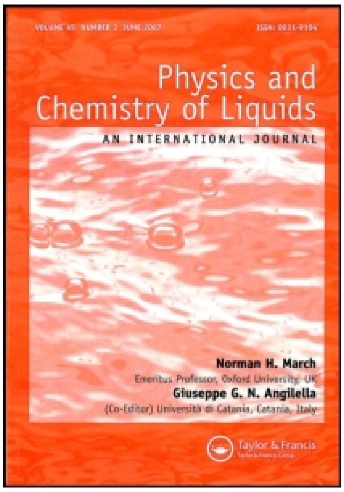

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Applicability of cubic equation of state mixing rules on correlation of excess molar volume of non-electrolyte binary mixtures - Part II

Mirjana LJ. Kijevčanin[a]; Bojan D. Djordjević[a]; Slobodan P. Šerbanović[a]; Ivona R. Radović[a]; Aleksandar Ž. Tasić[a]
[a] Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia and Montenegro

To cite this Article Kijevčanin, Mirjana LJ. , Djordjević, Bojan D. , Šerbanović, Slobodan P. , Radović, Ivona R. and Tasić, Aleksandar Ž.(2006) 'Applicability of cubic equation of state mixing rules on correlation of excess molar volume of non-electrolyte binary mixtures - Part II', Physics and Chemistry of Liquids, 44: 3, 233 — 247

To link to this Article: DOI: 10.1080/00319100600568962
URL: http://dx.doi.org/10.1080/00319100600568962

Physics and Chemistry of Liquids
Vol. 44, No. 3, June 2006, 233–247

Applicability of cubic equation of state mixing rules on correlation of excess molar volume of non-electrolyte binary mixtures – Part II

MIRJANA LJ. KIJEVČANIN*, BOJAN D. DJORDJEVIĆ,
SLOBODAN P. ŠERBANOVIĆ, IVONA R. RADOVIĆ
and ALEKSANDAR Ž. TASIĆ

Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4,
P.O. Box 35-03, Belgrade, Serbia and Montenegro

(*Received in final form 16 October 2005*)

The excess molar volume (V^E) data of the 24 binary highly non-ideal mixtures containing dicyclic ethers (593 data points) were correlated by the Peng–Robinson–Stryjek–Vera (PRSV) cubic equation of state (CEOS) coupled with two different classes of mixing rules: (i) the composition dependent van der Waals (vdW) mixing rule and (ii) the excess free energy mixing rules (CEOS/G^E) based on the approach of the Gupta–Rasmunssen–Fredenslund (GRF), as well as the Twu–Coon–Bluck–Tilton (TCBT) mixing rule; both rules with the NRTL equation as the G^E model. The results obtained by these models show that the type of applied mixing rules, including the number and position of interaction parameters are of great importance for a satisfactory correlation of V^E data. The GRF mixing rules gave mostly satisfactory results for V^E correlation of the non-ideal binary systems available at one isotherm of 298.15 K, while for the correlation in temperature range from 288.15 to 308.15 K the TCBT model can be recommended.

Keywords: Excess molar volume; Cubic equation of state; Correlation, mixing rules

1. Introduction

Cubic equations of state (CEOS) models are important thermodynamic tools used for the design of chemical processes and also for their further optimization. This part represents a continuation of our previous research [1] related to the correlation of the excess volume data of 21 binary non-electrolyte mixtures of monocyclic ethers with *n*-alkanes, 1-alcohols, cyclic and aromatic compounds, employing van der Waals (vdW) and Gupta–Rasmunssen–Fredenslund (GRF) as excess free energy mixing rules (CEOS/GE) coupled with the Peng–Robinson–Stryjek–Vera (PRSV) equation of state (PRSV CEOS). It was shown that in all cases, the GRF gave better results to those reached by the vdW models. Here, we have tried to extend further applicability of the

---

*Corresponding author. Tel.: +381-11-33-70-523. Fax: +381-11-33-70-387. Email: mirjana@tmf.bg.ac.yu

Physics and Chemistry of Liquids
ISSN 0031-9104 print: ISSN 1029-0451 online
DOI: 10.1080/00319100600568962

CEOS/G^{E}, involving the Twu–Coon–Bluck–Tilton (TCBT) models [2] to the correlation of excess molar volume of (V^{E}) data of the binary non-ideal systems of diverse structure and complexity, exhibiting very specific behavior. TCBT models were employed since in our recent papers [3,4] was shown that correlation with that kind of mixing rules led to exceptionally good results comparing to those obtained with the vdW models. Also, we considered together the results reached by the TCBT models and those achieved with models employed in our first paper (vdW1 and GRF). These analyses were performed for excess volume correlation quality for 24 mixtures of the dicyclic ethers with *n*-alkanes, 1-alcohols, and cyclohexane. The flexibility of the applied mixing rules to represent V^{E} data was tested, since the selected mixtures include non-ideal compounds, asymmetric shape of excess molar volume V^{E} *versus* composition (x_1) curve with very small or large excess values, etc.

2. Analysis of the data base

In the first part of our investigation [1] the V^{E} data of different kinds of systems with monoethers were correlated by the vdW and GRF models. This time, we decided to extend our work to the mixtures of dicyclic ethers with alkanes, alcohols, and cyclic organic compounds, since their V^{E} are almost 3 times larger, comparing to noticed for mixtures with monocyclic ethers [5–10], and generally, because the systems with diethers exhibit higher non-ideal behavior. This observation can be explained bearing in mind much stronger interactions present in pure diethers, which lead to much denser packing of molecules present in these compounds. This specific intermolecular order is deeply modified by adding of some other compound, causing a large positive excess molar volume effect.

Table 1 presents the binary systems investigated, the number of experimental data points and temperatures, as well as the source of the collected data.

All investigated systems were divided into two groups. The first group consists the experimental data at 298.15 K, whereas the second one is constituted by the data sets belonging to the temperature range from 288.15 to 308.15 K.

3. Cubic equation of state

As in the first part, the PRSV CEOS [16] was employed

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)}, \tag{1}$$

where P and T denote pressure and temperature, respectively, and R is the gas constant. For pure component i, the temperature dependent parameter a and parameter b are given by the following equations

$$a_i(T) = 0.457235\frac{(RT_{\mathrm{c}i})^2}{P_{\mathrm{c}i}}\left[1+m_i\left(1-T_{\mathrm{r}i}^{0.5}\right)\right]^2, \tag{2}$$

$$b_i = 0.077796\frac{RT_{\mathrm{c}i}}{P_{\mathrm{c}i}}, \tag{3}$$

Table 1. Binary systems used for V^E correlation.

System no.	System	No. of data points	T (K)	Reference
Dicyclic ether + alkane				
1	1,4-dioxane (1) + heptane (2)	46	288.15, 298.15, 308.15	[11]
2	1,4-dioxane (1) + octane (2)	46	288.15, 298.15, 308.15	[11]
3	1,4-dioxane (1) + nonane (2)	41	288.15, 298.15, 308.15	[11]
4	1,4-dioxane (1) + decane (2)	41	288.15, 298.15, 308.15	[11]
5	1,3-dioxolane (1) + heptane (2)	42	288.15, 298.15, 308.15	[12]
6	1,3-dioxolane (1) + octane (2)	42	288.15, 298.15, 308.15	[12]
7	1,3-dioxolane (1) + nonane (2)	41	288.15, 298.15, 308.15	[12]
8	1,3-dioxolane (1) + decane (2)	46	288.15, 298.15, 308.15	[12]
Dicyclic ether + alcohol				
9	1,4-dioxane (1) + butanol (2)	12	298.15	[13]
10	1,4-dioxane (1) + pentanol (2)	12	298.15	[13]
11	1,4-dioxane (1) + hexanol (2)	12	298.15	[13]
12	1,4-dioxane (1) + heptanol (2)	24	298.15	[13]
13	1,4-dioxane (1) + octanol (2)	12	298.15	[13]
14	1,4-dioxane (1) + nonanol (2)	33	298.15	[13]
15	1,4-dioxane (1) + decanol (2)	12	298.15	[13]
16	1,3-dioxolane (1) + butanol (2)	12	298.15	[14]
17	1,3-dioxolane (1) + pentanol (2)	11	298.15	[14]
18	1,3-dioxolane (1) + hexanol (2)	12	298.15	[14]
19	1,3-dioxolane (1) + heptanol (2)	12	298.15	[14]
20	1,3-dioxolane (1) + octanol (2)	22	298.15	[14]
21	1,3-dioxolane (1) + nonanol (2)	17	298.15	[14]
22	1,3-dioxolane (1) + decanol (2)	19	298.15	[14]
Dicyclic ether + cyclohexane				
23	1,4-dioxane (1) + cyclohexane (2)	13	298.15	[15]
24	1,3-dioxolane (1) + cyclohexane (2)	13	298.15	[15]

$$m_i = k_{0i} + k_{1i}\,(1 + T_{ri}^{0.5})\,(0.7 - T_{ri}), \tag{4}$$

$$k_{0i} = 0.378893 + 1.4897153\omega_i - 0.1713848\omega_i^2 + 0.0196554\omega_i^3. \tag{5}$$

In equations (2)–(5) subscripts c and r denote critical and reduced values, respectively, ω is the acentric factor, and k_{1i} is the pure component adjustable parameter [17].

4. Mixing rules

In order to examine the effect of the number and position of binary interaction parameters we used two different classes of mixing rules: (i) the composition dependent vdW one-fluid models [18] and (ii) two types of CEOS/G^E mixing rules – the general form based on the approach proposed by Gupta *et al.* (GRF) [19] and the mixing rule developed by Twu *et al.* (TCBT) [2].

4.1. *vdW one-fluid mixing rules*

For the parameters of mixture a and b, two forms of the vdW one-fluid rules were tested.

The energy parameter a, can be expressed by the following equation

$$a = \sum_i \sum_j x_i x_j a_{ij}. \tag{6}$$

The cross interaction parameter a_{ij}, has the form

$$a_{ij} = (a_i a_j)^{0.5}\big(1 - k_{ij} + l_{ij}(x_i - x_j)\big), \tag{7}$$

where equation (7) assumes $k_{ij} = k_{ji}$ and $l_{ij} = -l_{ji}$.

The covolumen parameter b can be defined in two ways; first, as a quadratic composition dependent function

$$b = \sum_i \sum_j x_i x_j b_{ij}, \tag{8}$$

where the cross interaction parameter b_{ij} is given by the equation

$$b_{ij} = \left(\frac{b_i + b_j}{2}\right)(1 - m_{ij}), \tag{9}$$

and second, as the linear composition dependence in the form

$$b = \sum_i x_i b_i. \tag{10}$$

Binary interaction parameters k_{ij}, l_{ij}, and m_{ij} can be treated as the linear temperature dependences by following equation:

$$k_{ij} = c_1 + c_2 T, \quad l_{ij} = c_3 + c_4 T, \quad m_{ij} = c_5 + c_6 T. \tag{11}$$

4.2. *Excess free energy mixing rules*

In the present article we used the general approach introduced by Gupta *et al.* (GRF) for VLE calculation since, as we illustrated in our first paper [1], it was successfully applied to V^{E} calculation in a very wide region of temperatures. Beside the GRF mixing rule we also used the TCBT mixing rule developed recently for VLE calculations at no reference pressure conditions and based on the vdW reference fluid.

The basic equation of the GRF mixing rule relates the excess Helmholtz free energy with the excess Gibbs energy [20]

$$\left(\frac{G^{\mathrm{E}}}{RT}\right)_{\mathrm{CEOS}} = \left(\frac{A^r - \sum_i x_i A^r i}{RT}\right) - \sum_i x_i \ln\left(\frac{V}{V_i}\right) + \frac{pV^{\mathrm{E}}}{RT}, \tag{12}$$

where Ar is the residual Helmholtz energy, and V and V_i are the molar volumes of mixture and of pure component i, respectively.

The form of $G^{\mathrm{E}}_{\mathrm{CEOS}}$ for the PRSV equation is

$$\left(\frac{G^{\mathrm{E}}}{RT}\right)_{\mathrm{CEOS}} = -\ln\left(1-\frac{b}{V}\right) + \sum_i x_i \ln\left(1-\frac{b_i}{V_i}\right) - \sum_i x_i \ln\left(\frac{V}{V_i}\right) + \frac{pV^{\mathrm{E}}}{RT} + \frac{a}{2\sqrt{2}bRT}\ln\left(\frac{V+(1-\sqrt{2})b}{V+(1+\sqrt{2})b}\right) - \sum_i x_i \frac{a_i}{2\sqrt{2}b_iRT}\ln\left(\frac{V_i+(1-\sqrt{2})b_i}{V_i+(1+\sqrt{2})b_i}\right). \tag{13}$$

The GRF mixing rule is obtained by equating the excess Gibbs energy from equation of state, equation (13) and the activity coefficient model

$$\left(\frac{G^{\mathrm{E}}}{RT}\right)_{\mathrm{CEOS}} = \left(\frac{G^{\mathrm{E}}}{RT}\right)_{G^{\mathrm{E}}_{\mathrm{model}}}. \tag{14}$$

The new, very attractive TCBT mixing rule can be presented as:

$$\frac{G^{\mathrm{E}}}{RT} - \frac{G^{\mathrm{E}}_{\mathrm{vdW}}}{RT} + (z - z_{\mathrm{vdW}}) = \ln\left[\left(\frac{V^*_{\mathrm{vdW}}-1}{V^*-1}\right)\left(\frac{b_{\mathrm{vdW}}}{b}\right)\right] - \frac{1}{w-u}\left[\frac{a^*}{b^*}\ln\left(\frac{V^*+w}{V^*+u}\right) - \frac{a^*_{\mathrm{vdW}}}{b^*_{\mathrm{vdW}}}\ln\left(\frac{V^*_{\mathrm{vdW}}+w}{V^*_{\mathrm{vdW}}+u}\right)\right] \tag{15}$$

where $G^{\mathrm{E}}_{\mathrm{vdW}}$ is calculated for the PRSV CEOS. Parameters a_{vdW} and b_{vdW} are determined by incorportating equations for k_{ij} and m_{ij} as interaction parameters of the vdW model.

The reduced parameters a^*, b^*, a^*_{vdW}, and b^*_{vdW} are obtained from the equations

$$a^* = Pa/R^2T^2, \quad b^* = Pb/RT \tag{16}$$

$V^* = V/b = z/b^*$ is the reduced liquid volume at P and T of the mixture. The compressibility factors z and z_{vdW} are calculated from equation (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. This mixing rule also involves the binary parameters introduced by an activity coefficient G^{E} model. Using this approach, a complex but very flexible TCBT mixing rule was established [21].

As an activity coefficient model for the G^{E} calculations the NRTL equation [22] was chosen

$$\frac{G^{\mathrm{E}}}{RT} = \sum_i x_i \frac{\sum_j x_j G_{ji}\tau_{ji}}{\sum_k x_k G_{ki}}. \tag{17}$$

For binary systems the following relations are valid

$$\begin{aligned} G_{12} &= \exp(-\alpha_{12}\tau_{12}), & G_{21} &= \exp(-\alpha_{21}\tau_{21}), \\ \tau_{12} &= (g_{12}-g_{22})/RT, & \tau_{21} &= (g_{21}-g_{11})/RT. \end{aligned} \tag{18}$$

The NRTL model binary parameters $g_{12}-g_{22}$ and $g_{21}-g_{11}$ a non-randomness parameter α_{12} ($\alpha_{12}=\alpha_{21}$) are given by the following linear temperature dependent forms:

$$\alpha_{12} = c_1 + c_2T, \quad g_{12}-g_{22} = c_3 + c_4T, \quad g_{21}-g_{11} = c_5 + c_6T. \tag{19}$$

Table 2. Thermodynamic CEOS and CEOS/G^{E} models used in the present work.

Model	Equations
vdW1	(6)–(9), (11); $c_2=c_6=0$, $l_{ij}=0$
vdW1-1	(6)–(9), (11); $l_{ij}=0$
MvdW1	(6), (7), (10), (11); $c_2=c_4=0$
MvdW1-1	(6), (7), (10), (11)
GRF1	(12)–(14), (17)–(19); $\alpha_{12}=0.3$; $c_4=c_6=0$
GRF2	(12)–(14), (17)–(19); $c_2=c_4=c_6=0$
GRF3	(12)–(14), (17)–(19)
TCBT1	(6)–(9), (15)–(19); $\alpha_{12}=0.3$; $c_4=c_6=0$, $l_{ij}=0$
TCBT2	(6)–(9), (15)–(19), $c_2=c_4=c_6=0$, $l_{ij}=0$
TCBT3	(6)–(9), (15–(19); $l_{ij}=0$

All CEOS and CEOS/G^{E} models obtained on the bases of the above mentioned equations are summarized in table 2.

4.3. *Representation of CEOS and CEOS/G^{E} models*

The general equation for the excess volume calculation is given as

$$V^{\mathrm{E}} = V - \sum_i x_i V_i. \tag{20}$$

The binary interaction parameters of the models were determined using the modified Marquardt optimization technique which incorporates principles of the Monte Carlo method, by minimizing the following objective function:

$$OF = \frac{1}{m}\sum_{i=1}^{m}\left(\frac{V_{\mathrm{exp}}^{\mathrm{E}} - V_{\mathrm{cal}}^{\mathrm{E}}}{V_{\mathrm{exp}}^{\mathrm{E}}}\right)_i^2 \rightarrow \min, \tag{21}$$

where m stands for the number of experimental data points.

The correlating results of V^{E} were assessed by the percentage average absolute deviation PD(V^{E}) defined as

$$\mathrm{PD}(V^{\mathrm{E}}) = \frac{100}{m}\sum_{i=1}^{m}\left|\frac{V_{\mathrm{exp}}^{\mathrm{E}} - V_{\mathrm{cal}}^{\mathrm{E}}}{\left(V_{\mathrm{exp}}^{\mathrm{E}}\right)_{\max}}\right|_i. \tag{22}$$

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

5. Results and discussion

Correlation of V^{E} data for the binary systems of dicyclic ethers, listed in table 1 was performed by the CEOS and CEOS/G^{E} models. Table 4 presents the results of the correlation at 298.15 K. Results of the correlation in entire temperature range are presented in tables 6 (for the models with temperature independent parameters) and in table 8 (for the models with temperature dependent parameters).

Table 3. Coefficients optimized at 298.15 K with the vdW1, MvdW1, GRF1, and GRF2 mixing rules.

				GRF2
	vdW1	MvdW1	GRF1[a]	c_1
	c_1	c_1	c_3 (J mol^{-1})	c_3 (J mol^{-1})
System no.	c_5	c_3	c_5 (J mol^{-1})	c_5 (J mol^{-1})
9	0.162613E−1	0.460393E−1	0.569537E+5	0.292204E+0
	−0.409048E−2	−0.499089E−2	0.275561E+4	0.590245E+5
				0.274552E+4
10	0.119640E−1	0.581766E−1	0.530866E+5	0.240172E+0
	−0.596683E−2	−0.118006E−1	0.289903E+4	0.715751E+5
				0.282474E+4
11	0.117344E−1	0.638712E−1	0.490815E+5	0.220478E+0
	−0.636964E−2	−0.168048E−1	0.447216E+4	0.770517E+5
				0.419977E+4
12	0.134540E−1	0.675962E−1	0.527508E+5	0.230433E+0
	−0.579510E−2	−0.244950E−1	0.203876E+4	0.735350E+5
				0.199964E+4
13	−0.818887E−2	0.386163E−1	0.560009E+5	0.754231E+0
	−0.478930E−2	−0.212791E−1	0.692172E+3	0.182065E+5
				0.725538E+3
14	0.657831E−3	0.652326E−1	−0.447820E+3	0.681225E+0
	−0.585411E−2	−0.367252E−1	0.298674E+4	0.203796E+5
				0.285157E+4
15	−0.154043E−1	0.181498E−1	−0.276978E+4	0.775570E+0
	−0.,292960E−2	−0.187566E−1	0.408601E+4	−0.140253E+4
				0.248362E+4
16	−0.834782E−2	0.452103E−1	−0.457472E+3	0.101734E+1
	−0.760712E−2	−0.151907E−1	0.335937E+4	0.107210E+4
				0.263786E+4
17	−0.723124E−2	0.528111E−1	−0.545723E+3	0.829163E+0
	−0.792876E−2	−0.220381E−1	0.315531E+4	0.106438E+4
				0.286670E+4
18	−0.961700E−2	0.557930E−1	−0.261640E+3	0.619030E+0
	−0.807564E−2	−0.276651E−1	0.429252E+4	0.934157E+3
				0.360220E+4
19	−0.119694E−1	0.542766E−1	−0.193262E+4	0.196579E+0
	−0.703734E−2	−0.360441E−1	0.484135E+4	−0.360929E+4
				0.639207E+4
20	−0.338188E−1	0.190890E−1	−0.381165E+4	0.615995E−1
	−0.534147E−2	−0.289288E−1	0.728898E+4	−0.123253E+5
				0.176126E+5
21	−0.245534E−1	0.494410E−1	−0.138927E+4	0.861558E−1
	−0.654409E−2	−0.483592E−1	0.750461E+4	−0.954972E+4
				0.159128E+5
22	−0.538582E−1	−0.134781E−1	0.337361E+4	0.260226E−2
	−0.340262E−2	−0.257662E−1	−0.431905E+4	−0.138650E+6
				0.159925E+6
23	0.102368E+0	0.112064E+0	0.420000E+4	0.471494E+0
	−0.177572E−2	−0.228809E−2	0.272072E+4	0.520585E+4
				0.388979E+4
24	0.690013E−1	0.937171E−1	0.212627E+4	0.606225E+0
	−0.468631E−2	−0.224996E−1	0.312730E+4	0.357139E+4
				0.404710E+4

[a] $\alpha_{12} = 0.30$, for GRF1 mixing rule.

Corresponding coefficients of the models are listed in table 3 (for the correlation at 298.15 K), table 5 (for the correlation in the temperature range using the models with temperature independent parameters), and table 7 (for the correlation in the temperature range using the models with temperature dependent parameters).

Table 4. Results of V^E correlation at 298.15 K with the vdW1, MvdW1, GRF1, and GRF2 mixing rules.

System no.	vdW1 PD(V^E)	MvdW1 PD(V^E)	GRF1 PD(V^E)	GRF2 PD(V^E)
9	1.99	2.34	0.98	0.92
10	1.43	1.95	0.94	0.66
11	1.83	2.38	1.65	1.01
12	0.92	1.57	0.86	0.77
13	1.43	1.90	1.14	1.00
14	1.23	1.97	1.34	0.80
15	1.22	1.56	1.08	1.00
16	2.42	3.18	2.14	1.09
17	2.01	2.75	1.82	1.40
18	1.27	2.06	1.04	0.71
19	1.41	2.34	1.04	1.05
20	2.07	2.58	1.55	1.40
21	2.65	3.51	2.23	2.18
22	1.82	2.21	2.95	1.02
23	2.30	2.47	1.94	0.35
24	6.09	2.62	2.26	0.57

For correlation at only one temperature the interaction parameters of the models can be treated as temperature independent, since the results presented in our previous paper [1] showed that in almost all cases the inclusion of the temperature dependence of parameters does not improve significantly the results of the V^E correlation. On the other hand the correlation in the temperature range demands a changing of the model.

From the table 4 it can be concluded that for the presented systems a considerable influence of the type of the correlation model exist. The GRF2 model gave the best agreement with experimental data, especially for the systems of dicyclic ethers with cyclohexane. Also, it is noticeable that almost all errors obtained for the systems of the 1,3-dioxolane with 1-alcohols, are higher then those obtained for the 1,4-dioxane and 1-alcohol systems. Very good results achieved with the GRF2 model indicate that it is not necessary to include more complex models for this type of correlation.

Figure 1(a) presents the results of V^E correlation obtained with the MvdW1 and GRF2 models for the system 1,3-dioxolane + 1-nonanol. Figure 1(b) shows the (V^E/x_1x_2)–x_1 relationship. As we emphasized in the first part [1], this kind of a graphical presentation is very illustrative, especially for high dilution regions. Also, the shape (non-linearity or dominant maximum or minimum) or strong slope could causes possible difficulties in the correlation with simple models. On this base, it can be noticed the inability of the MvdW1 model to follow the non-symmetric behavior of the (V^E/x_1x_2)–x_1 relationship, in spite of the fact that difference in deviations obtained with the MvdW1 and GRF1 models is not so large.

Table 6 illustrates that results reached with the TCBT models are much better than those obtained with the other models. In our previous paper was shown that for V^E correlation in temperature range, use of the temperature dependent parameters for the GRF and vdW models was necessary. For the data available in temperature range, we compared results obtained using models with temperature independent parameters (table 6) and models with temperature dependent parameters (table 8). Comparison of the results achieved by the TCBT2 and GRF3 models, resented in tables 6 and 8, respectively, led to the conclusion that all errors are very similar and it is acceptable to use the TCBT2 model, as model with less parameters. Although the TCBT3 model gave

Table 5. Coefficients optimized in temperature range 288.15−308.15 K with the vdW1, MvdW1, GRF1, GRF2, TCBT1, and TCBT2 mixing rules.

System no.	vdW1 c_1 c_5	MvdW1 c_1 $c3$	GRF1[a] c_3 (J mol^{-1}) c_5 (J mol^{-1})	GRF2 c_1 c_3 (J mol^{-1}) c_5 (J mol^{-1})	TCBT1[a] c_3 (J mol^{-1}) c_5 (J mol^{-1}) k_{ij} m_{ij}	TCBT2 c_1 c_3 (J mol^{-1}) c_5 (J mol^{-1}) k_{ij} m_{ij}
1	0.354978E−1	0.428206E−1	0.352506E+4	−0.146053E+0	0.440582E+3	−0.229084E+0
	−0.131322E−2	−0.108212E−1	0.987283E+3	−0.104439E+5	−0.238040E+3	0.302385E+3
				0.882905E+4	−0.396724E−1	−0.166711E+3
					0.187485E+0	−0.414222E−1
						0.176383E+0
2	−0.514433E−1	0.208527E−1	0.256645E+4	−0.990287E−1	−0.233139E+4	−0.122632E+0
	−0.104634E−1	−0.147455E−1	0.783137E+3	−0.110998E+5	0.299692E+4	−0.252422E+4
				0.973895E+4	−0.673848E−1	0.214759E+4
					−0.158262E+0	−0.439212E−1
						0.202312E+0
3	−0.830098E−1	−0.323777E−4	0.557236E+5	−0.178238E−1	−0.201922E+4	−0.538739E+0
	−0.106448E−1	−0.174228E−1	0.223395E+4	0.246238E+5	0.248195E+4	−0.188550E+4
				−0.273426E+5	−0.652582E−1	0.723166E+3
					−0.166951E+0	−0.580640E−1
						0.185839E+0
4	−0.930111E−1	−0.225814E−1	−0.941315E+3	−0.887069E−2	−0.513919E+3	−0.181911E+0
	−0.818811E−2	−0.179312E−1	0.254814E+4	−0.443597E+5	0.444440E+3	−0.396091E+4
				0.392881E+5	−0.693653E−1	0.248834E+4
					−0.252818E+0	−0.571664E−1
						0.161379E+0
5	−0.216974E−1	0.306345E−2	−0.176608E+3	0.287848E+0	0.865975E+5	−0.252693E+0
	−0.405209E−2	−0.256520E−1	0.244459E+4	−0.227050E+3	0.234177E+3	−0.219171E+4
				0.249662E+4	−0.456736E−1	0.207129E+4
					−0.842309E−2	−0.346295E−1
						0.119879E+0
6	−0.111044E+0	−0.201555E−1	−0.221547E+4	0.474980E+0	0.612097E+4	0.413008E+0
	−0.128237E−1	−0.300424E−1	0.494478E+4	−0.130874E+4	−0.655781E+4	0.473278E+4
				0.377691E+4	−0.181289E+0	−0.492707E+4
					0.950212E−1	−0.152340E+0
						0.398463E−1
7	−0.135544E+0	−0.445142E−1	−0.357616E+4	−0.145447E+0	−0.115898E+4	−0.584457E+0
	−0.115478E−1	−0.299351E−1	0.738127E+4	−0.115743E+5	0.139309E+4	−0.201477E+4
				0.663339E+4	−0.632366E−1	0.101488E+4
					−0.230923E+0	−0.573939E−1
						0.116928E−1
8	−0.133589E+0	−0.701548E−1	−0.450422E+4	−0.323499E+0	−0.231559E+3	−0.215187E+0
	−0.722607E−2	−0.247650E−1	0.961030E+4	−0.741905E+4	0.238964E+3	−0.398022E+4
				0.271041E+4	−0.672006E−1	0.247352E+4
					−0.279807E+0	−0.585289E−1
						0.403545E−1

[a] $\alpha_{12} = 0.30$, for GRF1 and TCBT1 mixing rules.

the best results, only for the system 1,3-dioxolane + octane it is necessary to use the most complex form of the TCBT model. In the case of the vdW models, results obtained with the MvdW1-1 model are better comparing with those obtained using the vdW1-1 model.

On the basis of all above mentioned results, the correlation of V^E data in a temperature range for the systems with dicyclic ethers can be successfully carried out by the TCBT2 model with five optimized parameters.

Table 6. Results of V^E correlation in temperature range 288.15–308.15 K with the vdW1, MvdW1, GRF1, GRF2, TCBT1, and TCBT2 mixing rules.

System no.	vdW1 PD(V^E)	MvdW1 PD(V^E)	GRF1 PD(V^E)	GRF2 PD(V^E)	TCBT1 PD(V^E)	TCBT2 PD(V^E)
1	4.79	2.80	4.30	2.81	0.57	0.50
2	3.87	2.62	3.63	2.50	0.93	0.54
3	2.21	2.49	3.06	1.93	1.21	0.47
4	1.45	2.06	2.26	1.47	1.17	0.44
5	8.53	1.64	1.92	1.92	1.56	1.56
6	6.62	2.22	2.11	2.07	1.60	1.40
7	3.44	1.72	3.10	2.28	1.68	1.42
8	3.04	2.15	4.29	2.53	2.38	1.97

Table 7. Coefficients optimized in temperature range 288.15–308.15 K with the vdW1-1, MvdW1-1, GRF3, and TCBT3 mixing rules.

System no.	vdW1-1 c_1 c_2 (K^{-1}) c_5 c_6 (K^{-1})	MvdW1-1 c_1 c_2 (K^{-1}) c_3 c_4 (K^{-1})	GRF3 c_1 c_2 (K^{-1}) c_3 ($J\,mol^{-1}$) c_4 ($J\,mol^{-1}K^{-1}$) c_5 ($J\,mol^{-1}$) c_6 ($J\,mol^{-1}K^{-1}$)	TCBT3 c_1 c_2 (K^{-1}) c_3 ($J\,mol^{-1}$) c_4 ($J\,mol^{-1}K^{-1}$) c_5 ($J\,mol^{-1}$) c_6 ($J\,mol^{-1}K^{-1}$) k_{ij} m_{ij}
1	0.336221E+0	0.108439E+0	−0.118404E+1	−0.682034E−2
	−0.851580E−3	−0.219627E−3	0.622311E−2	0.370435E−2
	0.255389E−1	−0.628879E−1	0.321501E+4	0.200078E+4
	−0.639362E−4	0.174458E−3	0.340434E+1	−0.721705E+0
			0.542100E+4	0.143621E+4
			−0.104136E+2	−0.318523E+1
				−0.139544E−1
				0.445590E−2
2	−0.909388E−1	0.107996E+0	−0.970327E+0	−0.740366E+0
	−0.202047E−3	−0.290105E−3	0.630758E−2	0.648331E−3
	0.175943E−1	−0.256837E−1	0.152995E+5	−0.435892E+5
	−0.138727E−3	0.375717E−4	−0.396954E+2	−0.216332E+1
			0.111377E+5	0.308113E+3
			−0.299927E+2	−0.118911E+1
				−0.414892E−1
				0.227936E+0
3	−0.277176E+0	0.931727E−1	0.225088E−1	0.311794E+0
	0.528986E−3	−0.311624E−3	0.122575E−2	−0.286515E−2
	−0.165552E−1	−0.592575E−1	−0.112931E+5	−0.561950E+4
	0.492777E−5	0.139783E−3	0.159183E+3	0.669354E+1
			0.897012E+4	0.998467E+2
			−0.225689E+2	−0.712994E+0
				−0.959606E−1
				0.219370E+0
4	−0.310170E+0	0.818032E−1	−0.936000E−1	−0.414411E−2
	0.706748E−3	−0.348889E−3	0.492444E−2	0.712233E−3
	−0.273740E−1	−0.101210E+0	−0.322313E+5	0.124471E+4
	0.620271E−4	0.278124E−3	0.135927E+3	−0.476533E+1
			0.158002E+5	0.730947E+5
			−0.466705E+2	0.204753E+3
				−0.424907E−1
				0.230566E+0

(Continued)

Table 7. Continued.

System no.	vdW1-1 c_1 c_2 (K^{-1}) c_5 c_6 (K^{-1})	MvdW1-1 c_1 c_2 (K^{-1}) c_3 c_4 (K^{-1})	GRF3 c_1 c_2 (K^{-1}) c_3 (J mol^{-1}) c_4 (J mol^{-1}K^{-1}) c_5 (J mol^{-1}) c_6 (J mol^{-1}K^{-1})	TCBT3 c_1 c_2 (K^{-1}) c_3 (J mol^{-1}) c_4 (J mol^{-1}K^{-1}) c_5 (J mol^{-1}) c_6 (J mol^{-1}K^{-1}) k_{ij} m_{ij}
5	−0.107938E+1	−0.106500E−1	0.103337E+0	−0.235138E+0
	0.300107E−2	0.459117E−4	0.961541E−3	0.402235E−3
	−0.955829E−1	−0.663351E−1	0.152998E+7	−0.841455E+4
	0.223933E−3	0.135964E−3	−0.480635E+4	0.110826E+2
			0.539104E+4	0.380513E+4
			−0.103559E+2	0.605436E+0
				−0.644611E−1
				−0.115812E+0
6	−0.106796E+1	−0.475623E−1	0.226952E+0	0.258924E+1
	0.280032E−2	0.917729E−4	−0.595875E−3	−0.123057E−1
	−0.696397E−1	−0.240841E+0	−0.203112E+4	−0.324402E+5
	0.137247E−3	0.704636E−3	−0.313275E+2	0.518787E+2
			0.248126E+5	0.493029E+4
			−0.285952E+2	−0.103236E+2
				0.358214E−1
				0.287219E+0
7	−0.429944E+0	−0.181020E−1	0.121503E+0	0.655731E+0
	0.875152E−3	−0.881738E−4	−0.197467E−3	−0.375524E−2
	−0.188905E−1	−0.115336E+0	−0.459054E+4	−0.125152E+6
	0.113778E−4	0.285362E−3	−0.262703E+2	0.259373E+3
			0.237645E+5	0.111329E+5
			−0.170092E+2	−0.209364E+2
				0.155720E+0
				0.379581E+0
8	−0.854983E+0	−0.539832E−1	−0.388261E+0	−0.121724E+0
	0.236874E−2	−0.537033E−4	0.717435E−3	−0.190662E−3
	−0.708168E−1	−0.250976E+0	−0.360274E+5	0.165260E+5
	0.208094E−3	0.755146E−3	0.855948E+2	−0.637182E+2
			0.503503E+4	0.117858E+5
			−0.189812E+0	0.303450E+1
				0.386283E+0
				0.629521E+0

Figure 2(a) and 2(b) presents the correlation of V^{E} data for the system 1,4-dioxane + heptane at 298.15 K with the model parameters generated in the temperature range 298.15–308.15 K. Applying the TCBT1 model a very good performance was obtained, while the GRF1 and GRF2 models show mutually very similar behavior, characterized by their inability to follow the tendency of experimental data point (figure 2b) specially at the ends of the concentration range.

Results of V^{E} correlation with the GRF1, GRF2, and TCBT2 models for the system 1,4-dioxane-nonane at 288.15 K are illustrated in figure 3(a) and 3(b). The GRF1 and GRF2 models work inadequately, unable to follow the non-linear variation of V^{E}/x_1x_2 with composition.

Figure 4(a) and 4(b) shows the fit of the V^{E} data obtained with the GRF1, GRF3, and TCBT3 models for the system 1,3-dioxolane + decane at 308.15 K. For this system an asymmetric shape of the (V^{E}/x_1x_2)–x_1 curve is satisfactorily followed with the

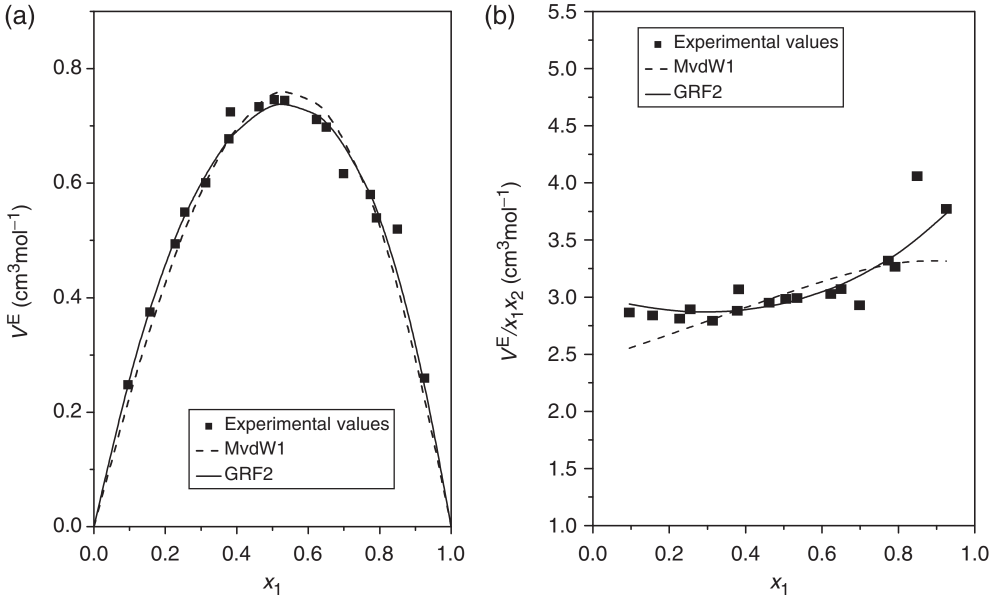

Figure 1. Correlation of V^E data at 298.15 K for the system 1,3-dioxolane + nonanol [14] in: (a) $V^E - x_1$ (b) $V^E/(x_1 x_2)$–x_1 diagrams. The symbols are experimental data. The lines present the results calculated by the various models.

Table 8. Results of V^E correlation in temperature range 288.15–308.15 K with the vdW1-1, MvdW1-1, GRF3, and TCBT3 mixing rules.

System no.	vdW1-1 PD(V^E)	MvdW1-1 PD(V^E)	GRF3 PD(V^E)	TCBT3 PD(V^E)
1	4.12	2.24	0.36	0.34
2	3.03	1.97	0.44	0.45
3	1.53	1.72	0.89	0.40
4	1.33	1.54	0.52	0.40
5	7.47	1.51	1.38	1.33
6	2.42	1.46	1.23	0.90
7	1.72	1.68	1.46	1.14
8	1.88	1.97	2.17	1.73

TCBT3 model. On the other hand the very non-linear (V^E/x_1x_2)–x_1 dependence for this system caused higher deviations obtained with the GRF1 (4.29%) and GRF3 (2.17%) models. Results of V^E correlation by all CEOS and CEOS/G^E models for the 1,4-dioxane + nonane system in temperature range is presented in figure 5. This type of graphical representation of deviation depending on the number of optimization coefficients used is very illustrative confirming the necessity of making use the TCBT model.

6. Conclusion

Results of correlation of the isothermal excess molar volume (V^E) data, using the cubic equation of state mixing rules for the systems of dicyclic ethers, with alcohol and

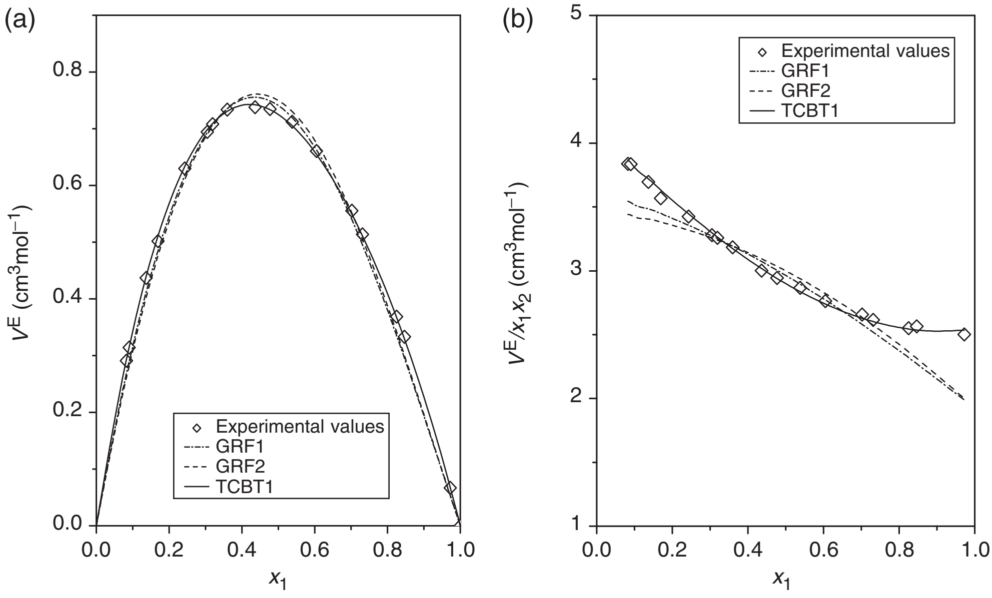

Figure 2. Correlation of V^E data at 298.15 K with the parameters of the models generated in temperature range 288.15–308.15 K, for the system 1,4-dioxane + heptane [11] in: (a) $V^E - x_1$ (b) (V^E/x_1x_2)–x_1 diagrams. The symbols are experimental data. The lines present the result calculated by the various models.

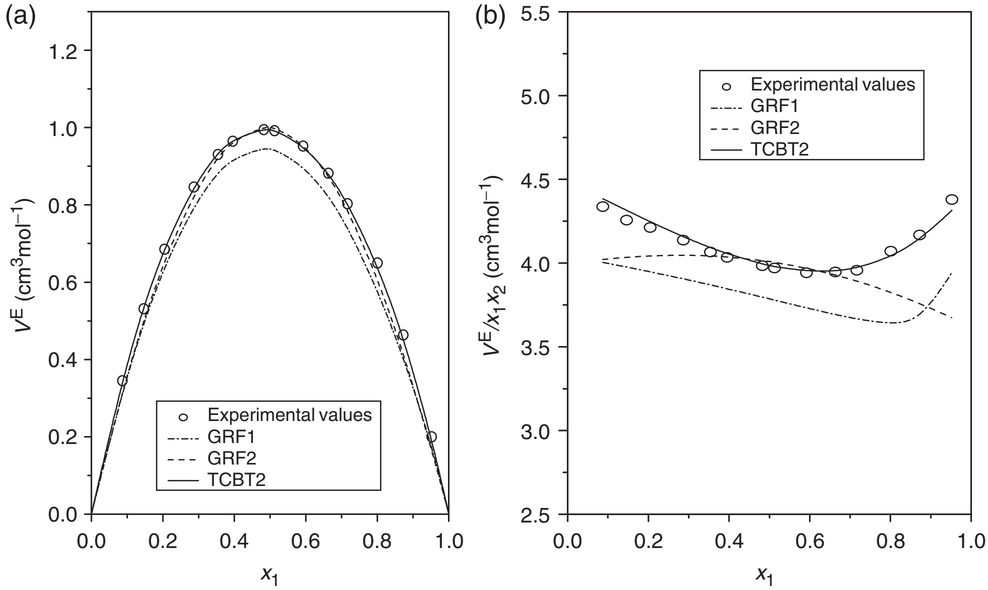

Figure 3. Correlation of V^E data at 288.15 K with the parameters of the models generated in temperature range 288.15–308.15 K, for the system 1,4-dioxane + nonane [11] in: (a) $V^E - x_1$ (b) (V^E/x_1x_2)–x_1 diagrams. The symbols are experimental data. The lines present the results calculated by the various models.

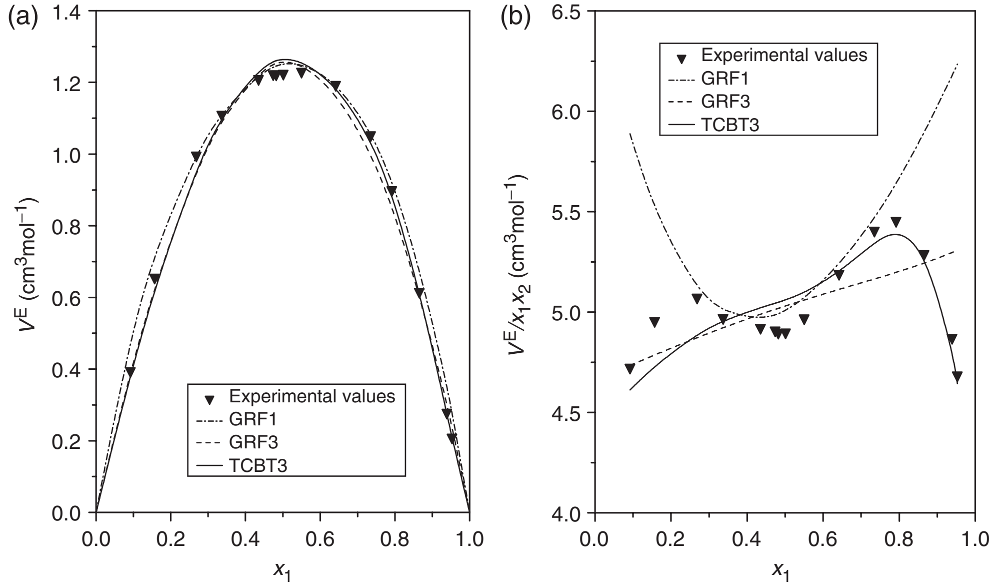

Figure 4. Correlation of V^E data at 308.15 K with the parameters of the models generated in temperature range 288.15–308.15 K, for the system 1,3-dioxolane + decane [12] in: (a) $V^E - x_1$ (b) $(V^E/x_1x_2)–x_1$ diagrams. The symbols are experimental data. The lines present the results calculated by the various models.

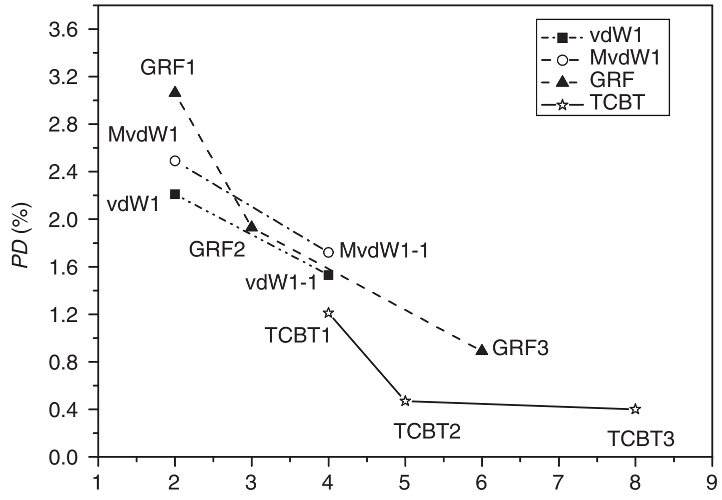

Figure 5. Comparison of the results of V^E data correlation using CEOS and CEOS/G^E models, with the parameters of the models generated in temperature range 288.15–308.15 K, for the system 1,4-dioxane + nonane [11].

cyclohexane, confirmed that use of the temperature dependent parameters of the cubic equation of state (CEOS) models was not necessary. The obtained results indicate that V^E correlation at only one isotherm can be successfully performed using the GRF models with no temperature dependent parameters of the NRTL equation.

For the correlation of the dicyclic ethers with alkanes in the temperature range, it was shown that use of the new TCBT model with no temperature dependent parameters are adequate. Alternatively, the GRF mixing rule with all temperature dependent parameters works satisfactorily.

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.

References

[1] M.Lj. Kijevčanin, B.D. Djordjević, S.P. Šerbanović, I.R. Grgurić, A.Ž. Tasić. *Phys. Chem. Liquids*, **42**, 147 (2004).

[2] C.H. Twu, J.E. Coon, D. Bluck, B. Tilton. *Fluid Phase Equilib.*, **158**, 271 (1999).

[3] I.R. Grgurić, S.P. Šerbanović, M.Lj. Kijevčanin, A.Ž. Tasić, B.D. Djordjević. *Thermochim. Acta*, **412**, 25 (2004).

[4] I.R. Grgurić, M.Lj. Kijevčanin, B.D. Djordjević, A.Ž. Tasić, S.P. Šerbanović. *J. Serb. Chem. Soc.*, **68**, 47 (2003).

[5] M. Pintos, A. Amigo, R. Bravo. *J. Chem. Thermodynam.*, **25**, 337 (1993).

[6] R. Bravo, M. Pintos, A. Amigo. *Can. J. Chem. Eng.*, **73**, 375 (1995).

[7] I. Castro, E. Calvo, R. Bravo, M. Pintos, A. Amigo. *J. Chem. Eng. Data*, **40**, 230 (1995).

[8] V. Alonso, E. Calvo, R. Bravo, M. Pintos, A. Amigo. *J. Chem. Eng. Data*, **39**, 926 (1994).

[9] A. Amigo, R. Bravo, M. Pintos. *J. Chem. Eng. Data*, **38**, 141 (1993).

[10] P. Brocos, A. Amigo, M. Pintos, E. Calvo, R. Bravo. *Thermochim. Acta*, **286**, 297 (1996).

[11] E. Calvo, P. Brocos, M. Pintos, A. Amigo, A.H. Roux, G. Roux-Desgranges. *J. Chem. Eng. Data*, **43**, 105 (1998).

[12] P. Brocos, E. Calvo, A. Amigo, R. Bravo, M. Pintos, A.H. Roux, G. Roux-Desgranges. *J. Chem. Eng. Data*, **43**, 112 (1998).

[13] E. Calvo, P. Brocos, A. Pineiro, M. Pintos, A. Amigo, R. Bravo, A.H. Roux, G. Roux-Desgranges. *J. Chem. Eng. Data*, **44**, 948 (1999).

[14] P. Brocos, E. Calvo, A. Pineiro, R. Bravo, A. Amigo, A.H. Roux, G. Roux-Desgranges. *J. Chem. Eng. Data*, **44**, 1341 (1999).

[15] P. Brocos, E. Calvo, R. Bravo, M. Pintos, A. Amigo, A.H. Roux, G. Roux-Desgranges. *J. Chem. Eng. Data*, **44**, 67 (1999).

[16] R. Stryjek, J.H. Vera. *Can. J. Chem. Eng.*, **64**, 323 (1986).

[17] R. Stryjek, J.H. Vera. *Can. J. Chem. Eng.*, **64**, 334 (1986).

[18] S. Malanowski, A. Anderko. *Modeling Phase Equilibria*, p. 153, John Wiley & Sons, New York (1992).

[19] P.A. Gupte, P. Rasmussen, Aa. Fredenslund. *Ind. Eng. Chem. Fundam.*, **25**, 636 (1986).

[20] K.C. Chao, R.L. Robinson Jr. *Equations of State*, p. 14, American Chemical Society, Washington, DC (1986).

[21] S.P. Šerbanović, M. Lj. Kijevčanin, I.R. Radović, B.D. Djordjeuić. *Fluid Phase Equilibria*, **239**, 69 (2006).

[22] H. Renon, J.M. Prausnitz. *AIChE J.*, **14**, 135 (1968).