fig. 1b, for the binary system of 1-butanol and n-heptane V^E values are positive in the entire composition range with asymmetric $V^E - x_1$ curves, shifted towards the lower 1-butanol mole fractions. Also, it is obvious that the V^E data values increase with temperature rising from 288.15 to 323.15 K. As it was discussed previously [33], the positive excess volumes in mixtures of n-alcohols and n-alkanes are the result of (i) the disruption of alcohol multimers due to breaking of hydrogen bonds (chemical contribution) and (ii) non-specific physical interactions between the real species in a mixture (physical contribution). Negative V^E values are mostly caused by interstitial accommodation and changes of free volumes (structural contribution). Since the chemical contribution of hydrogen bond breaking to V^E is negligible, except for small mole fractions, it is assumed that physical contribution comprises the major part of positive V^E values [33] in this system. The sharp increases of the V^E in the dilute 1-butanol region (Fig. 1b) suggest the dominance of the disruption of the H-bonds of alcohol multimers by unlike n-heptane molecules.

The system cyclohexylamine + n-heptane (Fig. 1c) also shows positive V^E values in a whole concentration range. In this case the highest values of V^E are obtained for the lowest temperature (288.15 K). It is assumed that the positive values are due to the breakdown of the hydrogen bonded structure of cyclohexylamine. H-bonds tend to be broken and V^E becomes larger with a temperature rising, and positive values of V^E in the mixture cyclohexylamine + n-heptane (Fig. 1c) are a consequence of the rupture of the compact hydrogen bonded structure of this amine.

Decreasing of V^E values with the temperature rising were probably the consequence of stronger amine–amine interactions at higher temperature.

The experimental results of V^E for the ternary mixture at 303.15 K are shown in Fig. 2 along with six different lines of constant ratio $z = x_1/x_3$. It is clear that a large amount of the 1-butanol (lines z_5 and z_6) gives the high approximately symmetrical contractive V^E with respect to x_2 mole fraction due to the cross-association between 1-butanol and cyclohexylamine molecules. Minimum obtained for z_6 is close to the minimum of the binary mixture 1-butanol + cyclohexylamine. Adding of a large amount of n-heptane causes expansion of V^E, showing nearly ideal behavior of the mixture for z_1.

Fig. 3 shows the isolines of ternary V^E at 303.15 K. It is evident that V^E of this system is mostly negative except for the region very close to binary mixtures of n-heptane with 1-butanol, or cyclohexylamine where a change in V^E sign occurs.

Fig. 4 shows the three-dimensional presentation of V^E ternary mixture at 313.15 K generated by Eq. (3). This surface follows and confirms all remarks given for binaries and ternary mixture.

4. Modelling of V^E data

4.1. Cubic EOS mixing rules

In the last few years the interest related to modelling of V^E by the CEOS and CEOS/G^E models has increased. In order to use these methods the comparative study of already adequate mixing rules is applied. For all calculations the PRSV cubic equation of state was selected [7] and applied with vdW1 [8] and TCBT [9] mixing rules, with the models previously established [1–3,5,6].

Table 3
Densities ρ and excess molar volumes V^E for 1-butanol(1) + cyclohexylamine(2) + n-heptane(3) from T = (288.15 to 323.15 K) and atmospheric pressure.

x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})
1-Butanol(1) + cyclohexylamine(2) + n-heptane(3)							
T = 288.15 K							
0.0900	0.1001	0.710879	−0.0508	0.5394	0.1010	0.763468	−0.3441
0.0806	0.2001	0.726010	−0.0503	0.4801	0.2000	0.777830	−0.6495
0.0698	0.3001	0.741383	−0.0111	0.4198	0.3003	0.791414	−0.8184
0.0615	0.3987	0.757477	0.0159	0.3600	0.4000	0.804131	−0.8709
0.0502	0.5005	0.774365	0.0584	0.3003	0.4997	0.816077	−0.8161
0.0400	0.6003	0.791821	0.0843	0.2399	0.6000	0.827615	−0.7074
0.0289	0.7008	0.810179	0.0877	0.1803	0.6994	0.838679	−0.5494
0.0200	0.7999	0.829525	0.0716	0.1197	0.8006	0.849752	−0.3676
0.0102	0.8998	0.849840	0.0481	0.0604	0.8994	0.860530	−0.1958
0.1799	0.1000	0.719997	−0.1501	0.7197	0.1003	0.791054	−0.4087
0.1586	0.2066	0.736287	−0.2447	0.6399	0.2002	0.803889	−0.7604
0.1401	0.3001	0.750604	−0.2458	0.5599	0.3001	0.815501	−0.9857
0.1204	0.4001	0.766182	−0.2076	0.4788	0.4016	0.826078	−1.0820
0.1000	0.5002	0.782130	−0.1574	0.4000	0.5000	0.835319	−1.0765
0.0802	0.6001	0.798605	−0.1000	0.3203	0.5996	0.843452	−0.9393
0.0597	0.7006	0.815802	−0.0637	0.2403	0.6996	0.851166	−0.7682
0.0404	0.7997	0.833474	−0.0252	0.1604	0.7995	0.858178	−0.5313
0.0211	0.8987	0.851937	−0.0118	0.0798	0.9002	0.865039	−0.2903
0.3603	0.0998	0.739972	−0.2554	0.8101	0.0998	0.806918	−0.4381
0.3198	0.2002	0.755320	−0.4970	0.7198	0.2001	0.818503	−0.8031
0.2802	0.3000	0.770031	−0.5900	0.6299	0.3001	0.828801	−1.0501
0.2402	0.3999	0.784335	−0.5850	0.5400	0.4000	0.837770	−1.1742
0.1998	0.5002	0.798549	−0.5275	0.4499	0.5002	0.845427	−1.1665
0.1599	0.6001	0.812677	−0.4260	0.3598	0.6002	0.851930	−1.0528
0.1201	0.7001	0.827008	−0.3170	0.2698	0.7002	0.857600	−0.8601
0.0801	0.7999	0.841517	−0.2124	0.1799	0.8001	0.862673	−0.6172
0.0401	0.9000	0.856197	−0.0913	0.0901	0.8998	0.867238	−0.3356
				0.4922	0.4415	0.838907	−1.1630
T = 293.15 K							
0.0900	0.1001	0.706609	−0.0463	0.5394	0.1010	0.759325	−0.3436
0.0806	0.2001	0.721740	−0.0532	0.4801	0.2000	0.773639	−0.6526
0.0698	0.3001	0.737112	−0.0201	0.4198	0.3003	0.787178	−0.8240
0.0615	0.3987	0.753183	0.0054	0.3600	0.4000	0.799862	−0.8794
0.0502	0.5005	0.770050	0.0462	0.3003	0.4997	0.811782	−0.8270
0.0400	0.6003	0.787478	0.0720	0.2399	0.6000	0.823306	−0.7217
0.0289	0.7008	0.805808	0.0752	0.1803	0.6994	0.834334	−0.5634
0.0200	0.7999	0.825120	0.0602	0.1197	0.8006	0.845361	−0.3797
0.0102	0.8998	0.845379	0.0407	0.0604	0.8994	0.856074	−0.2034
0.1799	0.1000	0.715732	−0.1446	0.7197	0.1003	0.787021	−0.4114
0.1586	0.2066	0.732012	−0.2463	0.6399	0.2002	0.799792	−0.7665
0.1401	0.3001	0.746325	−0.2530	0.5599	0.3001	0.811333	−0.9928
0.1204	0.4001	0.761890	−0.2184	0.4788	0.4016	0.821850	−1.0903
0.1000	0.5002	0.777821	−0.1705	0.4000	0.5000	0.831051	−1.0871
0.0802	0.6001	0.794271	−0.1136	0.3203	0.5996	0.839149	−0.9514
0.0597	0.7006	0.811442	−0.0777	0.2403	0.6996	0.846826	−0.7811
0.0404	0.7997	0.829072	−0.0370	0.1604	0.7995	0.853789	−0.5427
0.0211	0.8987	0.847480	−0.0196	0.0798	0.9002	0.860583	−0.2976
0.3603	0.0998	0.735746	−0.2505	0.8101	0.0998	0.802957	−0.4424
0.3198	0.2002	0.751066	−0.4976	0.7198	0.2001	0.814457	−0.8094
0.2802	0.3000	0.765761	−0.5959	0.6299	0.3001	0.824668	−1.0568
0.2402	0.3999	0.780050	−0.5949	0.5400	0.4000	0.833562	−1.1813
0.1998	0.5002	0.794250	−0.5408	0.4499	0.5002	0.841167	−1.1754
0.1599	0.6001	0.808351	−0.4399	0.3598	0.6002	0.847630	−1.0637
0.1201	0.7001	0.822652	−0.3308	0.2698	0.7002	0.853259	−0.8718
0.0801	0.7999	0.837117	−0.2241	0.1799	0.8001	0.858283	−0.6281
0.0401	0.9000	0.851740	−0.0989	0.0901	0.8998	0.862782	−0.3428
				0.4922	0.4415	0.834671	−1.1708
T = 298.15 K							
0.0900	0.1001	0.702316	−0.0404	0.5394	0.1010	0.755147	−0.3400
0.0806	0.2001	0.717447	−0.0547	0.4801	0.2000	0.769431	−0.6551
0.0698	0.3001	0.732824	−0.0287	0.4198	0.3003	0.782926	−0.8290
0.0615	0.3987	0.748878	−0.0056	0.3600	0.4000	0.795583	−0.8878
0.0502	0.5005	0.765727	0.0334	0.3003	0.4997	0.807483	−0.8385
0.0400	0.6003	0.783135	0.0581	0.2399	0.6000	0.818978	−0.7344
0.0289	0.7008	0.801429	0.0628	0.1803	0.6994	0.829977	−0.5765
0.0200	0.7999	0.820709	0.0488	0.1197	0.8006	0.840963	−0.3913
0.0102	0.8998	0.840918	0.0332	0.0604	0.8994	0.851615	−0.2106
0.1799	0.1000	0.711438	−0.1365	0.7197	0.1003	0.782966	−0.4129
0.1586	0.2066	0.727709	−0.2455	0.6399	0.2002	0.795667	−0.7704
0.1401	0.3001	0.742019	−0.2580	0.5599	0.3001	0.807146	−0.9988
0.1204	0.4001	0.757586	−0.2293	0.4788	0.4016	0.817606	−1.0975
0.1000	0.5002	0.773502	−0.1838	0.4000	0.5000	0.826765	−1.0962
0.0802	0.6001	0.789932	−0.1280	0.3203	0.5996	0.834835	−0.9628

Table 3 (*Continued*)

x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})
0.0597	0.7006	0.807074	−0.0917	0.2403	0.6996	0.842477	−0.7934
0.0404	0.7997	0.824666	−0.0488	0.1604	0.7995	0.849393	−0.5534
0.0211	0.8987	0.843021	−0.0274	0.0798	0.9002	0.856124	−0.3046
0.3603	0.0998	0.731497	−0.2442	0.8101	0.0998	0.798974	−0.4454
0.3198	0.2002	0.746793	−0.4973	0.7198	0.2001	0.810393	−0.8148
0.2802	0.3000	0.761467	−0.5999	0.6299	0.3001	0.820518	−1.0625
0.2402	0.3999	0.775747	−0.6038	0.5400	0.4000	0.829340	−1.1876
0.1998	0.5002	0.789937	−0.5535	0.4499	0.5002	0.836892	−1.1831
0.1599	0.6001	0.804022	−0.4546	0.3598	0.6002	0.843318	−1.0735
0.1201	0.7001	0.818289	−0.3445	0.2698	0.7002	0.848912	−0.8831
0.0801	0.7999	0.832711	−0.2355	0.1799	0.8001	0.853890	−0.6387
0.0401	0.9000	0.847278	−0.1060	0.0901	0.8998	0.858325	−0.3498
				0.4922	0.4415	0.830424	−1.1780
			T= 303.15 K				
0.0900	0.1001	0.697998	−0.0343	0.5394	0.1010	0.750943	−0.3361
0.0806	0.2001	0.713136	−0.0571	0.4801	0.2000	0.765197	−0.6571
0.0698	0.3001	0.728515	−0.0373	0.4198	0.3003	0.778657	−0.8344
0.0615	0.3987	0.744562	−0.0179	0.3600	0.4000	0.791285	−0.8960
0.0502	0.5005	0.761393	0.0196	0.3003	0.4997	0.803165	−0.8494
0.0400	0.6003	0.778782	0.0436	0.2399	0.6000	0.814642	−0.7476
0.0289	0.7008	0.797047	0.0492	0.1803	0.6994	0.825613	−0.5898
0.0200	0.7999	0.816293	0.0373	0.1197	0.8006	0.836557	−0.4024
0.0102	0.8998	0.836453	0.0260	0.0604	0.8994	0.847156	−0.2179
0.1799	0.1000	0.707118	−0.1280	0.7197	0.1003	0.778883	−0.4140
0.1586	0.2066	0.723390	−0.2459	0.6399	0.2002	0.791520	−0.7743
0.1401	0.3001	0.737700	−0.2643	0.5599	0.3001	0.802935	−1.0041
0.1204	0.4001	0.753261	−0.2398	0.4788	0.4016	0.813343	−1.1044
0.1000	0.5002	0.769168	−0.1973	0.4000	0.5000	0.822466	−1.1054
0.0802	0.6001	0.785583	−0.1429	0.3203	0.5996	0.830507	−0.9737
0.0597	0.7006	0.802698	−0.1060	0.2403	0.6996	0.838115	−0.8049
0.0404	0.7997	0.820255	−0.0609	0.1604	0.7995	0.844991	−0.5639
0.0211	0.8987	0.838557	−0.0346	0.0798	0.9002	0.851663	−0.3113
0.3603	0.0998	0.727218	−0.2368	0.8101	0.0998	0.794962	−0.4479
0.3198	0.2002	0.742496	−0.4967	0.7198	0.2001	0.806299	−0.8192
0.2802	0.3000	0.757158	−0.6049	0.6299	0.3001	0.816348	−1.0680
0.2402	0.3999	0.771428	−0.6131	0.5400	0.4000	0.825103	−1.1939
0.1998	0.5002	0.785612	−0.5667	0.4499	0.5002	0.832605	−1.1908
0.1599	0.6001	0.799677	−0.4688	0.3598	0.6002	0.838995	−1.0832
0.1201	0.7001	0.813919	−0.3586	0.2698	0.7002	0.844553	−0.8937
0.0801	0.7999	0.828304	−0.2475	0.1799	0.8001	0.849485	−0.6483
0.0401	0.9000	0.842818	−0.1134	0.0901	0.8998	0.853865	−0.3564
				0.4922	0.4415	0.826157	−1.1846
			T= 308.15 K				
0.0900	0.1001	0.693647	−0.0258	0.5394	0.1010	0.746705	−0.3308
0.0806	0.2001	0.708795	−0.0576	0.4801	0.2000	0.760931	−0.6577
0.0698	0.3001	0.724180	−0.0447	0.4198	0.3003	0.774360	−0.8387
0.0615	0.3987	0.740221	−0.0291	0.3600	0.4000	0.786965	−0.9036
0.0502	0.5005	0.757042	0.0061	0.3003	0.4997	0.798830	−0.8601
0.0400	0.6003	0.774414	0.0294	0.2399	0.6000	0.810287	−0.7599
0.0289	0.7008	0.792653	0.0360	0.1803	0.6994	0.821235	−0.6024
0.0200	0.7999	0.811869	0.0260	0.1197	0.8006	0.832144	−0.4134
0.0102	0.8998	0.831986	0.0188	0.0604	0.8994	0.842690	−0.2245
0.1799	0.1000	0.702762	−0.1167	0.7197	0.1003	0.774765	−0.4139
0.1586	0.2066	0.719040	−0.2443	0.6399	0.2002	0.787347	−0.7780
0.1401	0.3001	0.733356	−0.2697	0.5599	0.3001	0.798702	−1.0093
0.1204	0.4001	0.748918	−0.2503	0.4788	0.4016	0.809057	−1.1106
0.1000	0.5002	0.764818	−0.2108	0.4000	0.5000	0.818148	−1.1139
0.0802	0.6001	0.781218	−0.1573	0.3203	0.5996	0.826161	−0.9837
0.0597	0.7006	0.798307	−0.1195	0.2403	0.6996	0.833742	−0.8161
0.0404	0.7997	0.815832	−0.0721	0.1604	0.7995	0.840580	−0.5739
0.0211	0.8987	0.834090	−0.0418	0.0798	0.9002	0.847198	−0.3177
0.3603	0.0998	0.722902	−0.2270	0.8101	0.0998	0.790918	−0.4499
0.3198	0.2002	0.738170	−0.4949	0.7198	0.2001	0.802181	−0.8236
0.2802	0.3000	0.752822	−0.6087	0.6299	0.3001	0.812151	−1.0727
0.2402	0.3999	0.767087	−0.6217	0.5400	0.4000	0.820843	−1.1995
0.1998	0.5002	0.781263	−0.5787	0.4499	0.5002	0.828298	−1.1978
0.1599	0.6001	0.795318	−0.4829	0.3598	0.6002	0.834652	−1.0918
0.1201	0.7001	0.809532	−0.3716	0.2698	0.7002	0.840180	−0.9036
0.0801	0.7999	0.823887	−0.2590	0.1799	0.8001	0.845073	−0.6575
0.0401	0.9000	0.838353	−0.1204	0.0901	0.8998	0.849400	−0.3625
				0.4922	0.4415	0.821873	−1.1910
			T= 313.15 K				
0.0900	0.1001	0.689263	−0.0165	0.5394	0.1010	0.742427	−0.3240
0.0806	0.2001	0.704427	−0.0584	0.4801	0.2000	0.756634	−0.6579
0.0698	0.3001	0.719820	−0.0524	0.4198	0.3003	0.770034	−0.8424

Table 3 (*Continued*)

x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})
0.0615	0.3987	0.735861	−0.0411	0.3600	0.4000	0.782622	−0.9111
0.0502	0.5005	0.752672	−0.0078	0.3003	0.4997	0.794474	−0.8705
0.0400	0.6003	0.770031	0.0147	0.2399	0.6000	0.805921	−0.7728
0.0289	0.7008	0.788252	0.0217	0.1803	0.6994	0.816844	−0.6149
0.0200	0.7999	0.807436	0.0146	0.1197	0.8006	0.827718	−0.4236
0.0102	0.8998	0.827511	0.0121	0.0604	0.8994	0.838218	−0.2307
0.1799	0.1000	0.698368	−0.1037	0.7197	0.1003	0.770609	−0.4130
0.1586	0.2066	0.714660	−0.2424	0.6399	0.2002	0.783140	−0.7809
0.1401	0.3001	0.728984	−0.2747	0.5599	0.3001	0.794441	−1.0140
0.1204	0.4001	0.744551	−0.2607	0.4788	0.4016	0.804750	−1.1168
0.1000	0.5002	0.760449	−0.2246	0.4000	0.5000	0.813810	−1.1223
0.0802	0.6001	0.776834	−0.1715	0.3203	0.5996	0.821799	−0.9936
0.0597	0.7006	0.793906	−0.1336	0.2403	0.6996	0.829352	−0.8265
0.0404	0.7997	0.811401	−0.0835	0.1604	0.7995	0.836155	−0.5828
0.0211	0.8987	0.829619	−0.0489	0.0798	0.9002	0.842725	−0.3233
0.3603	0.0998	0.718545	−0.2153	0.8101	0.0998	0.786838	−0.4513
0.3198	0.2002	0.733810	−0.4920	0.7198	0.2001	0.798029	−0.8274
0.2802	0.3000	0.748459	−0.6122	0.6299	0.3001	0.807928	−1.0773
0.2402	0.3999	0.762720	−0.6299	0.5400	0.4000	0.816560	−1.2049
0.1998	0.5002	0.776895	−0.5909	0.4499	0.5002	0.823971	−1.2045
0.1599	0.6001	0.790940	−0.4966	0.3598	0.6002	0.830294	−1.1002
0.1201	0.7001	0.805139	−0.3856	0.2698	0.7002	0.835792	−0.9128
0.0801	0.7999	0.819458	−0.2699	0.1799	0.8001	0.840649	−0.6660
0.0401	0.9000	0.833882	−0.1271	0.0901	0.8998	0.844928	−0.3679
				0.4922	0.4415	0.817569	−1.1973
			T= 318.15 K				
0.0900	0.1001	0.684842	−0.0047	0.5394	0.1010	0.738104	−0.3131
0.0806	0.2001	0.700027	−0.0576	0.4801	0.2000	0.752299	−0.6550
0.0698	0.3001	0.715430	−0.0589	0.4198	0.3003	0.765679	−0.8444
0.0615	0.3987	0.731477	−0.0528	0.3600	0.4000	0.778252	−0.9170
0.0502	0.5005	0.748287	−0.0227	0.3003	0.4997	0.790095	−0.8797
0.0400	0.6003	0.765631	−0.0002	0.2399	0.6000	0.801533	−0.7845
0.0289	0.7008	0.783839	0.0068	0.1803	0.6994	0.812435	−0.6263
0.0200	0.7999	0.802991	0.0032	0.1197	0.8006	0.823281	−0.4334
0.0102	0.8998	0.823032	0.0049	0.0604	0.8994	0.833739	−0.2367
0.1799	0.1000	0.693933	−0.0872	0.7197	0.1003	0.766410	−0.4083
0.1586	0.2066	0.710248	−0.2387	0.6399	0.2002	0.778898	−0.7810
0.1401	0.3001	0.724582	−0.2783	0.5599	0.3001	0.790147	−1.0161
0.1204	0.4001	0.740158	−0.2703	0.4788	0.4016	0.800417	−1.1211
0.1000	0.5002	0.756061	−0.2385	0.4000	0.5000	0.809441	−1.1278
0.0802	0.6001	0.772434	−0.1860	0.3203	0.5996	0.817415	−1.0018
0.0597	0.7006	0.789487	−0.1472	0.2403	0.6996	0.824947	−0.8359
0.0404	0.7997	0.806960	−0.0951	0.1604	0.7995	0.831720	−0.5914
0.0211	0.8987	0.825137	−0.0556	0.0798	0.9002	0.838245	−0.3286
0.3603	0.0998	0.714144	−0.1995	0.8101	0.0998	0.782718	−0.4493
0.3198	0.2002	0.729412	−0.4862	0.7198	0.2001	0.793843	−0.8283
0.2802	0.3000	0.744064	−0.6138	0.6299	0.3001	0.803677	−1.0797
0.2402	0.3999	0.758331	−0.6375	0.5400	0.4000	0.812251	−1.2081
0.1998	0.5002	0.772503	−0.6020	0.4499	0.5002	0.819622	−1.2094
0.1599	0.6001	0.786544	−0.5099	0.3598	0.6002	0.825917	−1.1071
0.1201	0.7001	0.800732	−0.3994	0.2698	0.7002	0.831389	−0.9210
0.0801	0.7999	0.815019	−0.2809	0.1799	0.8001	0.836212	−0.6736
0.0401	0.9000	0.829402	−0.1334	0.0901	0.8998	0.840448	−0.3729
				0.4922	0.4415	0.813235	−1.2010
			T= 323.15 K				
0.0900	0.1001	0.680384	0.0090	0.5394	0.1010	0.733739	−0.3026
0.0806	0.2001	0.695593	−0.0554	0.4801	0.2000	0.747939	−0.6546
0.0698	0.3001	0.711013	−0.0649	0.4198	0.3003	0.761296	−0.8475
0.0615	0.3987	0.727073	−0.0650	0.3600	0.4000	0.773854	−0.9232
0.0502	0.5005	0.743885	−0.0379	0.3003	0.4997	0.785704	−0.8908
0.0400	0.6003	0.761216	−0.0151	0.2399	0.6000	0.797136	−0.7977
0.0289	0.7008	0.779421	−0.0090	0.1803	0.6994	0.808016	−0.6383
0.0200	0.7999	0.798541	−0.0082	0.1197	0.8006	0.818835	−0.4429
0.0102	0.8998	0.818546	−0.0012	0.0604	0.8994	0.829257	−0.2423
0.1799	0.1000	0.689460	−0.0691	0.7197	0.1003	0.762168	−0.4052
0.1586	0.2066	0.705809	−0.2354	0.6399	0.2002	0.774627	−0.7839
0.1401	0.3001	0.720151	−0.2814	0.5599	0.3001	0.785825	−1.0202
0.1204	0.4001	0.735749	−0.2813	0.4788	0.4016	0.796058	−1.1268
0.1000	0.5002	0.751662	−0.2539	0.4000	0.5000	0.805064	−1.1362
0.0802	0.6001	0.768014	−0.1997	0.3203	0.5996	0.813015	−1.0108
0.0597	0.7006	0.785058	−0.1609	0.2403	0.6996	0.820526	−0.8452
0.0404	0.7997	0.802511	−0.1063	0.1604	0.7995	0.827274	−0.5995
0.0211	0.8987	0.820656	−0.0623	0.0798	0.9002	0.833759	−0.3331
0.3603	0.0998	0.709700	−0.1825	0.8101	0.0998	0.778556	−0.4498
0.3198	0.2002	0.724979	−0.4802	0.7198	0.2001	0.789624	−0.8318
0.2802	0.3000	0.739645	−0.6164	0.6299	0.3001	0.799395	−1.0840

Table 3 (*Continued*)

x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	x_1	x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})
0.2402	0.3999	0.753912	−0.6446	0.5400	0.4000	0.807924	−1.2140
0.1998	0.5002	0.768090	−0.6133	0.4499	0.5002	0.815255	−1.2160
0.1599	0.6001	0.782133	−0.5236	0.3598	0.6002	0.821523	−1.1148
0.1201	0.7001	0.796315	−0.4137	0.2698	0.7002	0.826969	−0.9289
0.0801	0.7999	0.810574	−0.2919	0.1799	0.8001	0.831768	−0.6812
0.0401	0.9000	0.824918	−0.1391	0.0901	0.8998	0.835963	−0.3772
				0.4922	0.4415	0.808885	−1.2072

Table 4
Parameters A_p of Eq. (2) and the corresponding PD and σ of the fits for the binary systems.

T (K)	A_0	A_1	A_2	A_3	A_4	PD (%)	σ (cm^3 mol^{-1})
1-Butanol (1) + cyclohexylamine (2)							
288.15	−4.9739	−0.9516	0.7023	0.4039		0.32	0.0051
293.15	−5.0031	−0.9213	0.6499	0.3867		0.33	0.0052
298.15	−5.0293	−0.8900	0.6059	0.3746		0.32	0.0051
303.15	−5.0540	−0.8627	0.5612	0.3680		0.32	0.0050
308.15	−5.0756	−0.8377	0.5060	0.3435		0.34	0.0051
313.15	−5.0984	−0.8135	0.4846	0.3432		0.32	0.0049
318.15	−5.1092	−0.7783	0.4584	0.3377		0.30	0.0047
323.15	−5.1324	−0.7509	0.4439	0.2854		0.29	0.0047
1-Butanol (1) + n-heptane (2)							
288.15	0.6041	−0.6367	0.1188	−0.2357	0.3376	0.93	0.0021
293.15	0.6647	−0.6839	0.0740	−0.3176	0.4949	1.05	0.0028
298.15	0.7387	−0.7319	0.0185	−0.4031	0.6618	1.03	0.0030
303.15	0.8184	−0.7838	−0.0179	−0.4943	0.8115	1.07	0.0035
308.15	0.9107	−0.8386	−0.0530	−0.6071	0.9734	1.06	0.0039
313.15	1.0113	−0.8951	−0.0820	−0.7304	1.1441	1.11	0.0046
318.15	1.1330	−0.9522	−0.1015	−0.8466	1.3644	1.10	0.0050
323.15	1.2605	−1.0223	−0.1169	−0.9907	1.5496	1.11	0.0053
Cyclohexylamine (1) + n-heptane (2)							
288.15	1.2537	−0.5444	0.3720	0.2252		0.41	0.0017
293.15	1.2065	−0.5553	0.3288	0.2399		0.42	0.0016
298.15	1.1583	−0.5640	0.2953	0.2351		0.43	0.0016
303.15	1.1035	−0.5708	0.2718	0.2351		0.48	0.0018
308.15	1.0471	−0.5766	0.2592	0.2168		0.50	0.0018
313.15	0.9869	−0.5830	0.2406	0.2185		0.56	0.0018
318.15	0.9238	−0.5905	0.2248	0.2139		0.59	0.0018
323.15	0.8596	−0.5919	0.2151	0.1979		0.50	0.0015

For the determination of PRSV parameters of a mixture (a and b), two different types of mixing rules are used: vdW1 and TCBT.

The vdW1 mixing rule [8] can be expressed by the following equations:

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2} [1 - k_{ij} + l_{ij}(x_i - x_j)] \quad (6)$$

$$b = \sum_i \sum_j x_i x_j (b_i b_j)^{1/2} (1 - m_{ij}) \quad (7)$$

where k_{ij}, l_{ij} and m_{ij} are the binary interaction parameters. The TCBT mixing rule [9] developed for no reference pressure conditions, relates the excess molar Gibbs energy, G^E, to the excess molar Gibbs energy based on the van der Waals reference fluid (vdW), G^E_{vdW}, can be presented as:

$$\frac{G^E}{RT} - \frac{G^E_{vdW}}{RT} + (Z - Z_{vdW}) = \ln\left[\left(\frac{V^*_{vdW} - 1}{V^* - 1}\right)\left(\frac{b_{vdW}}{b}\right)\right] - \frac{1}{w-u}\left[\frac{a^*}{b^*}\ln\left(\frac{V^* + w}{V^* + u}\right) - \frac{a^*_{vdW}}{b^*_{vdW}}\ln\left(\frac{V^*_{vdW} + w}{V^*_{vdW} + u}\right)\right] \quad (8)$$

where G^E_{vdW} is calculated for the PRSV CEOS.

Table 5
Parameters B_i of Eq. (3) and the corresponding PD and σ of the fits for the 1-butanol (1) + cyclohexylamine (2) + n-heptane (3) system.

T (K)	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15
1-Butanol(1) + cyclohexylamine(2) + n-heptane(3)								
B_0	-1.6919×10^{-2}	-1.6751×10^{-2}	-1.6544×10^{-2}	-1.6400×10^{-2}	-1.6268×10^{-2}	-1.6111×10^{-2}	-1.5950×10^{-2}	-1.5760×10^{-2}
B_1	-3.2063×10^{-2}	-3.1811×10^{-2}	-3.1234×10^{-2}	-3.0879×10^{-2}	-3.0565×10^{-2}	-3.0251×10^{-2}	-2.9764×10^{-2}	-2.9353×10^{-2}
B_2	-3.0218×10^{-2}	-2.9946×10^{-2}	-2.9738×10^{-2}	-2.9609×10^{-2}	-2.9530×10^{-2}	-2.9271×10^{-2}	-2.8993×10^{-2}	-2.8394×10^{-2}
B_3	2.4032×10^{-2}	2.4608×10^{-2}	2.4918×10^{-2}	2.5443×10^{-2}	2.6158×10^{-2}	2.6774×10^{-2}	2.6868×10^{-2}	2.7546×10^{-2}
B_4	1.0109×10^{-2}	1.0444×10^{-2}	1.1550×10^{-2}	1.2297×10^{-2}	1.3102×10^{-2}	1.3440×10^{-2}	1.3856×10^{-2}	1.3493×10^{-2}
B_5	4.0160×10^{-2}	3.9717×10^{-2}	3.8388×10^{-2}	3.7578×10^{-2}	3.6888×10^{-2}	3.6402×10^{-2}	3.5638×10^{-2}	3.4614×10^{-2}
B_6	-8.1166×10^{-3}	-8.6672×10^{-3}	-9.3075×10^{-3}	-1.0006×10^{-2}	-1.0944×10^{-2}	-1.1547×10^{-2}	-1.1726×10^{-2}	-1.2577×10^{-2}
B_7	7.4599×10^{-3}	7.0070×10^{-3}	5.8249×10^{-3}	5.0969×10^{-3}	4.3155×10^{-3}	3.9007×10^{-3}	3.3531×10^{-3}	3.5053×10^{-3}
B_8	-4.1141×10^{-3}	-5.0603×10^{-3}	-5.1071×10^{-3}	-5.5693×10^{-3}	-6.1328×10^{-3}	-7.2428×10^{-3}	-7.6723×10^{-3}	-8.1544×10^{-3}
PD (%)	0.60	0.59	0.59	0.58	0.58	0.58	0.57	0.58
σ (cm^3 mol^{-1})	0.0097	0.0096	0.0095	0.0095	0.0094	0.0094	0.0093	0.0094

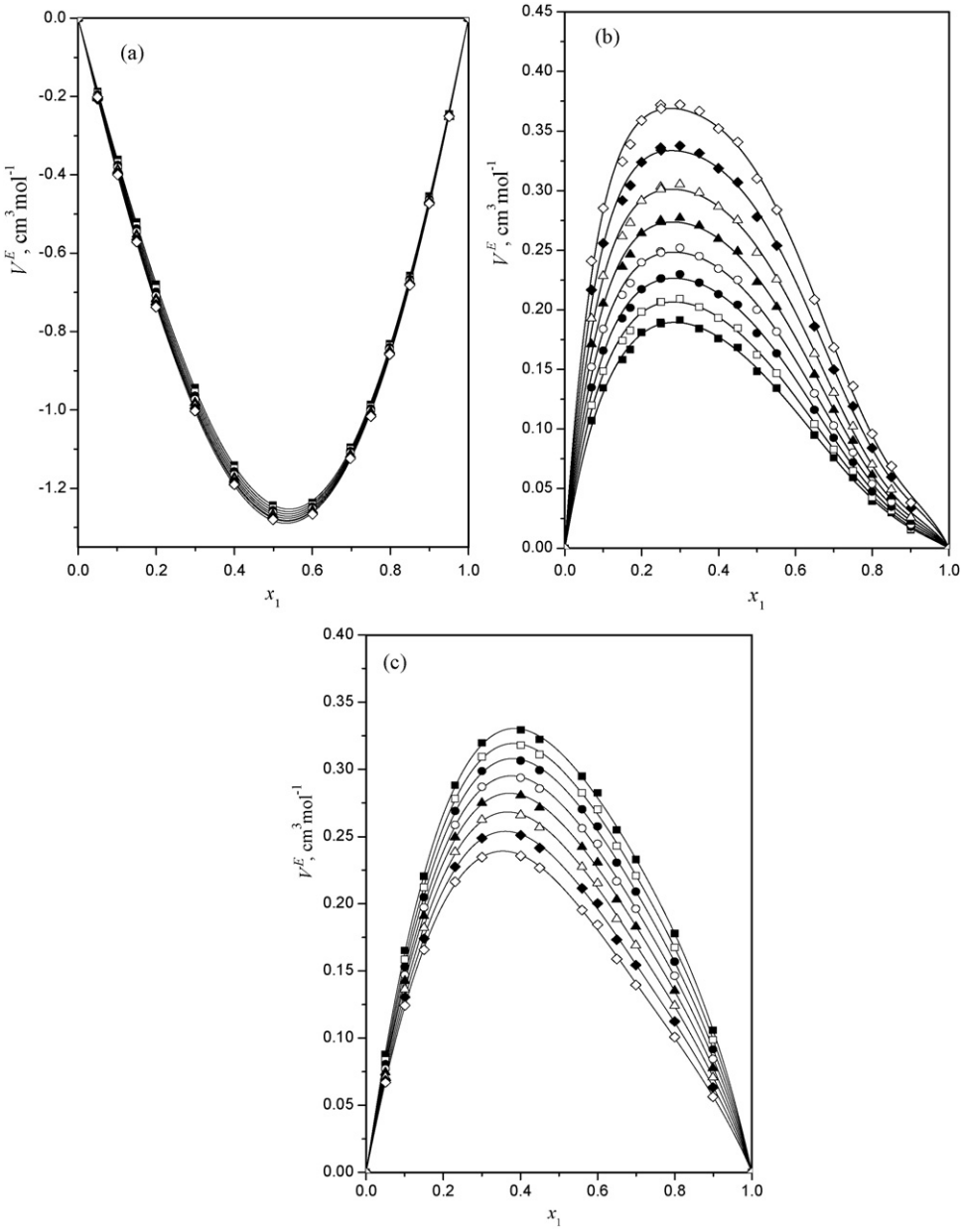

Fig. 1. Experimental values of V^E data for system (a) 1-butanol (1) + cyclohexylamine (2), (b) 1-butanol (1) + n-heptane (2), (c) cyclohexylamine (1) + n-heptane (2). Symbols refer to experimental points at: (■) 288.15 K; (□) 293.15 K; (●) 298.15 K; (○) 303.15 K; (▲) 308.15 K; (△) 313.15 K; (♦) 318.15 K; (◊) 323.15 K, while the lines represent the results calculated by the Eq. (2).

Parameters a_{vdW} and b_{vdW} are determined by Eqs. (11) and (12), whereas the reduced parameters a^*, b^*, a^*_{vdW} and b^*_{vdW} are obtained from the equations:

$$a^* = \frac{Pa}{R^2T^2} \quad b^* = \frac{Pb}{RT} \tag{9}$$

$V^* = V/b = Z/b^*$ is the reduced liquid volume at P and T of the mixture. The compressibility factors Z and Z_{vdW} are calculated from PRSV equation. Bearing in mind that equation for V^* evaluation does not have an explicit solution, an iterative technique was required for the calculation.

In this work, the NRTL equation [34] is used as the G^E model:

$$\frac{G^E}{RT} = \sum_i x_i \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_k x_k G_{ki}} \tag{10}$$

For a binary mixture the following equations are incorporated:

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \quad G_{21} = \exp(-\alpha_{12}\tau_{21})$$
$$\tau_{12} = \frac{(g_{12} - g_{22})}{RT} = \frac{\Delta g_{12}}{RT} \quad \tau_{21} = \frac{(g_{21} - g_{11})}{RT} = \frac{\Delta g_{21}}{RT} \tag{11}$$

and for a ternary mixture:

$$\tau'_{ij} = \tau_{ij} + \frac{\sum_{k=1}^{n} x_k \Delta g_{ijk}}{RT} \tag{12}$$

The Δg_{12} and Δg_{21} denote the binary energy parameters, while Δg_{ijk} is the ternary contribution.

For the temperature range, model parameters were used as temperature dependent:

$$Y = Y_1 + Y_2 T \tag{13}$$

where $Y = k_{ij}$, l_{ij}, m_{ij}, Δg_{12} and Δg_{21}. All models used here for V^E calculations are obtained applying sets of corresponding equations

Table 6
Correlation of the V^E data by the temperature independent PRSV CEOS models for the investigated binary systems from T=(288.15 to 323.15 K) and atmospheric pressure.

T (K)	$k_{ij,1}$	$l_{ij,1}$	$m_{ij,1}$	$\Delta g_{12,1}$ (J mol^{-1})	$\Delta g_{21,1}$ (J mol^{-1})	PD (%)	σ (cm^3 mol^{-1})
1-Butanol (1) + cyclohexylamine (2)							
288.15							
vdW1-2[a]	0.1774		0.0412			3.30	0.0502
vdW1-3[b]	0.0196	−0.0307	0.0214			1.50	0.0216
TCBT-2[c]				-0.373112×10^4	0.559453×10^4	1.65	0.0286
TCBT-3[d]	0.0957			0.265661×10^4	0.221502×10^4	0.52	0.0078
293.15							
vdW1-2	0.1720		0.0413			3.20	0.0491
vdW1-3	0.0205	−0.0285	0.0217			1.39	0.0203
TCBT-2				-0.378598×10^4	0.570172×10^4	1.36	0.0228
TCBT-3	0.0942			0.254508×10^4	0.208372×10^4	0.51	0.0078
298.15							
vdW1-2	0.1654		0.0411			3.14	0.0481
vdW1-3	0.0211	−0.0263	0.0218			1.31	0.0191
TCBT-2				-0.378103×10^4	0.555980×10^4	1.56	0.0260
TCBT-3	0.0963			0.258348×10^4	0.205619×10^4	0.46	0.0073
303.15							
vdW1-2	0.1586		0.0409			3.09	0.0472
vdW1-3	0.0217	−0.0243	0.0220			1.23	0.0180
TCBT-2				-0.380179×10^4	0.553076×10^4	1.55	0.0264
TCBT-3	0.0952			0.249640×10^4	0.194296×10^4	0.45	0.0071
308.15							
vdW1-2	0.1512		0.0405			3.08	0.0466
vdW1-3	0.0220	−0.0225	0.0221			1.15	0.0169
TCBT-2				-0.382402×10^4	0.551632×10^4	1.52	0.0260
TCBT-3	0.0928			0.237077×10^4	0.180111×10^4	0.43	0.0070
313.15							
vdW1-2	0.1425		0.0399			3.08	0.0464
vdW1-3	0.0240	−0.0209	0.0225			1.08	0.0160
TCBT-2				-0.383838×10^4	0.548593×10^4	1.49	0.0251
TCBT-3	0.0931			0.234511×10^4	0.173797×10^4	0.42	0.0068
318.15							
vdW1-2	0.1297		0.0385			3.05	0.0457
vdW1-3	0.0234	−0.0191	0.0224			1.07	0.0158
TCBT-2				-0.387932×10^4	0.555983×10^4	1.20	0.0202
TCBT-3	−0.0395			0.743235×10^4	-0.549749×10^4	0.39	0.0070
323.15							
vdW1-2	0.1169		0.0370			3.12	0.0463
vdW1-3	0.0233	−0.0181	0.0225			1.05	0.0151
TCBT-2				-0.389693×10^4	0.553953×10^4	1.17	0.0208
TCBT-3	0.0938			0.231350×10^4	0.160995×10^4	0.35	0.0065
288.15–323.15							
vdW1-2	0.0339		0.0237			3.84	0.0559
vdW1-3	0.0087	−0.0238	0.0203			1.36	0.0205
TCBT-2				0.187199×10^4	-0.221204×10^4	2.69	0.0443
TCBT-3	−0.0104			0.190331×10^4	-0.261544×10^4	1.85	0.0276
1-Butanol (1) + n-heptane (2)							
288.15							
vdW1-2	0.0503		−0.0237			5.69	0.0129
vdW1-3	−0.1621	−0.0617	−0.0515			1.25	0.0030
TCBT-2				0.376634×10^4	0.227849×10^3	3.66	0.0091
TCBT-3	−0.0620			0.355326×10^3	0.764664×10^5	1.36	0.0034
293.15							
vdW1-2	0.0544		−0.0230			6.02	0.0153
vdW1-3	−0.1649	−0.0632	−0.0528			1.54	0.0045
TCBT-2				0.370477×10^4	0.161360×10^3	4.32	0.0119
TCBT-3	−0.0608			0.375858×10^3	0.772363×10^5	0.96	0.0023
298.15							
vdW1-2	0.0582		−0.0223			6.15	0.0177
vdW1-3	−0.1688	−0.0648	−0.0543			1.75	0.0059
TCBT-2				0.366426×10^4	0.866426×10^2	4.79	0.0156
TCBT-3	−0.0597			0.386906×10^3	0.773314×10^5	0.78	0.0021
303.15							
vdW1-2	0.0621		−0.0216			6.42	0.0205
vdW1-3	−0.1694	−0.0654	−0.0555			1.95	0.0075
TCBT-2				0.357706×10^4	0.463472×10^2	5.30	0.0171
TCBT-3	−0.0589			0.390291×10^3	0.772120×10^5	0.78	0.0025

Table 6 (*Continued*)

T (K)	$k_{ij,1}$	$l_{ij,1}$	$m_{ij,1}$	$\Delta g_{12,1}$ (J mol^{-1})	$\Delta g_{21,1}$ (J mol^{-1})	PD (%)	σ (cm^3 mol^{-1})
308.15							
vdW1-2	0.0664		−0.0208			6.73	0.0238
vdW1-3	−0.1702	−0.0662	−0.0567			2.15	0.0094
TCBT-2				0.353250×10^4	-0.164733×10^2	5.49	0.0207
TCBT-3	−0.0578			0.401707×10^3	0.775918×10^5	0.73	0.0026
313.15							
vdW1-2	0.0705		−0.0200			7.04	0.0276
vdW1-3	−0.1694	−0.0664	−0.0578			2.42	0.0117
TCBT-2				0.348922×10^4	-0.736984×10^2	5.79	0.0244
TCBT-3	−0.0562			0.442648×10^3	0.790414×10^5	0.91	0.0032
318.15							
vdW1-2	0.0739		−0.0193			7.49	0.0325
vdW1-3	−0.1625	−0.0647	−0.0581			2.78	0.0146
TCBT-2				0.344477×10^4	-0.125838×10^3	6.26	0.0290
TCBT-3	−0.0563			0.404658×10^3	0.782284×10^5	0.70	0.0029
323.15							
vdW1-2	0.0783		−0.0184			7.83	0.0374
vdW1-3	−0.1618	−0.0651	−0.0593			3.06	0.0173
TCBT-2				0.339621×10^4	-0.173275×10^3	6.53	0.0334
TCBT-3	0.0160			0.407822×10^4	0.776788×10^5	0.83	0.0038
288.15–323.15							
vdW1-2	0.0601		−0.0220			7.47	0.0274
vdW1-3	0.0448	−0.0066	−0.0244			6.56	0.0228
TCBT-2				0.337307×10^4	0.149487×10^3	85.58	0.2829
TCBT-3	−0.1257			0.342645×10^4	-0.413447×10^4	10.32	0.0391
Cyclohexylamine (1) + n-heptane (2)							
288.15							
vdW1-2	0.0446		−0.0120			3.41	0.0127
vdW1-3	−0.0527	−0.0209	−0.0256			1.84	0.0075
TCBT-2				0.208254×10^4	-0.118697×10^3	2.86	0.0125
TCBT-3	−0.0977			0.623552×10^4	-0.497534×10^4	0.58	0.0023
293.15							
vdW1-2	0.0423		−0.0121			3.15	0.0114
vdW1-3	−0.0497	−0.0198	−0.0254			1.66	0.0065
TCBT-2				0.207913×10^4	-0.134042×10^3	2.59	0.0121
TCBT-3	−0.0988			0.622172×10^4	-0.500575×10^4	0.60	0.0024
298.15							
vdW1-2	0.0407		−0.0122			2.88	0.0102
vdW1-3	−0.0454	−0.0186	−0.0250			1.38	0.0054
TCBT-2				0.211042×10^4	-0.172676×10^3	2.38	0.0105
TCBT-3	−0.1007			0.627303×10^4	-0.507006×10^4	0.42	0.0019
303.15							
vdW1-2	0.0387		−0.0123			2.82	0.0095
vdW1-3	−0.0444	−0.0181	−0.0250			1.49	0.0052
TTCBT-2				0.212412×10^4	-0.200050×10^3	2.35	0.0103
TCBT-3	−0.1042			0.644987×10^4	-0.520206×10^4	0.82	0.0030
308.15							
vdW1-2	0.0373		−0.0123			2.79	0.0091
vdW1-3	−0.0425	−0.0175	−0.0249			1.45	0.0048
TCBT-2				0.214298×10^4	-0.229477×10^3	2.36	0.0098
TCBT-3	−0.1056			0.645284×10^4	-0.523901×10^4	0.88	0.0030
313.15							
vdW1-2	0.0354		−0.0124			2.73	0.0084
vdW1-3	−0.0374	−0.0161	−0.0243			1.49	0.0045
TCBT-2				0.217017×10^4	-0.264962×10^3	2.35	0.0090
TCBT-3	−0.1062			0.638214×10^4	-0.523970×10^4	0.81	0.0028
318.15							
vdW1-2	0.0338		−0.0125			2.68	0.0079
vdW1-3	−0.0315	−0.0146	−0.0236			1.46	0.0043
TCBT-2				0.218914×10^4	-0.293958×10^3	2.34	0.0086
TCBT-3	−0.1081			0.641189×10^4	-0.529331×10^4	0.84	0.0027
323.15							
vdW1-1							
vdW1-2	0.0321		−0.0126			2.69	0.0074
vdW1-3	−0.0272	−0.0134	−0.0230			1.41	0.0038
TCBT-2				0.221445×10^4	-0.327500×10^3	2.34	0.0081
TCBT-3	−0.1118			0.657565×10^4	-0.541694×10^4	0.71	0.0020

Table 6 (*Continued*)

T (K)	$k_{ij,1}$	$l_{ij,1}$	$m_{ij,1}$	$\Delta g_{12,1}$ (J mol^{-1})	$\Delta g_{21,1}$ (J mol^{-1})	PD (%)	σ (cm^3 mol^{-1})
288.15–323.15							
vdW1-2	0.0186		−0.0154			6.46	0.0224
vdW1-3	−0.0040	−0.0091	−0.0190			1.91	0.0068
TCBT-2				0.212858×10^4	-0.218262×10^3	16.82	0.0581
TCBT-3	−0.0221			0.126546×10^4	-0.418681×10^3	2.51	0.0092

[a] Eqs. (6), (7) and (13); $l_{ij} = 0$.
[b] Eqs. (6), (7) and (13).
[c] Eqs. (8)–(11) and (13); $k_{ij} = l_{ij} = m_{ij} = 0$; $\alpha_{ij} = 0.3$ (found by trial and error and set to 0.3 in all cases).
[d] Eqs. (8)–(11) and (13); $l_{ij} = m_{ij} = 0$; $\alpha_{ij} = 0.3$.

Table 7
Correlation of the V^E data by the temperature dependent PRSV CEOS models for the investigated binary systems from T = (288.15 to 323.15 K) and atmospheric pressure.

	$k_{ij,1}$ $k_{ij,2}$ (K^{-1})	$l_{ij,1}$ $l_{ij,2}$ (K^{-1})	$m_{ij,1}$ $m_{ij,2}$ (K^{-1})	$\Delta g_{12,1}$ (J mol^{-1}) $\Delta g_{12,2}$ (J mol^{-1} K^{-1})	$\Delta g_{21,1}$ (J mol^{-1}) $\Delta g_{22,2}$ (J mol^{-1} K^{-1})	PD (%)	σ (cm^3 mol^{-1})
1-Butanol (1) + cyclohexylamine (2)							
vdW1-2[a]	0.3402		0.252×10^{-1}			3.14	0.0476
	-0.610×10^{-3}		0.499×10^{-4}				
vdW1-3[b]	-0.523×10^{-1}	−0.1371	0.740×10^{-2}			1.22	0.0180
	0.242×10^{-3}	0.371×10^{-3}	0.478×10^{-4}				
TCBT-2[c]				-0.293541×10^4	0.691550×10^4	1.80	0.0297
				-0.276804×10^1	-0.480520×10^1		
TCBT-3[d]	0.396×10^{-1}			0.529623×10^3	0.373858×10^4	1.21	0.0200
				0.539652×10^4	-0.825143×10^1		
1-Butanol (1) + n-heptane (2)							
vdW1-2	−0.1263		-0.583×10^{-1}			6.76	0.0250
	0.624×10^{-3}		0.122×10^{-3}				
vdW1-3	−0.5273	−0.1492	-0.336×10^{-1}			2.15	0.0104
	0.117×10^{-2}	0.272×10^{-3}	-0.736×10^{-4}				
TCBT-2				0.403468×10^4	0.548120×10^4	10.53	0.0467
				-0.117304×10^1	-0.180907×10^2		
TCBT-3	-0.687×10^{-1}			0.344494×10^4	-0.462240×10^4	6.79	0.0257
				-0.189291×10^2	0.257277×10^2		
Cyclohexylamine (1) + n-heptane (2)							
vdW1-2	0.959×10^{-1}		-0.157×10^{-1}			2.98	0.0101
	-0.190×10^{-3}		0.109×10^{-4}				
vdW1-3	−0.1288	-0.516×10^{-1}	-0.260×10^{-1}			1.58	0.0055
	0.283×10^{-3}	0.111×10^{-3}	0.389×10^{-5}				
TCBT-2				0.211291×10^3	0.219229×10^4	3.66	0.0118
				0.655445×10^1	-0.804924×10^1		
TCBT-3	-0.338×10^{-1}			-0.849853×10^4	-0.421199×10^3	2.43	0.0083
				0.429689×10^4	0.224698×10^1		

[a] Eqs. (6), (7) and (13); $l_{ij} = 0$.
[b] Eqs. (6), (7) and (13).
[c] Eqs. (6)–(11) and (13); $k_{ij} = l_{ij} = m_{ij} = 0$; $\alpha_{ij} = 0.3$
[d] Eqs. (6)–(11) and (13); $l_{ij} = m_{ij} = 0$; $\alpha_{ij} = 0.3$.

Table 8
Prediction of V^E by the PRSV CEOS models for the investigated ternary system from T = (288.15 to 323.15 K) and atmospheric pressure.

T (K)	vdW1-2[a]		vdW1-3[b]		TCBT-2[c]		TCBT-3[d]	
	PD (%)	σ (cm^3 mol^{-1})	PD (%)	σ (cm^3 mol^{-1})	PD (%)	σ (cm^3 mol^{-1})	PD (%)	σ (cm^3 mol^{-1})
1-Butanol(1) + cyclohexylamine(2) + n-heptane(3)								
288.15	15.86	0.2366	14.77	0.2186	10.68	0.1501	16.15	0.2707
293.15	15.88	0.2385	14.93	0.2215	11.31	0.1603	15.60	0.2642
298.15	15.90	0.2402	15.11	0.2244	11.46	0.1635	15.82	0.2668
303.15	15.90	0.2417	15.42	0.2292	11.78	0.1686	16.08	0.2630
308.15	15.89	0.2430	15.68	0.2334	12.20	0.1757	15.57	0.2538
313.15	15.82	0.2433	15.85	0.2366	12.32	0.1785	15.19	0.2523
318.15	15.67	0.2423	16.12	0.2408	12.68	0.1852	15.06	0.2419
323.15	15.45	0.2405	16.33	0.2450	13.05	0.1915	23.23	0.4065
288.15–323.15[e]	12.98	0.1980	12.94	0.1966	9.63	0.1659	16.26	0.2453
288.15–323.15[f]	15.96	0.2431	15.58	0.2322	11.06	0.1608	21.02	0.3267

[a] Eqs. (6), (7) and (13); $l_{ij} = 0$.
[b] Eqs. (6), (7) and (13).
[c] Eqs. (6)–(11) and (13); $k_{ij} = l_{ij} = m_{ij} = 0$; $\alpha_{ij} = 0.3$.
[d] Eqs. (6)–(11) and (13); $l_{ij} = m_{ij} = 0$; $\alpha_{ij} = 0.3$.
[e] Prediction of V^E using temperature independent binary parameters.
[f] Prediction of V^E using temperature dependent binary parameters.

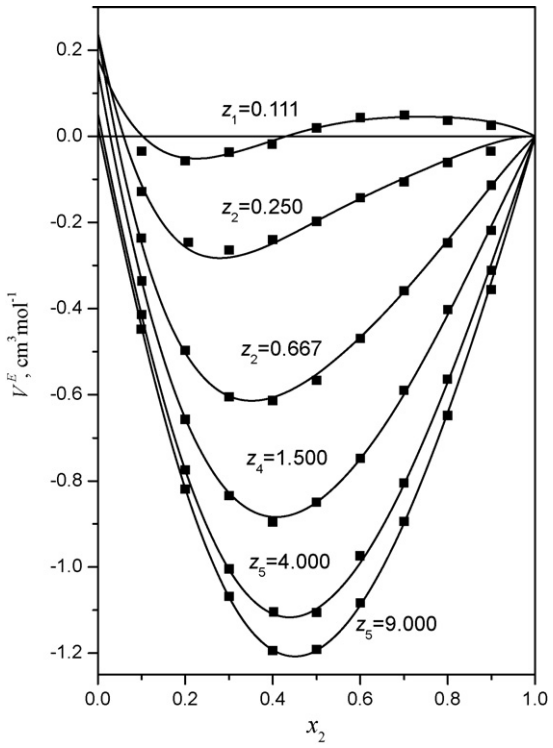

Fig. 2. Excess molar volume V^E for the ternary system 1-butanol (1) + cyclohexylamine (2) + n-heptane (3), at 303.15 K and atmospheric pressure, along the curves of constant ratio $z = x_1/x_3$ as a function of the cyclohexylamine composition. Symbols represent the experimental points. Solid curves were calculated by the Eq. (3).

as listed in the footnote of Tables 6–9. Parameters of these models were generated by minimizing the objective function Eq. (14) using the Marquardt optimisation technique [35]:

$$OF = \frac{1}{N}\sum_{i=i}^{N}\left(\frac{V^{E}_{exp} - V^{E}_{cal}}{V^{E}_{exp}}\right)^{2}_{i} \rightarrow \min \qquad (14)$$

Modelling of the binary and ternary V^E data was performed by the PRSV CEOS with the vdW1 and TCBT mixing rules and the values of the model parameters, PD(V^E) and the corresponding σ of binary data are presented in Table 6 (correlation with temperature independent models) and Table 7 (correlation with temperature dependent models), while the results of prediction and correlation for the ternary system are given in Tables 8 and 9, respectively. Inspection of Table 6 indicates that for all systems, at each temperature separately, the best results are obtained by the three parameter TCBT-3 model, and the superiority of TCBT-3 model is the most obvious in the case of 1-butanol + n-heptane system, especially comparing to two-parameter vdW1-2 and TCBT-2 models. The other three parameter model, vdW1-3 gave satisfactory results for this system at lower temperature but errors increase with temperature rising.

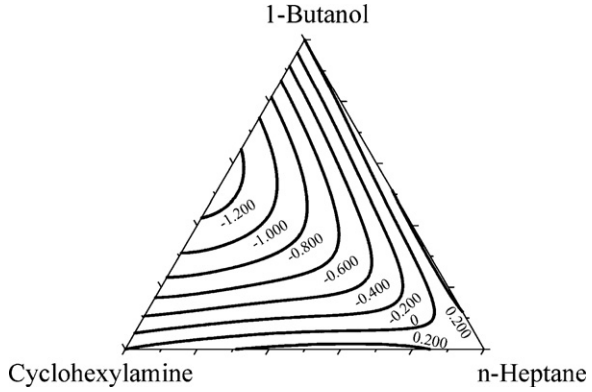

Fig. 3. Curves of constant V^E_{123} (cm^3 mol^{-1}) for the ternary system 1-butanol (1) + cyclohexylamine (2) + n-heptane (3), at 303.15 K. The lines represent results calculated by the Eq. (3).

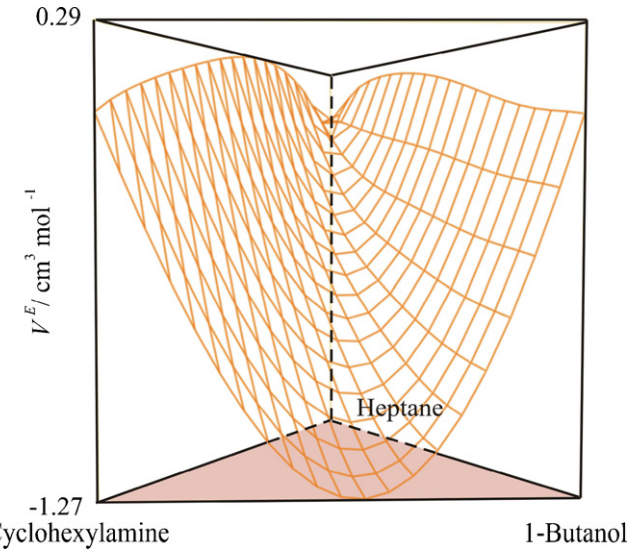

Fig. 4. Three-dimensional surface of V^E for the ternary system 1-butanol (1) + cyclohexylamine (2) + n-heptane (3), at 313.15 K, generated by the Eq. (3).

However, the influence of temperature on the V^E values is significant for the systems 1-butanol + n-heptane. Therefore, for the generation of unique set of parameters in the entire temperature range, it is recommendable to employ the temperature dependent models, especially in the case of TCBT-2 model, where the improvement of fit quality is obvious. On the other hand, in the case of 1-butanol + cyclohexylamine and cyclohexylamine + n-heptane systems, the temperature independent CEOS and CEOS/G^E models could be recommended.

Correlation of the binary V^E by temperature dependent models (Table 7) confirms that vdW1-3 as a simpler model shows the best results for each binary, while the TCBT-3 model gives good result only for the 1-butanol + cyclohexylamine system.

Prediction of V^E for the ternary system 1-butanol + cyclohexylamine + n-heptane at each temperature separately, and in the entire temperature range with unique set of parameters was performed with CEOS and CEOS/G^E models, and the results are presented in Table 8.

Correlations of V^E data for the ternary system 1-butanol + cyclohexylamine + n-heptane were performed by both CEOS/G^E models. Table 9 shows very good results obtained for both temperature independent models TCBT-2 and TCBT-3.

The TCBT-3 model is superior for the correlation in whole temperature range using temperature independent binary parameters, while the TCBT-2 model is better, when the temperature dependent binary parameters are employed.

The results of prediction obtained by all models could be treated as fair, particularly results of the TCBT-2 model which uses temperature independent binary parameters.

4.2. Prediction of V^E by empirical models

As an alternative to the CEOS and CEOS/G^E models, the prediction of V^E for multicomponent systems performed by empirical equations is proposed in the literature. Frequently used models

Table 9
Correlation of V^E by the PRSV CEOS models for the investigated ternary system from T = (288.15 to 323.15 K) and atmospheric pressure.

T (K)	Δg_{123} (J mol^{-1}) Δg_{132} (J mol^{-1})	Δg_{213} (J mol^{-1}) Δg_{231} (J mol^{-1})	Δg_{312} (J mol^{-1}) Δg_{321} (J mol^{-1})	PD (%)	σ (cm^3 mol^{-1})
1-Butanol(1) + cyclohexylamine(2) + n-heptane(3)					
T = 288.15					
TCBT-	-0.357380×10^4	-0.641159×10^4	0.454997×10^4	0.86	0.0138
2[a]	-0.46906×10^4	0.949585×10^4	0.583439×10^4		
TCBT-	-0.673764×10^4	-0.289614×10^4	-0.757649×10^5	0.67	0.0097
3	-0.140200×10^4	-0.357216×10^4	0.432792×10^4		
[b]					
T = 293.15					
TCBT-	-0.708047×10^3	-0.106954×10^5	0.563769×10^4	0.75	0.0126
2	0.183013×10^4	-0.256667×10^4	0.682319×10^4		
TCBT-	-0.657262×10^4	-0.274857×10^4	-0.748581×10^5	0.68	0.0099
3	-0.130778×10^4	-0.346002×10^4	0.424927×10^4		
T = 298.15					
TCBT-	0.708708×10^4	-0.713011×10^4	0.976606×10^3	0.79	0.0125
2	0.735977×10^4	-0.391644×10^4	-0.569624×10^4		
TCBT-	-0.702986×10^4	-0.266184×10^4	-0.714532×10^5	0.65	0.0097
3	-0.131532×10^4	-0.242071×10^4	0.425553×10^4		
T = 303.15					
TCBT-	0.712070×10^4	-0.702540×10^4	0.902317×10^3	0.81	0.0127
2	0.707879×10^4	-0.382281×10^4	-0.575759×10^4		
TCBT-	-0.655057×10^4	-0.258778×10^4	-0.748755×10^5	0.61	0.0089
3	-0.145959×10^4	-0.366334×10^4	0.446984×10^4		
T = 308.15					
TCBT-	-0.258511×10^4	-0.847090×10^4	0.413001×10^4	0.73	0.0115
2	-0.471288×10^2	0.106526×10^5	0.437853×10^4		
TCBT-	-0.693752×10^4	-0.237310×10^4	-0.703785×10^5	0.59	0.0090
3	-0.130291×10^4	-0.242369×10^4	0.434140×10^4		
T = 313.15					
TCBT-	-0.263193×10^4	-0.845300×10^4	0.415607×10^4	0.68	0.0109
2	-0.465262×10^4	0.102419×10^5	0.468745×10^4		
TCBT-	-0.717926×10^4	-0.225725×10^4	-0.668025×10^5	0.61	0.0093
3	-0.124640×10^4	-0.139781×10^4	0.424719×10^4		
T = 318.15					
TCBT-	-0.199020×10^4	-0.897819×10^4	0.353732×10^4	0.62	0.0107
2	-0.452180×10^4	0.101976×10^5	0.391305×10^4		
TCBT-	-0.706878×10^4	-0.207473×10^4	-0.662629×10^5	0.56	0.0084
3	-0.131071×10^4	-0.113721×10^4	0.426482×10^4		
T = 323.15					
TCBT-	-0.215684×10^4	-0.888451×10^4	0.358430×10^4	0.61	0.0106
2	-0.429425×10^4	0.915531×10^4	0.478824×10^4		
TCBT-	0.411612×10^4	-0.215534×10^4	-0.380491×10^5	0.65	0.0101
3	0.468795×10^3	-0.143234×10^4	-0.289743×10^3		
T = 288.15-323.15[c]					
TCBT-	-0.644843×10^4	0.605223×10^4	-0.141562×10^4	7.05	0.1138
2	-0.232910×10^4	-0.259398×10^4	0.388333×10^4		
TCBT-	-0.525349×10^4	-0.631499×10^4	0.665577×10^4	0.89	0.0135
3	-0.472423×10^4	0.108354×10^5	-0.117799×10^4		
T = 288.15-323.15[d]					
TCBT-	-0.151474×10^4	-0.826044×10^4	0.348138×10^4	1.12	0.0180
2	-0.475506×10^4	0.126732×10^5	0.302990×10^3		
TCBT-	0.434980×10^5	0.835418×10^3	-0.609880×10^4	2.80	0.0440
3	0.337098×10^4	0.131118×10^4	-0.595839×10^3		

[a] Eqs. (6)–(13); $k_{ij} = l_{ij} = m_{ij} = 0$; $\alpha_{ij} = 0.3$.
[b] Eqs. (6)–(13); $l_{ij} = m_{ij} = 0$; $\alpha_{ij} = 0.3$.
[c] Correlation of V^E using prediction results obtained with temperature independent binary parameters.
[d] Correlation of V^E using prediction results obtained with temperature dependent binary parameters.

are known as symmetric and asymmetric polynomials. Symmetric or geometrical polynomials used here are Kohler [10], Colinet [11], Radojković et al. [12], Rastogi et al. [13] and Jacob–Fitzner [14]. Asymmetric models applied in this work are the Scatchard et al. [15], Tsao–Smith [16] and Toop [17]. In symmetric polynomials the contribution of the three binaries to the ternary excess property are treated equally while asymmetric models indicate different individual contribution of one of the binaries [36].

The results of the V^E calculation performed by CEOS and empirical models were assessed by the root-mean-square deviation σ, Eq. (4), and by the percentage average absolute deviation PD(V^E), Eq. (5). Table 10 presents results of both the symmetric and asymmetric models considered in this work, and it can be seen that the satisfactory predictions of the experimental ternary V^E data were obtained by symmetric equations of Radojković et al., and Jacob–Fitzner, whereas the most inadequate estimation by this type of equation was with the equation of Rastogi et al. For all asymmetric equations, better PD and σ were obtained with n-heptane as the asymmetric component (Tsao–Smith[c], Toop[c] and Scatchard et al.[c]), while quite poor predictions were in the arrangement where 1-butanol was the asymmetric component. Also, Table 10 indicates that polynomial equations with cyclohexylamine as the asymmet-

Table 10
Prediction of the V^E data by the empirical models for the investigated ternary system and the corresponding PD(%) and σ ($cm^3\ mol^{-1}$).

T(K)	288.15		293.15		298.15		303.15		308.15		313.15		318.15		323.15	
	PD	σ	PD	σ	PD	σ	PD	σ	PD	σ	PD	σ	PD	σ	PD	σ
1-Butanol(1) + cyclohexylamine(2) + n-heptane(3)																
Radojković	13.60	0.1981	13.73	0.2008	13.88	0.2039	14.05	0.2072	14.24	0.2107	14.44	0.2142	14.69	0.2185	14.94	0.2229
Kohler	14.34	0.2072	14.44	0.2100	14.57	0.2131	14.73	0.2166	14.91	0.2204	15.12	0.2244	15.41	0.2293	15.69	0.2344
Jacob–Fitzner	13.60	0.1981	13.73	0.2008	13.88	0.2039	14.05	0.2072	14.24	0.2107	14.44	0.2142	14.69	0.2185	14.94	0.2229
Colinet	14.18	0.2061	14.30	0.2087	14.46	0.2116	14.64	0.2150	14.84	0.2186	15.07	0.2225	15.38	0.2273	15.67	0.2323
Tsao–Smith[a]	18.81	0.2684	18.85	0.2706	18.93	0.2732	19.04	0.2761	19.20	0.2797	19.39	0.2835	19.64	0.2880	19.94	0.2936
Tsao–Smith[b]	15.15	0.2203	15.49	0.2256	15.91	0.2319	16.35	0.2386	16.84	0.2461	17.38	0.2542	18.08	0.2641	18.73	0.2742
Tsao–Smith[c]	3.56	0.0471	3.52	0.0469	3.51	0.0470	3.52	0.0474	3.54	0.0479	3.59	0.0488	3.73	0.0508	3.85	0.0526
Toop[a]	16.24	0.2343	16.42	0.2379	16.63	0.2419	16.87	0.2464	17.17	0.2515	17.49	0.2570	17.88	0.2633	18.33	0.2706
Toop[b]	13.46	0.2003	13.64	0.2035	13.86	0.2072	14.09	0.2112	14.34	0.2155	14.61	0.2200	14.98	0.2256	15.29	0.2310
Toop[c]	12.99	0.1852	12.98	0.1863	13.00	0.1876	13.04	0.1891	13.08	0.1907	13.15	0.1925	13.30	0.1951	13.42	0.1976
Scatchard[a]	16.12	0.2326	16.31	0.2364	16.54	0.2405	16.80	0.2451	17.10	0.2503	17.44	0.2559	17.84	0.2623	18.29	0.2696
Scatchard[b]	13.29	0.1972	13.44	0.1999	13.64	0.2032	13.84	0.2067	14.06	0.2103	14.29	0.2142	14.59	0.2190	14.86	0.2236
Scatchard[c]	12.55	0.1811	12.58	0.1824	12.62	0.1839	12.69	0.1857	12.75	0.1875	12.84	0.1895	13.01	0.1923	13.13	0.1948
Rastogi	24.28	0.3434	24.49	0.3472	24.74	0.3511	25.05	0.3552	25.37	0.3592	25.71	0.3635	26.09	0.3682	26.46	0.3731

[a] 1-Butanol is asymmetric component.
[b] Cyclohexylamine is asymmetric component.
[c] n-Heptane is asymmetric component.

ric component (Tsao–Smith[b], Toop[b] and Scatchard et al.[b]) have some limitations. Increasing of the system temperature has no influence on calculations by the investigated polynomials (PD are slightly higher). Among the polynomials applied to ternary V^E prediction, the best results were obtained by Tsao–Smith[c] equation. This model presents the advantage of using only binary data, which are more available in literature.

Finally, it is interesting to compare the predicting results of polynomials (Table 10) with the corresponding results obtained by CEOS and CEOS/G^E models (Table 8). It is evident that the Tsao–Smith[c] model works much better than two and three parameters CEOS and CEOS/G^E models, while some of aforementioned polynomials are slightly better than the applied cubic equation of state models.

Acknowledgements

This work was supported by a grant from the Research Fund of Ministry of Science and Environmental Protection, Serbia and the Faculty of Technology and Metallurgy, University of Belgrade (project no. 142064).

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