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Volumetric properties of the ternary system ethanol + 2-butanone + benzene by the van der Waals and Twu–Coon–Bluck–Tilton mixing rules: experimental data, correlation and prediction

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Abstract

Densities of the ternary system ethanol + 2-butanone + benzene and its binaries ethanol + 2-butanone, ethanol + benzene and 2-butanone + benzene were measured at $T = 298.15\,\mathrm{K}$ and atmospheric pressure. From these densities excess molar volumes (V^E) were calculated and fitted to the Redlich–Kister equation for all binary mixtures and to the Nagata and Tamura equation; for the ternary system. The V^E data of the binary systems were correlated by the van der Waals (vdW1) and Twu–Coon–Bluck–Tilton (TCBT) mixing rules coupled with the Peng–Robinson–Stryjek–Vera (PRSV) equation of state. The prediction and correlation of V^E data for the ternary system were performed by the same models.

Keywords: Excess molar volume data; Equation of state; Mixing rules; Correlation; Prediction

1. Introduction

In our previous works [1–3], we investigated rigorous cubic equation of state (CEOS) models applied to the estimation of experimental excess molar volumes (V^E) of binary systems of acetonitrile with alcohols and other non-ideal binary systems such as diethers with alkanes.

In the present paper, we continue our studies by correlating and predicting the V^E for the ternary system by the modern Peng–Robinson–Stryjek–Vera (PRSV) equation of state [4] using two different mixing rules: (i) the van der Waals (vdW1) and (ii) the Twu–Coon–Bluck–Tilton (TCBT) [5]. Various forms of the vdW1 mixing rules were already successfully applied for correlation V^E data of diverse binary mixtures [6–9]. The TCBT mixing rule has been widely applied for calculation of vapor–liquid equilibria. This approach, based on the CEOS incorporating the G^E equation (CEOS/G^E models), was also used for fitting of V^E data [2,3].

Here, we present the experimental V^E data of the ethanol + 2-butanone + benzene system at 298.15 K for which no literature data are available, as well as the corresponding binaries. Binary and ternary data were fitted by the Redlich–Kister [10], and Nagata and Tamura [11] equation, respectively. Correlation and prediction of volumetric properties of these systems were performed by various vdW1 and TCBT models.

2. Experimental

Ethanol was supplied by Riedel-de Haën with a purity >99.8 mass%, 2-butanone and benzene were supplied by Aldrich with a purity >99.5 mass% (HPLC) and >99.9 mass% (HPLC), respectively. Table 1 lists the densities of the liquids measured in this work together with the values found in the literature. Since the agreement is good, no further purification was performed. All mixtures were prepared by mass using the cell and the procedure described previously [12,13]; presently, a Mettler balance with a precision of $\pm 1 \times 10^{-4}$ g was used. Error in mole fraction was estimated to be less than $\pm 1 \times 10^{-4}$.

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Table 1
Comparison of the measured densities of pure substances at 298.15 K with literature values

Component	Density ($g\,cm^{-3}$)	
	Measured	Literature
Ethanol	0.78525	0.78517 [14]
2-Butanone	0.79978	0.79985 [15]
Benzene	0.87362	0.87360 [8]

Densities were determined by means of an Anton Paar DMA 55 digital vibrating tube densimeter having a precision $\pm 1 \times 10^{-5}\,g\,cm^{-3}$. Calibration of the apparatus was performed periodically using ambient air and distilled (Millipore quality) water. Vibrating tube of the apparatus was thermostated at (298.15±0.01 K) using a system of the Heto Birkerød 04 PT 623 and Lauda R52 thermostatic water baths, ensuring a temperature stability of ±0.005 K. Temperature of water bath was measured by means of Beckman thermometer having a resolution of 0.002 K. This thermometer was calibrated at 298.15 K using a thermostatic bath with an accuracy of ±0.001 K, hence, it is believed that temperature accuracy in the measuring cell was within ±0.01 K.

3. Results and discussion

Excess molar volume V^E was computed using the following expression:

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

where M_i, x_i and ρ_i are the molar mass, mole fraction and density of the pure liquid i, respectively, ρ stands for the density of the mixture, and n denotes the number of components in the mixture.

Experimental densities and the corresponding excess molar volumes of the investigated binaries at $T = 298.15\,K$ are reported in Table 2 and plotted in Fig. 1a. Data for the binary mixtures were fitted to the Redlich–Kister type equation [10]:

$$V_{ij}^E = x_i x_j \sum_{p=0}^{k} A_p (x_i - x_j)^p \tag{2}$$

where adjustable parameters A_p were obtained by a least-squares method; k is the number of adjustable parameters determined by means of the F-test [16].

Adjustable parameters of the fits and the corresponding standard deviations, defined by the equation

$$\sigma = \left(\frac{\sum_{i=1}^{m} (V_{exp}^E - V_{cal}^E)^2}{m}\right)^{1/2} \tag{3}$$

are given in Table 3. In Eq. (3), m denotes the number of experimental data points.

Experimental densities and excess molar volumes of the present ternary system at $T = 298.15\,K$ are given in Table 4, while the curves of constant excess molar volumes are plotted in Fig. 2.

The excess ternary volumes were fitted using the expression proposed by Nagata and Tamura [11]:

$$V_{123}^E = V_{12}^E + V_{13}^E + V_{23}^E + x_1 x_2 x_3 RT(B_0 - B_1 x_1 - B_2 x_2 - B_3 x_1^2 - B_4 x_2^2 - B_5 x_1 x_2 - B_6 x_1^3 - B_7 x_2^3 - B_8 x_1^2 x_2) \tag{4}$$

Table 2
Experimental densities and excess molar volumes for the binary mixtures at 298.15 K

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 ($cm^3\,mol^{-1}$)
Ethanol (1) + 2-butanone (2)								
0.1013	0.79891	−0.013	0.4548	0.79537	−0.066	0.8001	0.79009	−0.066
0.2039	0.79802	−0.033	0.5047	0.79477	−0.073	0.8494	0.78907	−0.057
0.2975	0.79710	−0.047	0.6032	0.79339	−0.075	0.8960	0.78807	−0.049
0.3590	0.79646	−0.056	0.6557	0.79263	−0.078	0.9468	0.78669	−0.022
0.3993	0.79604	−0.064	0.7480	0.79109	−0.074			
Ethanol (1) + benzene (2)								
0.0523	0.87000	0.058	0.4042	0.84587	0.048	0.7634	0.81409	−0.040
0.1016	0.86676	0.075	0.5032	0.83807	0.023	0.8208	0.80788	−0.045
0.1994	0.86028	0.090	0.5687	0.83262	0.001	0.9035	0.79808	−0.035
0.3027	0.85319	0.078	0.6092	0.82903	−0.008	0.9659	0.79002	−0.019
0.3527	0.84967	0.063	0.6784	0.82266	−0.029			
2-Butanone (1) + benzene (2)								
0.0982	0.86652	−0.022	0.3181	0.85082	−0.086	0.6775	0.82445	−0.108
0.1614	0.86199	−0.039	0.3738	0.84684	−0.103	0.7134	0.82174	−0.101
0.1656	0.86168	−0.039	0.5037	0.83741	−0.122	0.7192	0.82134	−0.104
0.2033	0.85901	−0.052	0.5268	0.83572	−0.124	0.7746	0.81707	−0.083
0.2058	0.85879	−0.049	0.5681	0.83268	−0.125	0.8267	0.81306	−0.064
0.252	0.85552	−0.065	0.6570	0.82600	−0.112	0.9049	0.80711	−0.040
0.2993	0.85212	−0.077						

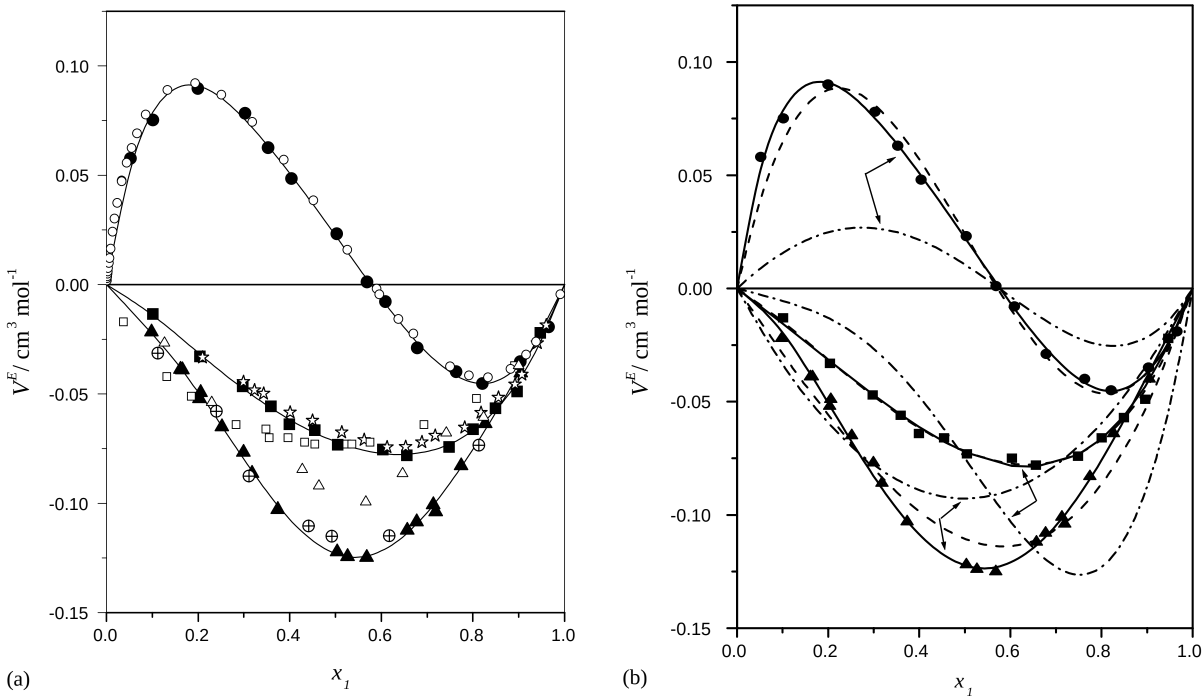

Fig. 1. Excess molar volumes V^E at 298.15 K. (a) Experimental values: ethanol (1) + 2-butanone (2): (■) this work, (☆) Letcher and Nevines [17], (□) Inarrea et al. [18]; ethanol (1) + benzene (2): (●) this work, (○) Marsh and Burfitt [19]; 2-butanone (1) + benzene (2): (▲) this work, (⊕) Grolier et al. [15], (△) Malhotra and Mahl [20]; ( ) Redlich–Kister equation. (b) Symbols represent experimental values. Models: (—) TCBT-3; (–·–·–·–) vdW1–1; (-----) vdW1–3.

Here V_{ij}^E are the binary contributions obtained from Eq. (2) and B_i denotes the adjustable parameters computed by the least-squares method. The fitting parameters of Eq. (4), along with the corresponding standard deviations σ calculated according to Eq. (3), are given in Table 3.

The V^E data at 298.15 K for the binaries investigated here, have been reported previously by several authors [15,17–20]. From Fig 1a it can be seen that our results of V^E for the system ethanol + 2-butanone are some what lower than those of Letcher and Nevines [17] with the same asymmetric shape of the V^E–x curve, while Inarrea et al. [18] obtained the symmetric shape of this curve. For the system, ethanol + benzene our V^E results agree very well with those of Marsh and Burfitt [19]. The V^E data for the 2-butanone + benzene system obtained here agree very well with those of Grolier et al. [15], while the results of Malhotra and Mahl [20] are more higher. Disagreements between our results and those reported earlier could be attributed to the different experimental techniques used.

Various interactions between the species present in the investigated mixtures result in the different shapes of V^E–x curves: dipole-induced dipole interactions between alkanol or ketone and polarizable benzene molecules; association between the keto group of ketone and proton of the hydroxy group of alkanol; self-association between alkanol molecules due to the hydrogen bonding.

As can be seen from Fig. 2, the V^E values for the ternary system are negative in the majority of the ternary composition field. It seems reasonable to assume that negative values of the ternary V^E data are mainly due

Table 3
Parameters A_p of Eq. (2), B_i of Eq. (4) and the corresponding standard deviations σ (cm^3 mol^{-1}) of the fits

Ethanol + 2-butanone					
$A_0 = -2.8437 \times 10^{-1}$	$A_1 = 1.5028 \times 10^{-1}$	$A_2 = -9.9479 \times 10^{-2}$	$A_3 = 9.7634 \times 10^{-2}$	$A_4 = 8.6984 \times 10^{-2}$	0.002
Ethanol + benzene					
$A_0 = 8.1345 \times 10^{-2}$	$A_1 = 5.8169 \times 10^{-1}$	$A_2 = 2.0470 \times 10^{-1}$	$A_3 = 3.4989 \times 10^{-1}$		0.003
2-Butanone + benzene					
$A_0 = -4.9162 \times 10^{-1}$	$A_1 = 1.5332 \times 10^{-1}$	$A_2 = 3.7165 \times 10^{-1}$	$A_3 = -4.5856 \times 10^{-2}$	$A_4 = -2.3929 \times 10^{-1}$	0.002
Ethanol + 2-butanone + benzene					
$B_0 = 3.2713 \times 10^{-3}$	$B_1 = 1.2833 \times 10^{-2}$	$B_2 = 6.7695 \times 10^{-3}$	$B_3 = -2.0800 \times 10^{-2}$	$B_4 = 4.9759 \times 10^{-4}$	0.004
$B_5 = -9.1976 \times 10^{-3}$	$B_6 = 2.4760 \times 10^{-2}$	$B_7 = -5.5281 \times 10^{-3}$	$B_8 = -6.5600 \times 10^{-3}$		

Table 4
Experimental densities and excess molar volumes for the system ethanol (1) + 2-butanone (2) + benzene (3) at 298.15 K

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})
0.0565	0.8926	0.80300	−0.027	0.2980	0.5985	0.80607	−0.096
0.0973	0.7100	0.81426	−0.085	0.2990	0.1505	0.84236	−0.048
0.0978	0.8051	0.80667	−0.051	0.3035	0.3482	0.82648	−0.125
0.0992	0.6085	0.82211	−0.113	0.3051	0.4436	0.81850	−0.128
0.0993	0.5025	0.83031	−0.124	0.3482	0.3067	0.82612	−0.117
0.1017	0.4455	0.83443	−0.117	0.3493	0.3458	0.82271	−0.115
0.1018	0.5450	0.82682	−0.119	0.3547	0.1473	0.83844	−0.064
0.1022	0.3373	0.84253	−0.101	0.3556	0.2503	0.83015	−0.108
0.1034	0.1944	0.85295	−0.052	0.3580	0.5411	0.80534	−0.095
0.1046	0.6404	0.81919	−0.106	0.3623	0.4402	0.81366	−0.117
0.1050	0.3967	0.83792	−0.116	0.3934	0.1177	0.83773	−0.054
0.1497	0.6497	0.81477	−0.099	0.4006	0.3482	0.81808	−0.119
0.1505	0.3494	0.83823	−0.114	0.4034	0.1452	0.83466	−0.064
0.1509	0.4457	0.83086	−0.132	0.4041	0.2447	0.82648	−0.104
0.1510	0.0980	0.85707	−0.036	0.4453	0.0982	0.83509	−0.050
0.1512	0.5453	0.82303	−0.124	0.4496	0.1527	0.83029	−0.081
0.1515	0.7480	0.80673	−0.071	0.4524	0.4467	0.80458	−0.103
0.1530	0.2460	0.84572	−0.073	0.4582	0.3415	0.81339	−0.118
0.1533	0.6958	0.81084	−0.093	0.4609	0.2443	0.82159	−0.111
0.1996	0.4504	0.82663	−0.125	0.5027	0.2456	0.81766	−0.112
0.2004	0.2464	0.84238	−0.086	0.5065	0.1475	0.82574	−0.081
0.2006	0.6982	0.80654	−0.084	0.5463	0.3512	0.80387	−0.108
0.2008	0.1512	0.84952	−0.045	0.5518	0.2478	0.81297	−0.129
0.2009	0.3469	0.83463	−0.114	0.5527	0.1469	0.82164	−0.089
0.2011	0.5460	0.81888	−0.120	0.6075	0.0973	0.82095	−0.083
0.2471	0.2440	0.83903	−0.082	0.6212	0.1864	0.81173	−0.124
0.2486	0.3519	0.83057	−0.120	0.6548	0.2458	0.80248	−0.111
0.2506	0.4488	0.82269	−0.131	0.6560	0.1457	0.81193	−0.114
0.2528	0.5440	0.81469	−0.118	0.6956	0.1058	0.81144	−0.093
0.2624	0.6363	0.80614	−0.092	0.7507	0.098	0.80622	−0.085
0.2937	0.2513	0.83489	−0.090	0.7533	0.1491	0.80115	−0.110

to specific interactions between different species predominating the effect of dissociation of the alcohol molecules.

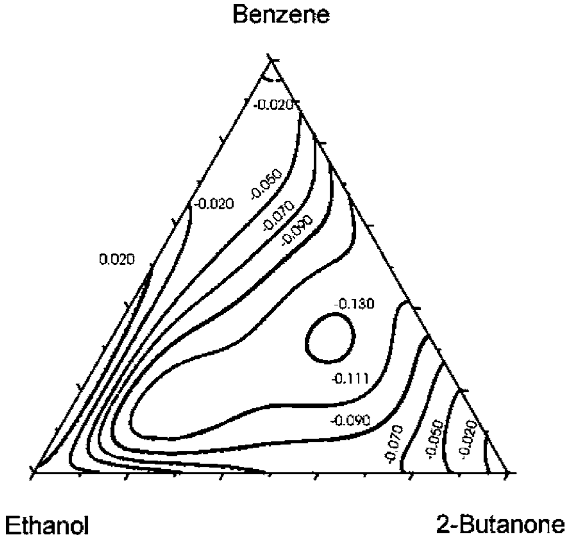

Fig. 2. Isolines of V^E (cm^3 mol^{-1}) for the system ethanol (1)+ 2-butanone (2)+ benzene (3) at 298.15 K.

4. Modeling by cubic equation of state

The general two-parameter cubic equation of state (CEOS) has the form:

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+ub)(V+wb)} \tag{5}$$

where the CEOS dependent constants u and w for the Peng–Robinson–Stryjek–Vera equation applied here are: $u = 1 - \sqrt{2}$ and $w = 1 + \sqrt{2}$. For the pure substance the energy a_i and covolume b_i parameters are determined by the following set of equations

$$a_i(T) = 0.457235\frac{(RT_{ci})^2}{P_{ci}}[1 + m_i(1 - T_{ri}^{1/2})]^2 \tag{6}$$

$$b_i = 0.077796\frac{RT_{ci}}{P_{ci}} \tag{7}$$

$$m_i = k_{0i} + k_{1i}(1 + T_{ri}^{1/2})(0.7 - T_{ri}) \tag{8}$$

$$\begin{aligned} k_{0i} &= 0.378893 + 1.4897153\omega_i - 0.1713848\omega_i^2 \\ &\quad + 0.0196554\omega_i^3 \end{aligned} \tag{9}$$

where R is the gas constant, T_{ci} and P_{ci} the critical temperature and pressure of component i, T_{ri} stands for the reduced temperature (T/T_{ci}), ω is; the acentric factor, and k_{1i} represents the pure substance adjustable parameter [4].

For the mixtures, two different types of mixing rules were incorporated in the PRSV CEOS as already mentioned: vdW1 and TCBT. vdW1 can be expressed in the general form as follows:

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2} [1 - k_{ij} + l_{ij}(x_i - x_j)] \tag{10}$$

$$b = \sum_i \sum_j x_i x_j (b_i b_j)^{1/2} (1 - m_{ij}) \tag{11}$$

where k_{ij}, l_{ij} and m_{ij} are the binary interaction parameters. New, very attractive TCBT mixing rule [5] developed recently for no reference pressure conditions and based on the van der Waals reference fluid (vdW) can be presented as:

$$\begin{aligned} &\frac{G^{\mathrm{E}}}{RT} - \frac{G^{\mathrm{E}}_{\mathrm{vdW}}}{RT} + (z - z_{\mathrm{vdW}}) \\ &\quad = \ln\left[\left(\frac{V^*_{\mathrm{vdW}} - 1}{V^* - 1}\right)\left(\frac{b_{\mathrm{vdW}}}{b}\right)\right] - \frac{1}{w - u} \\ &\qquad \times \left[\frac{a^*}{b^*} \ln\left(\frac{V^* + w}{V^* + u}\right) - \frac{a^*_{\mathrm{vdW}}}{b^*_{\mathrm{vdW}}} \ln\left(\frac{V^*_{\mathrm{vdW}} + w}{V^*_{\mathrm{vdW}} + u}\right)\right] \end{aligned} \tag{12}$$

where $G^{\mathrm{E}}_{\mathrm{vdW}}$ is calculated for the PRSV CEOS.

Parameters a_{vdW} and b_{vdW}; are determined by using Eqs. (10) and (11), whereas the reduced parameters a^*, b^*, a^*_{vdW} and b^*_{vdW} are obtained from the equations

$$a^* = \frac{Pa}{R^2T^2}, \qquad b^* = \frac{Pb}{RT} \tag{13}$$

$V^* = V/b = z/b^*$ is the reduced liquid volume at P and T of the mixture. The compressibility factors z and z_{vdW} are calculated from Eq. (1) expressed in the z form. Bearing in mind that V^* does not have an explicit solution, an iterative technique was required for the calculation.

The NRTL equation (21) in the following form

$$\frac{G^{\mathrm{E}}}{RT} = \sum_i x_i \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_k x_k G_{ki}} \tag{14}$$

was used as the G^{E} model [21], where for a binary mixture

$$\begin{aligned} G_{12} &= \exp(-\alpha_{12}\tau_{12}), \qquad G_{21} = \exp(-\alpha_{12}\tau_{21}), \\ \tau_{12} &= \frac{g_{12} - g_{22}}{RT}, \qquad \tau_{21} = \frac{g_{21} - g_{11}}{RT} \end{aligned} \tag{15}$$

and for a ternary mixture

$$\tau'_{ij} = \tau_{ij} + \frac{\sum_{k=1}^{n} x_k \Delta g_{ijk}}{RT} \tag{16}$$

Table 5
Correlation of the V^{E} data by the vdW1 and TCBT models for the investigated binary systems at 298.15 K

Model	Ethanol + 2-butanone	Ethanol + benzene	2-Butanone + benzene
vdW1–1 (Eqs. (5)–(11); $l_{ij} = m_{ij} = 0$)			
k_{ij}	1.1911×10^{-1}	7.4747×10^{-2}	-4.2557×10^{-4}
PD(V^{E}) (%)	35.90	30.19	13.57
σ (cm^3 mol^{-1})	0.033	0.034	0.020
vdW1–2 (Eqs. (5)–(11); $l_{ij} = 0$)			
k_{ij}	2.3731×10^{-2}	1.2930×10^{-1}	-6.1454×10^{-2}
m_{ij}	-1.7324×10^{-2}	9.6311×10^{-3}	-9.9751×10^{-3}
PD(V^{E}) (%)	2.33	19.51	8.70
σ (cm^3 mol^{-1})	0.002	0.027	0.012
vdW1–3 (Eqs. (5)–(11))			
k_{ij}	-1.3585×10^{-1}	-5.6028×10^{-2}	-4.6901×10^{-4}
l_{ij}	-2.2591×10^{-2}	-2.8492×10^{-2}	-4.0870×10^{-3}
m_{ij}	-4.2912×10^{-2}	-2.1890×10^{-2}	3.1079×10^{-4}
PD(V^{E}) (%)	1.96	4.95	5.24
σ (cm^3 mol^{-1})	0.002	0.007	0.008
TCBT-2 (Eqs. (5)–(15); $k_{ij} = l_{ij} = m_{ij} = 0$; $\alpha_{ij} = 0.3$)			
$g_{12}-g_{22}$ (J mol^{-1})	2.5433×10^{3}	8.5804×10^{2}	-2.6924
$g_{21}-g_{11}$ (J mol^{-1})	-7.6401×10^{2}	7.6123×10^{4}	7.5836×10^{4}
PD(V^{E}) (%)	2.27	4.05	3.56
σ (cm^3 mol^{-1})	0.002	0.004	0.006
TCBT-3 (Eqs. (5)–(15); $l_{ij} = m_{ij} = 0$; $\alpha_{ij} = 0.3$)			
$g_{12}-g_{22}$ (J mol^{-1})	4.4371×10^{2}	1.4365×10^{1}	1.3283×10^{3}
$g_{21}-g_{11}$ (J mol^{-1})	-3.6623×10^{3}	7.7585×10^{4}	2.5269×10^{3}
k_{ij}	-1.4391×10^{-1}	1.2893×10^{-2}	9.3404×10^{-2}
PD(V^{E}) (%)	2.16	2.30	1.53
σ (cm^3 mol^{-1})	0.002	0.003	0.002

Table 6
Prediction and correlation of the V^E for the ethanol (1) + 2-butanone (2) + benzene (3) system at 298.15 K

	Model		
Prediction			
	vdW1-1	vdW1-2	vdW1-3
PD(V^E) %	34.08	30.21	16.75
σ (cm^3 mol^{-1})	0.048	0.043	0.025
Correlation			
	TCBT-2[a]	TCBT-3[b]	
Δg_{123} (J mol^{-1})	-3.15956×10^5	3.05376×10^5	
Δg_{132} (J mol^{-1})	2.10641×10^5	-1.48092×10^5	
Δg_{213} (J mol^{-1})	1.11151×10^5	3.27865×10^5	
Δg_{231} (J mol^{-1})	-2.12988×10^5	-3.62213×10^4	
Δg_{312} (J mol^{-1})	-1.94874×10^6	2.32565×10^6	
Δg_{321} (J mol^{-1})	-3.73688×10^5	-7.34111×10^4	
PD(V^E) (%)	4.69	4.35	
σ (cm^3 mol^{-1})	0.007	0.007	

[a] Eqs. (5)–(16); $k_{ij} = l_{ij} = m_{ij} = 0$; $\alpha_{ij} = 0.3$.
[b] Eqs. (5)–(16); $l_{ij} = m_{ij} = 0$; $\alpha_{ij} = 0.3$.

$g_{12} - g_{22}$ and $g_{21} - g_{11}$ denote binary energy parameters, while Δg_{ijk} is the ternary contribution. Models used here for all calculations were obtained by applying sets of corresponding equations as listed in Table 5. Parameters of these models were generated by minimizing the objective function Eq. (17) using the Marquardt optimization technique [22]

$$\mathrm{OF} = \frac{1}{m}\sum_{i=1}^{m}\left(\frac{V^E_{\mathrm{exp}} - V^E_{\mathrm{cal}}}{V^E_{\mathrm{exp}}}\right)^2_i \rightarrow \min \qquad (17)$$

The results of the V^E calculation were assessed by the percentage average absolute deviation PD(V^E)

$$\mathrm{PD}(V^E) = \frac{100}{m}\sum_{i=1}^{m}\left|\frac{V^E_{\mathrm{exp}} - V^E_{\mathrm{cal}}}{(V^E_{\mathrm{exp}})_{\mathrm{max}}}\right|_i \qquad (18)$$

where $(V^E_{\mathrm{exp}})_{\mathrm{max}}$ denotes the maximum value of experimental V^E.

Modeling of the binary V^E data was performed by the PRSV CEOS with the vdW1 and TCBT mixing rules. Values of the model parameters, PD(V^E) and the corresponding σ are presented in Table 5. Inspection of this table indicates that for all systems the best results are obtained by the three parameter TCBT-3 model except in the case of the ethanol + 2-butanone system where vdW1–3 model worked slightly better. Good performance of the TCBT-3 model is, also, illustrated in Fig. 1b.

Binary interaction parameters of all aforementioned models (Table 5) were used for the V^E prediction of the ternary system ethanol + 2-butanone + benzene at 298.15 K. In Table 6 the corresponding PD(V^E) and σ are listed. Very high deviations obtained for the prediction by the TCBT models has been excluded from this table. On the other hand, agreement between experimental and predicted values obtained by the vdW1–1 and vdW1–2 models could be treated as fair, while the results corresponding to the vdW1–3 model are very good. Correlation of the same ternary was performed only by the TCBT models that include ternary contribution in the NRTL model as given by Eq. (16). Fitting of the ternary data performed by both TCBT models could be regarded as acceptable and very similar.

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