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Publisher *Taylor & Francis*

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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

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To cite this Article Kijevčanin, Mirjana Lj. , Djordjević, Bojan D. , Šerbanović, Slobodan P. , Grgurić, Ivona R. and Tasić, Aleksandar Ž(2004) 'Applicability of cubic equation of state mixing rules on correlation of excess molar volume of Non-Electrolyte binary mixtures', *Physics and Chemistry of Liquids*, 42: 2, 147 – 158

To link to this Article: DOI: 10.1080/00319100310001634828

URL: <http://dx.doi.org/10.1080/00319100310001634828>

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APPLICABILITY OF CUBIC EQUATION OF STATE MIXING RULES ON CORRELATION OF EXCESS MOLAR VOLUME OF NON-ELECTROLYTE BINARY MIXTURES

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(Received 30 August 2003)

The excess molar volume V^E data of the binary liquid systems were correlated by the Peng–Robinson–Stryjek–Vera equation of state coupled with two different types of mixing rules: composition dependent van der Waals mixing rule (vdW) and the mixing rule based on the Gupta–Rasmussen–Fredenslund method (GRF), with the NRTL equation as G^E model. The results obtained by these models show that type of applied mixing rule, a number and position of interaction parameters are of great importance for a satisfactory correlation of V^E data. The GRF mixing rules coupled with the NRTL model gave mostly satisfactory results for V^E correlation of the nonideal binary systems of diverse complexity.

Keywords: Excess molar volume; CEOS; NRTL; Correlation; Mixing rules

1. INTRODUCTION

Cubic equations of state models are important tools used to design the thermodynamic behavior of chemical processes and, also for their further optimization. Usually, they provide a framework for the correlation of VLE and LLE data, but also a thermodynamically consistent way for single or simultaneous estimation [1–4] of other important thermophysical properties, such as excess properties (excess volume, excess enthalpy, excess heat capacity, etc.). In this work the ability of composition dependent CEOS (vdW) and CEOS/ G^E mixing rules (GRF with, incorporated, the NRTL equation as G^E model) to correlate the excess molar volume (V^E) of non-electrolyte binary mixtures was investigated.

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The influence of applied mixing rule (CEOS or CEOS/ G^E), as well as the influence of incorporated temperature dependent interaction parameters on correlation of V^E data was tested.

These analyses were performed for very complex mixtures, where the possibility of the change of excess volume correlation quality for several series – monocyclic ethers with n -alkanes, 1-alcohols, cyclic or aromatic compounds was investigated. Also, the flexibility of applied mixing rules to represent V^E data of systems with very diverse structure and complexity was tested, since the selected mixtures include nonideal compounds, asymmetric shape of excess volume $V^E - x_1$ curve with very small or large excess values, etc.

2. ANALYSIS OF THE DATA BASE

Table I summarizes investigated binary systems, number of experimental data points and temperatures, as well as the references for the collected data. These data sets represent very complex mixtures of monocyclic ethers and some organic compounds belonging to several different classes – alkanes and alcohols, cyclic and aromatic compounds.

These kinds of data allow the following change of correlation quality of excess volume by increase/decrease in number of carbon atoms in hydrocarbon chain for chosen n -alkane or 1-alcohol series. Also, systems show very diverse structure and

TABLE I Binary systems used for V^E correlation

System No.	System	No. of data points	T (K)	References
<i>Monocyclic ether + alkane</i>				
1	THP ^a + hexane	14	298.15	[5]
2	THP + heptane	41	288.15, 298.15, 308.15	[5, 6]
3	THP + octane	40	288.15, 298.15, 308.15	[5, 6]
4	THP + nonane	43	288.15, 298.15, 308.15	[5, 6]
5	THP + decane	13	298.15	[7]
6	THF ^b + hexane	13	298.15	[5]
7	THF + heptane	14	298.15	[5]
8	THF + octane	14	298.15	[5]
9	THF + nonane	15	298.15	[5]
<i>Monocyclic ether + alcohol</i>				
10	THP + hexanol	41	288.15, 298.15, 308.15	[8, 9]
11	THP + heptanol	41	288.15, 298.15, 308.15	[8, 9]
12	THP + octanol	41	288.15, 298.15, 308.15	[8, 9]
13	THP + nonanol	16	298.15	[9]
14	THF + hexanol	15	298.15	[9]
15	THF + heptanol	15	298.15	[9]
16	THF + octanol	14	298.15	[9]
17	THF + nonanol	16	298.15	[9]
<i>Monocyclic ether + cyclohexane</i>				
18	THP + cyclohexane	39	288.15, 298.15, 308.15	[10]
19	THF + cyclohexane	39	288.15, 298.15, 308.15	[10]
<i>Monocyclic ether + toluene</i>				
20	THP + toluene	39	288.15, 298.15, 308.15	[10]
21	THF + toluene	39	288.15, 298.15, 308.15	[10]

^aTHP – tetrahydropyran; ^bTHF – tetrahydrofuran.

complexity, such as nonideal, asymmetric behavior, with very small or large excess values, etc.

All systems were divided into two groups according to the nature of performed calculations. In the first case experimental data were available at only one isotherm of 298.15 K, and in the second case the data were available for temperature range from 288.15 to 308.15 K.

3. CUBIC EQUATION OF STATE

In this work the Peng–Robinson–Stryjek–Vera cubic equation of state (PRSV CEOS) [11] was employed

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

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 following equations

$$a_i(T) = 0.457235 \frac{(RT_{ci})^2}{P_{ci}} [1 + m_i(1 - T_{ri}^{0.5})]^2, \quad (2)$$

$$b_i = 0.077796 \frac{RT_{ci}}{P_{ci}}, \quad (3)$$

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

$$k_{0i} = 0.378893 + 1.4897153\omega_i - 0.1713848\omega_i^2 + 0.0196554\omega_i^3 \quad (5)$$

In Eqs. (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 [12].

4. MIXING RULES

For all calculations performed by the CEOS models, we used two different types of mixing rules – composition dependent van der Waals (vdW) one-fluid models [13] and general excess free energy mixing rules based on the approach given by Gupte *et al.* [14].

4.1. Van der Waals One-fluid Mixing Rules

In order to examine the effect of the position of binary interaction parameters in parameters of mixture a and b , two forms of the vdW rules were tested.

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

$$a = \sum_i \sum_j x_i x_j a_{ij}. \quad (6)$$

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

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

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

The covolumen parameter b is defined in two ways. First, as a quadratic composition dependent

$$b = \sum_i \sum_j x_i x_j b_{ij}, \quad (8)$$

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

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

and second, as the linear composition dependent in the form

$$b = \sum_i x_i b_i. \quad (10)$$

Binary interaction parameters k_{ij} , l_{ij} and m_{ij} can be treated as linear temperature dependent as follows:

$$k_{ij} = c_1 + c_2 T, \quad (11)$$

$$l_{ij} = c_3 + c_4 T, \quad (12)$$

$$m_{ij} = c_5 + c_6 T. \quad (13)$$

4.2. Excess Free Energy Mixing Rules

In the last decades there have been several proposals which include excess free energy (excess Gibbs or excess Helmholtz energy) into a cubic equation of state through its mixing rules. In this article we used general approach introduced by Gupta–Rasmussen–Fredenslund (GRF) [14] for VLE calculation, since it can be applied in very wide region of temperatures and pressures.

The basic equation of this approach connects the excess Helmholtz free energy and the excess Gibbs energy [15]

$$\left(\frac{G^E}{RT} \right)_{\text{CEOS}} = \left(\frac{A^r - \sum_i x_i A_i^r}{RT} \right) - \sum_i x_i \ln \left(\frac{V}{V_i} \right) + \frac{pV^E}{RT}, \quad (14)$$

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

The form for the PRSV equation is

$$\begin{aligned} \left(\frac{G^E}{RT}\right)_{\text{CEOS}} = & -\ln\left(1 - \frac{b}{V}\right) + \sum_i x_i \ln\left(1 - \frac{b_i}{V_i}\right) - \sum_i x_i \ln\left(\frac{V}{V_i}\right) + \frac{pV^E}{RT} \\ & + \frac{a}{2\sqrt{2}bRT} \ln\left(\frac{V + (1 - \sqrt{2})b}{V + (1 + \sqrt{2})b}\right) - \sum_i x_i \frac{a_i}{2\sqrt{2}b_iRT} \ln\left(\frac{V_i + (1 - \sqrt{2})b_i}{V_i + (1 + \sqrt{2})b_i}\right). \end{aligned} \quad (15)$$

The GRF mixing rule is obtained by equating the excess Gibbs energy from equation of state, Eq. (15), to that from an activity coefficient model

$$\left(\frac{G^E}{RT}\right)_{\text{CEOS}} = \left(\frac{G^E}{RT}\right)_{G^E \text{ model}}. \quad (16)$$

The final form for the parameter a calculation is

$$\begin{aligned} a = & 2\sqrt{2}bRT \left[\ln\left(\frac{V + (1 + \sqrt{2})b}{V + (1 - \sqrt{2})b}\right) \right] \left[\ln\left(1 - \frac{b}{V}\right) - \sum_i x_i \ln\left(1 - \frac{b_i}{V_i}\right) - \frac{pV^E}{RT} \right. \\ & \left. + \sum_i x_i \ln\left(\frac{V}{V_i}\right) + \sum_i x_i \frac{a_i}{2\sqrt{2}b_iRT} \ln\left(\frac{V_i + (1 - \sqrt{2})b_i}{V_i + (1 + \sqrt{2})b_i}\right) + \left(\frac{G^E}{RT}\right)_{G^E \text{ model}} \right]. \end{aligned} \quad (17)$$

As an activity coefficient model for the G^E calculations the NRTL equation [16] was chosen

$$\frac{G^E}{RT} = \sum_i x_i \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_k x_k G_{ki}}, \quad (18)$$

For binary systems

$$\begin{aligned} G_{12} = \exp(-\alpha_{12} \tau_{12}), \quad G_{21} = \exp(-\alpha_{21} \tau_{21}), \\ \tau_{12} = (g_{12} - g_{22})/RT, \quad \tau_{21} = (g_{21} - g_{11})/RT. \end{aligned} \quad (19)$$

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

$$\alpha_{12} = c_1 + c_2 T, \quad (20)$$

$$g_{12} - g_{22} = c_3 + c_4 T, \quad (21)$$

$$g_{21} - g_{11} = c_5 + c_6 T. \quad (22)$$

All CEOS and CEOS/ G^E models obtained on the basis of all above mentioned equations are summarized in Table II.

TABLE II Thermodynamic CEOS and CEOS/ G^E models used in the present work

<i>Model</i>	<i>Equations</i>
vdW1	(6)–(9), (11), (13); $c_2 = c_6 = 0$
vdW1-1	(6)–(9), (11), (13)
MvdW1	(6), (7), (10)–(12); $c_2 = c_4 = 0$
MvdW1-1	(6), (7), (10)–(12)
GRF1	(14)–(22); $\alpha_{12} = 0.3$; $c_2 = c_4 = c_6 = 0$
GRF2	(14)–(22); $c_2 = c_4 = c_6 = 0$
GRF3	(14)–(22)

4.3. Representation of CEOS and CEOS/ G^E Models

The general equation for the excess volume calculation is given as

$$V^E = V - \sum_i x_i V_i, \quad (23)$$

The binary interaction parameters were determined using the modified Marquardt optimization technique with incorporated principles of Monte Carlo method by minimizing the following objective function:

$$OF = \frac{1}{m} \sum_{i=1}^m \left(\frac{V_{\text{exp}}^E - V_{\text{cal}}^E}{V_{\text{exp}}^E} \right)_i^2 \rightarrow \min, \quad (24)$$

where m stands for the number of experimental data points.

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

$$PD(V^E) = \frac{100}{m} \sum_{i=1}^m \left| \frac{V_{\text{exp}}^E - V_{\text{cal}}^E}{(V_{\text{exp}}^E)_{\text{max}}}_i \right|. \quad (25)$$

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

5. RESULTS AND DISCUSSION

The correlation of V^E data for the binary systems of monocyclic ethers using the CEOS and CEOS/ G^E models, listed in Table II, was performed. Bearing in mind that some experimental data were available at only one isotherm and the other in temperature ranges (Table I), all systems were divided into two groups and all results were summarized separately. Table IV presents the results of the correlation at 298.15 K while Table VI gives the results of the correlation in whole temperature range. Corresponding coefficients are listed in Table III (for the correlation at 298.15 K) and Table V (for correlation in temperature range). For a fitting of data at only one

TABLE III Coefficients optimized at 298.15 K with the vdW1, MvdW1, GRF1 and GRF2 mixing rules

System No.	vdW1	MvdW1	GRF1*	GRF2
	c_1 c_5	c_1 c_3	c_3 (J mol ⁻¹) c_5 (J mol ⁻¹)	c_1 c_3 (J mol ⁻¹) c_5 (J mol ⁻¹)
1	0.105592E-1 -0.108807E-4	0.105182E-1 -0.340312E-3	0.226727E + 4 -0.506282E + 3	0.722820E + 0 0.186255E + 4 0.237701E + 5
5	-0.588637E-1 0.158858E-2	-0.217957E-1 -0.123761E-3	0.277558E + 4 -0.361244E + 4	-0.258524E-1 -0.188821E + 5 0.139345E + 5
6	0.652230E-1 0.141864E-1	-0.830983E-2 -0.662429E-2	-0.120300E + 3 0.926934E + 3	-0.552771E-1 0.396489E + 4 -0.352483E + 4
7	-0.115639E + 0 -0.134088E-1	-0.317193E-1 -0.727450E-2	-0.294121E + 4 0.446095E + 4	0.474836E-1 -0.108433E + 5 0.135461E + 5
8	-0.723078E-1 -0.223342E-2	-0.568594E-1 -0.319592E-2	-0.433044E + 4 0.705320E + 4	0.683573E-2 -0.524973E + 5 0.600597E + 5
9	-0.758370E-1 0.629759E-3	-0.807065E-1 0.148891E-2	0.311036E + 4 -0.384010E + 4	-0.424340E + 0 -0.365734E + 4 0.371808E + 3
13	0.814325E-2 -0.215199E-2	0.317352E-1 -0.150545E-1	-0.320318E + 4 0.459002E + 4	0.543250E + 0 -0.216754E + 4 0.342909E + 4
14	0.139876E-1 -0.174670E-2	0.278742E-1 -0.670056E-2	0.598296E + 3 0.104015E + 4	0.864443E + 0 0.827295E + 3 0.101619E + 4
15	0.904488E-2 -0.197906E-2	0.274622E-1 -0.110590E-1	0.377096E + 4 -0.326459E + 4	0.147363E + 0 -0.581124E + 4 0.743260E + 4
16	-0.130603E-1 0.278142E-3	-0.157935E-1 0.164565E-2	0.120440E + 3 -0.226113E + 4	0.791339E + 0 -0.610654E + 3 -0.144501E + 4
17	-0.403068E-2 -0.142050E-2	0.119863E-1 -0.113196E-1	0.191188E + 4 -0.286149E + 4	0.902957E + 0 0.223892E + 5 -0.134841E + 4

* $\alpha_{12}=0.30$, for GRF1 mixing rule.

isotherm the interaction parameters can be treated as temperature independent, since our preliminary results showed that in almost all cases further increase in number of parameters (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 models with temperature dependent parameters.

It can be concluded from Table IV that particularly unreliable results were obtained by the GRF2 with errors over 6% and over 10% with the other models for the THP + hexane system. In that case it was necessary to include the temperature dependent parameters; only the GRF3 model gave satisfactory result of 1.94% (signed with asterisk). The obtained results indicate a considerable influence of the number

TABLE IV 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 $PD(V^E)$
1	10.89	10.88	11.35	6.25 (1.94)*
5	0.88	0.86	0.48	0.22
6	6.57	1.14	1.00	1.00
7	2.12	1.49	1.93	1.30
8	1.40	1.39	3.29	1.05
9	0.55	0.55	2.02	0.54
13	0.66	1.74	0.60	0.57
14	2.33	2.34	2.18	2.05
15	1.12	2.34	1.67	0.84
16	1.02	1.00	1.09	0.98
17	0.80	1.42	0.83	0.78

*Results in brackets is obtained with the GRF3 model, with following parameters: $c_1 = 0.459930E - 1$; $c_2 (K^{-1}) = 0.522600E - 2$; $c_3 (J mol^{-1}) = 0.409091E + 0$; $c_4 (J mol^{-1} K^{-1}) = 0.504498E + 1$; $c_5 (J mol^{-1}) = -0.260214E + 1$; $c_6 (J mol^{-1} K^{-1}) = 0.256751E + 1$.

TABLE V Coefficients optimized in temperature range 288.15–308.15 K with the vdW1-1, MvdW1-1 and GRF3 mixing rules

System No.	vdW1-1	MvdW1-1	GRF3	System No.	vdW1-1	MvdW1-1	GRF3
	c_1	c_1	c_1		c_1	c_1	c_1
	$c_2 (K^{-1})$	$c_2 (K^{-1})$	$c_2 (K^{-1})$		$c_2 (K^{-1})$	$c_2 (K^{-1})$	$c_2 (K^{-1})$
	c_5	c_3	$c_3 (J mol^{-1})$		c_5	c_3	$c_3 (J mol^{-1})$
	$c_6 (K^{-1})$	$c_4 (K^{-1})$	$c_4 (J mol^{-1} K^{-1})$		$c_6 (K^{-1})$	$c_4 (K^{-1})$	$c_4 (J mol^{-1} K^{-1})$
			$c_5 (J mol^{-1})$				$c_5 (J mol^{-1})$
			$c_6 (J mol^{-1} K^{-1})$				$c_6 (J mol^{-1} K^{-1})$
2	-0.261687E-1	-0.530410E-2	-0.232889E+0	12	0.164603E-1	0.714757E-1	0.129073E+0
	-0.205807E-4	-0.109391E-4	-0.293354E-2		-0.494185E-4	-0.222947E-3	0.697020E-3
	0.434165E-2	0.123802E-2	-0.192409E+2		-0.488784E-2	-0.355974E-1	-0.888082E+2
	-0.273924E-4	-0.492666E-5	-0.401244E+1		0.152794E-4	0.113493E-3	0.169268E+2
			0.113811E+4				-0.250270E+4
			0.357897E+0				-0.417300E+1
3	-0.463940E+0	0.308515E-1	0.910432E+0	18	-0.757876E-1	0.914723E-1	-0.198986E+0
	0.147588E-2	-0.199070E-3	-0.293354E-2		0.422523E-3	-0.197632E-3	0.114134E-2
	-0.741053E-1	0.670975E-2	-0.117083E+5		-0.356571E-1	-0.316665E-2	0.307448E+6
	0.251182E-3	-0.201836E-4	0.637942E+2		0.130172E-3	0.412433E-5	-0.507510E+3
			0.281046E+5				0.504069E+4
			-0.117062E+3				-0.117102E+2
4	0.648467E-2	0.617682E-2	-0.860511E+0	19	-0.281583E+0	0.159591E+0	-0.161076E+0
	-0.166474E-3	-0.186981E-3	0.144185E-2		0.661420E-3	-0.388887E-3	0.149215E-2
	-0.159272E-2	0.161323E-2	0.175097E+4		-0.326235E-1	-0.499860E-1	0.994347E+5
	0.816133E-5	-0.443251E-6	-0.125544E+2		0.339243E-4	0.142389E-3	-0.123805E+3
			-0.417103E+3				0.989026E+4
			0.332912E+1				-0.261301E+2
10	0.665495E-1	0.749132E-1	-0.705246E+1	20	-0.150996E+0	-0.858564E-1	-0.668452E+0
	-0.137140E-3	-0.137575E-3	0.273491E-1		0.476963E-3	0.212201E-3	0.194262E-2
	0.102609E-2	-0.595020E-2	0.180664E+4		-0.141093E-1	-0.335207E-3	-0.218344E+4
	-0.689700E-5	0.892046E-5	-0.976028E+0		0.544052E-4	0.548607E-5	0.320629E+1
			0.105268E+3				-0.264136E+4
			0.392703E+1				0.948371E+1
11	0.116441E+0	0.154412E+0	-0.353274E+0	21	0.337168E-1	-0.186304E+0	0.156676E+0
	-0.319091E-3	-0.389535E-3	0.230690E-2		-0.164808E-3	0.440400E-3	-0.393297E-3
	-0.633790E-4	-0.319106E-1	0.139383E+5		0.218790E-1	0.410045E-1	0.175437E+5
	-0.596497E-5	0.767283E-4	-0.351912E+2		-0.530246E-4	-0.113640E-3	0.101210E+1
			-0.788480E+4				-0.725475E+4
			0.182988E+2				-0.283826E+2

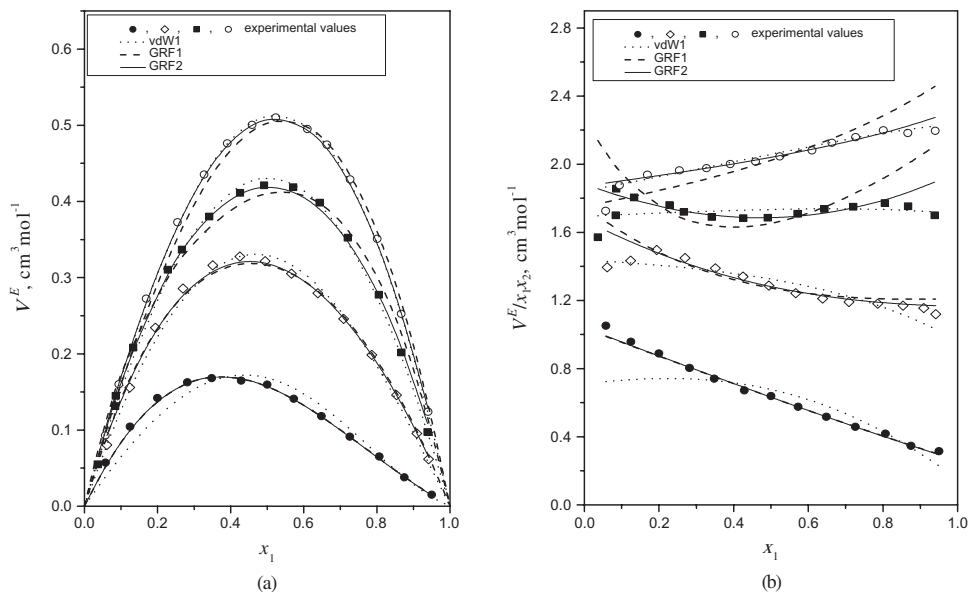


FIGURE 1 Correlation of V^E data at 298.15K for the systems THF+*n*-alkane [5] in: (a) $V^E - x_1$; (b) $V^E/(x_1 x_2) - x_1$ diagrams. The symbols are experimental data of the systems: ● – THF(1)+hexane (2), ◇ – THF (1)+heptane (2), ■ – THF (1)+octane (2), ○ – THF (1)+nonane (2). The lines present the results calculated by the various models.

of interaction parameters, as well as the influence of temperature dependent parameters for the asymmetric systems with very small V^E values. The similar results were obtained for the THF + *n*-alkane systems, also presented in Table IV and in Fig. 1.

Comparison of the results presented in Table IV shows that in all cases the GRF2 model gave the best agreement with experimental data. Also, very good results were obtained with the MvdW1 model. It can be seen from Table IV that for the systems with 1-alcohol all models gave very good results with the corresponding errors less than 2% (an exception is the system THF + hexanol where all models gave higher errors).

Figure 1(a) presents the result of the V^E correlation for mixtures of THF with homologous series of *n*-alkane (from hexane to nonane) with the vdW1, GRF1 and GRF2 models. Figure 1(b) shows $V^E/x_1 x_2 - x_1$ relationship. This kind of a graphical presentation is very illustrative, especially for infinite and high dilution region. Also, the shape (nonlinearity or dominant maximum or minimum) or large slope indicates possible difficulties in the correlation with simple models, for these systems. On this basis it can be concluded that the large deviation obtained with the GRF1 model for the system THF + octane is a consequence of its inability to follow the nonsymmetric behavior of the $V^E/x_1 x_2 - x_1$ relationship in high dilution region.

As one said before, for the data available in temperature range, it was necessary to carry out the V^E correlation using models with the temperature dependent parameters. Comparison of the results achieved by the vdW1-1, MvdW1-1 and GRF3 models, presented in Table VI, led to the conclusion that in most cases the GRF3 model gave the best results, with errors less than 1%. In the case of the vdW models choice of the position of the optimized parameters was not crucial, since the results are almost the same.

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

System No.	vdW1-1 $PD(V^E)$	MvdW1-1 $PD(V^E)$	GRF3 $PD(V^E)$
2	1.78	1.95	1.91
3	1.95	2.44	0.41
4	0.77	0.76	0.63
10	2.83	3.44	1.10
11	2.17	2.24	2.15
12	1.98	1.97	1.70
18	1.76	1.36	1.10
19	2.53	1.72	0.80
20	1.05	1.04	1.00
21	0.61	0.74	0.63

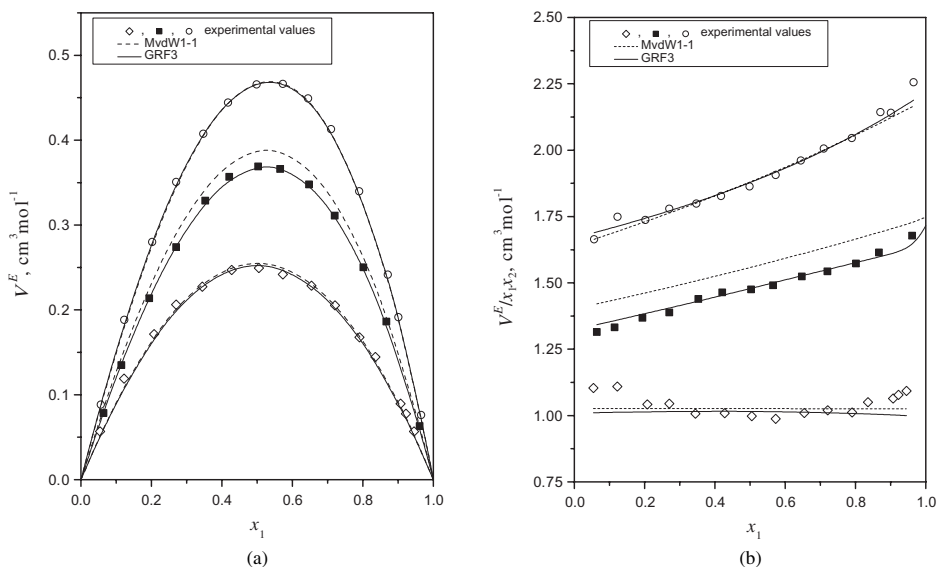


FIGURE 2 Correlation of V^E data at 298.15 K with the parameters of the models generated in temperature range 288.15–308.15 K, for the systems THP + n -alkane [5] in: (a) $V^E - x_1$; (b) $V^E/(x_1 x_2) - x_1$ diagrams. The symbols are experimental data of the systems: \diamond – THP (1) + heptane (2), \blacksquare – THP (1) + octane (2), \circ – THP (1) + nonane (2). The lines present the results calculated by the various models.

On the basis of all the above mentioned results, the correlation of V^E data in temperature range can be carried out by the GRF3 model which uses all optimized parameters.

Figure 2(a) and (b) presents the correlation of V^E data at 298.15 K with the parameters generated in temperature range 298.15–308.15 K for the system THP + n -alkane. The MvdW1-1 and GRF3 models show very similar behavior, with the exception of the THP + octane system where the poor performance of the MvdW1-1 was obtained.

Results of the V^E correlation with the MvdW1-1 and GRF3 models for the systems THP + hexanol, + heptanol and + octanol, at 298.15 K are presented in Fig. 3(a) and (b). The MvdW1-1 and GRF3 models work inadequately in high dilution region, unable to follow the nonlinear variation of $V^E/x_1 x_2$ with composition.

Figure 4(a) and (b) shows the fitting of the V^E data obtained for the systems of monocyclic ethers with cyclohexane and toluene at 298.15 K, with the vdW1-1 and

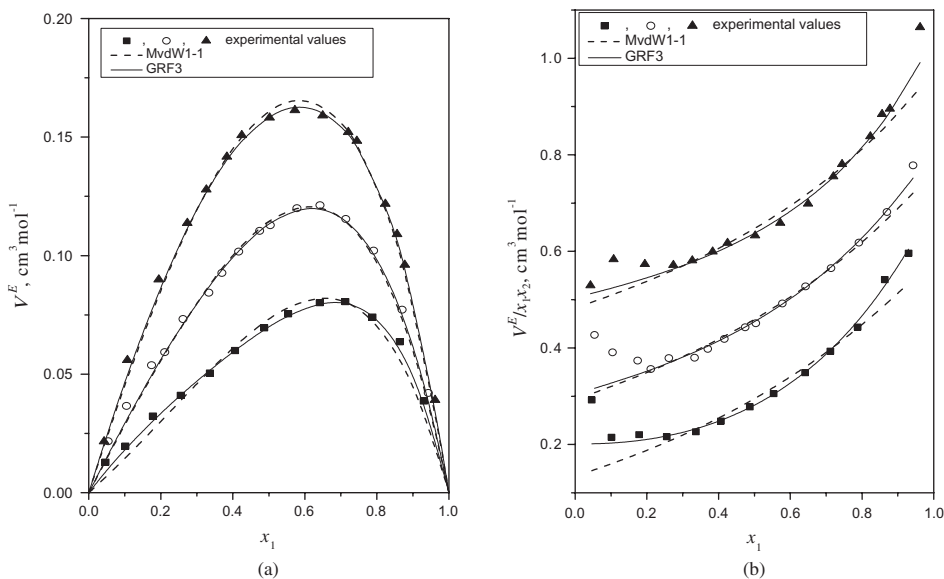


FIGURE 3 Correlation of V^E data at 298.15 K with the parameters of the models generated in temperature range 288.15–308.15 K, for the systems THP + 1-alcohols [9] in: (a) $V^E - x_1$ b) $V^E/(x_1 x_2) - x_1$ diagrams. The symbols are experimental data of the systems: \blacksquare – THP (1) + hexanol (2), \circ – THP (1) + heptanol (2), \blacktriangle – THP (1) + octanol (2). The lines present the results calculated by the various models.

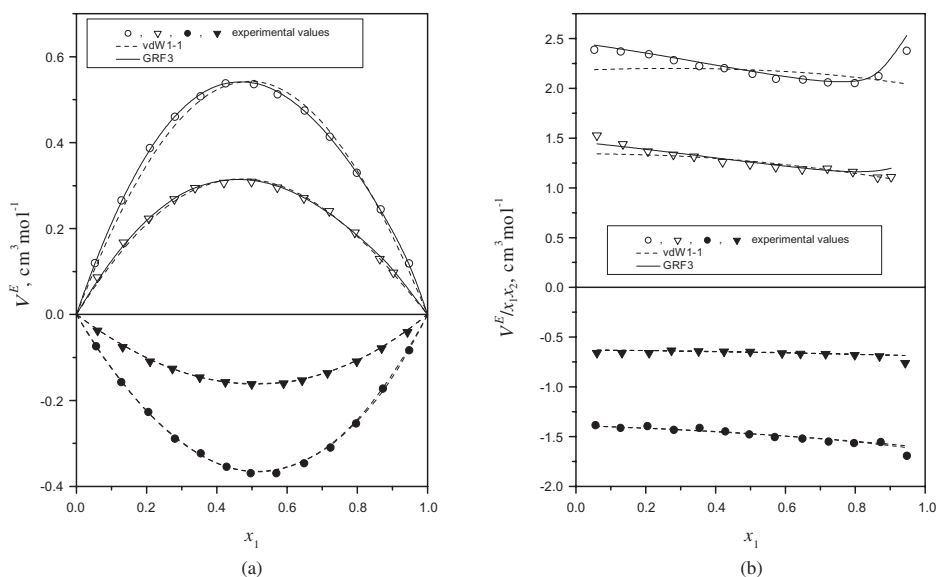


FIGURE 4 Correlation of V^E data at 298.15 K with the parameters of the models generated in temperature range 288.15–308.15 K, for the systems monocyclic ethers + cyclohexane, or + toluene [10] in: (a) $V^E - x_1$; (b) $V^E/(x_1 x_2) - x_1$ diagrams. The symbols are experimental data of the systems: ∇ – THP (1) + cyclohexane (2), \circ – THF (1) + cyclohexane (2), \blacktriangledown – THP (1) + toluene (2), \bullet – THF (1) + toluene (2). The lines present the results calculated by the various models.

GRF3 models. For the systems with toluene which have negative but symmetric shape of $V^E - x_1$ curve and linear $V^E/x_1x_2 - x_1$ dependence, the results obtained with both models are very good. On the other hand, the nonlinear $V^E/x_1x_2 - x_1$ dependence for the system THF + cyclohexane caused the higher deviations obtained with the vdW1-1 (2.53%) and MvdW1-1 (1.72%) models.

6. CONCLUSION

Results of the correlation of the experimental excess molar volume data by cubic equation of state mixing rules for the systems of monocyclic ethers, with different type of organic compounds (alkane, alcohol, cyclohexane and toluene) at only one isotherm, show that the use of the temperature dependent parameters of the cubic equation of state models was not necessary. The obtained results indicate that the V^E correlation at only one isotherm can be successfully performed using the GRF or vdW models with no-temperature dependent parameters of the NRTL equation. However, for the correlation in temperature range, the obtained results indicate that it is necessary to incorporate more flexible GRF3 mixing rule, where all temperature dependent interaction parameters were used.

References

- [1] B.D. Djordjević, M. Lj. Kijevčanin, J.P. Orlović and S.P. Šerbanović (2001). *J. Serb. Chem. Soc.*, **66**, 213.
- [2] S.P. Šerbanović, B.D. Djordjević and D.K. Grozdanić (1990). *Fluid Phase Equilibria*, **57**, 47.
- [3] B.D. Djordjević, D.K. Grozdanić and S.P. Šerbanović (1994). *Can. J. Chem. Eng.*, **72**, 171.
- [4] M. Kijevčanin, D. Djurdjević, J. Smiljanić, S. Šerbanović and B. Djordjević (2001). *The Fifth Italian Conference of Chemical and Process Engineering*. Florence, Italy.
- [5] M. Pintos, A. Amigo and R. Bravo (1993). *J. Chem. Thermodynamics*, **25**, 337.
- [6] R. Bravo, M. Pintos and A. Amigo (1995). *Can. J. Chem. Eng.*, **73**, 375.
- [7] I. Castro, E. Calvo, R. Bravo, M. Pintos and A. Amigo (1995). *J. Chem. Eng. Data*, **40**, 230.
- [8] V. Alonso, E. Calvo, R. Bravo, M. Pintos and A. Amigo (1994). *J. Chem. Eng. Data*, **39**, 926.
- [9] A. Amigo, R. Bravo and M. Pintos (1993). *J. Chem. Eng. Data*, **38**, 141.
- [10] P. Brocos, A. Amigo, M. Pintos, E. Calvo and R. Bravo (1996). *Thermochimica Acta*, **286**, 297.
- [11] R. Stryjek, and J.H. Vera (1986). *Can. J. Chem. Eng.*, **64**, 323.
- [12] R. Stryjek, and J.H. Vera (1986). *Can. J. Chem. Eng.*, **64**, 334.
- [13] S. Malanowski and A. Anderko (1992). *Modeling Phase Equilibria*, p. 153. John Wiley & Sons, New York.
- [14] P.A. Gupte, P. Rasmussen and Aa. Fredenslund (1986). *Ind. Eng. Chem. Fundam.*, **25**, 636.
- [15] K.C. Chao, and R.L. Robinson Jr. (1986). *Equations of State*, p. 14. American Chemical Society, Washington, DC.
- [16] H. Renon and J.M. Prausnitz (1968). *AIChE J.*, **14**, 135.