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Excess molar volume of acetonitrile + alcohol systems at 298.15 K. Part II: Correlation by cubic equation of state

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Abstract: The excess molar volume V^E of the binary liquid systems acetonitrile + methanol and acetonitrile + ethanol, experimentally determined in the previous part, were correlated by the PRSV CEOS coupled with the vdW and TCBT mixing rules. The results obtained show that the number and position of the interaction parameters of these models are of great importance for a satisfactory fitting of V^E data.

Keywords: excess molar volume, CEOS, correlation, alcohol, acetonitrile.

INTRODUCTION

Over the past last decade, very accurate equation of state models have been developed for describing the vapour–liquid equilibria (VLE) behavior of fluids composed of complex molecules. The correlation of these data requires complex and unphysical mixing rules with temperature dependent parameters. The modern development of combining cubic equation of state (CEOS) with Gibbs free energy models (G^E), known as CEOS/ G^E models, presents a quite effective method for correlating VLE data of highly non-ideal systems. However, it is extremely desirable that CEOS/ G^E models can be used for the single and simultaneous correlation of other thermodynamic properties, such as excess enthalpy, excess heat capacity *etc*., as shown in several papers.[1–5] In recent years, some efforts have been made in the correlation of excess molar volume (V^E) using CEOS models mostly with various forms of van der Waals one fluid mixing rules.[6–11] In the second part of our work, we have tried to extend the applicability of the CEOS/ G^E model of Twu *et al.*[12] to the correlation of V^E data of the systems acetonitrile+methanol and acetonitrile+ethanol measured in the first part[13] of this work.

PENG-ROBINSON-STRYJEK-VERA CEOS

In the present work, the Peng-Robinson-Stryjek-Vera equation of state[14] (PRSV CEOS), in the form

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

was employed, where

$$u = 1-\sqrt{2},\ w = 1+\sqrt{2}$$

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

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

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

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

and k_{1i} is the pure compound adjustable parameter.[14]

MIXING RULES

Van der Waals one-fluid mixing rules

In order to examine the effect of the number of binary interaction parameters, present in this type of mixing rules, and of their position in various parameters, several forms of the van der Waals mixing rules were tested.

The energy parameter a, present in the original two parameter van der Waals one-fluid mixing rule (vdW1), which is a quadratic dependence on composition, can be expressed by the follwing equation

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

where a_{ij}, the cross interaction coefficient, has the form

$$a_{ij} = (a_i a_j)^{0.5}(1-k_{ij}) \tag{7}$$

In this equation, a_i and a_j are the parameters of the pure component, whereas k_{ij} denotes the binary interaction parameter.

The covolumen parameter b is given by the linear composition dependence in the form

$$b = \sum_i x_i b_i \tag{8}$$

Modifications of the vdW1 mixing rule in order to examine the importance of the position of the binary interaction parameters of parameters a and b on the VLE calculation were investigated by several authors.[15]

The modified form of Eq. (7) is as follows

$$a_{ij} = (a_i a_j)^{0.5}[1 - k_{ij}' + l_{ij}'(x_i - x_j)] \tag{9}$$

where $k_{ij}' = k_{ji}'$ and $l_{ij}' = -l_{ji}'$. Equations (6), (8) and (9) represent the modified two parameter van der Waals one-fluid mixing rule (MvdW1-1).

To increase the flexibility of the above mentioned simple mixing rules, the three parameter mixing rule of the van der Waals type was introduced, where parameter a is given by Eqs. (6) and (9), similarly to the case of the MvdW1-1 mixing rule, whereas for determination of the parameter b, the quadratic composition dependence

$$b = \sum_i \sum_j x_i x_j b_{ij} \tag{10}$$

was employed.

The cross interaction parameter b_{ij} is defined by the following equations

$$b_{ij} = \left(\frac{b_i + b_j}{2}\right)(1 - m_{ij}) \tag{11}$$

or

$$b_{ij} = (b_i b_j)^{0.5}(1 - m_{ij}') \tag{12}$$

Here b_i and b_j stand for the parameters of the pure component and m_{ij} and m_{ij}' represent the binary interaction parameters.

Twu-Coon-Bluck-Tilton mixing rule

Recently, Twu *et al.* introduced a new group of mixing rules[4] based on the van der Waals referent fluid, which also include the second virial coefficient. These mixing rules were derived for various conditions of reference pressure, leading to models of various complexities. In the present work, the Twu-Coon-Bluck-Tilton (TCBT)[12] mixing rule was used to correlate the excess volume data given in the first part of the present investigation.

The TCBT mixing rule, developed for no reference pressure conditions, can be presented by the following equation

$$\frac{A^{\mathrm{E}}}{RT} - \frac{A^{\mathrm{E}}_{\mathrm{vdW}}}{RT} = \ln\left[\left(\frac{V^*_{\mathrm{vdW}} - 1}{V^* - 1}\right)\left(\frac{b_{\mathrm{vdW}}}{b}\right)\right] - \\ - \frac{1}{w - u}\left[\frac{a^*}{b^*}\ln\left(\frac{V^* + w}{V^* + u}\right) - \frac{a^*_{\mathrm{vdW}}}{b^*_{\mathrm{vdW}}}\ln\left(\frac{V^*_{\mathrm{vdW}} + w}{V^*_{\mathrm{vdW}} + u}\right)\right] \tag{13}$$

The excess Helmholtz energy is related to the excess Gibbs energy by the following equation

$$\frac{A^{\mathrm{E}}}{RT} - \frac{A^{\mathrm{E}}_{\mathrm{vdW}}}{RT} = \frac{G^{\mathrm{E}}}{RT} - \frac{G^{\mathrm{E}}_{\mathrm{vdW}}}{RT} + (z - z_{\mathrm{vdW}}) \tag{14}$$

where $G^{\mathrm{E}}_{\mathrm{vdW}}$ is calculated from PRSV equation.

Parameters a_{vdW} and b_{vdW} can be determined by mean of the vdW1 mixing rule, Eqs. (6), (7), (10) and (11), whereas the reduced parameters a^*, b^*, $a_{\mathrm{vdW}}{}^*$ and $b_{\mathrm{vdW}}{}^*$ can be obtained from the equations

$$a^* = Pa/R^2T^2; \quad b^* = Pb/RT \tag{15}$$

V^* is the reduced liquid volume at the pressure and temperature of the system and is defined as

$$V^* = V/b = z/b^* \tag{16}$$

The compressibility factor z and z_{vdW}, are calculated from

$$z^3 + [(u + w - 1)b^* - 1]z^2 + [(uw - u - w)b^{*2} - (u + w)b^* + a^*]z - (uwb^{*3} + \\ + uwb^{*2} + a^*b^*) = 0 \tag{17}$$

Since V^* is an implicit function of a^* and b^* (Eq. (13)), a^*/b^* does not have an explicit solution so an iterative technique is required for the calculation.

NRTL equation for CEOS/$\mathrm{G^E}$ *models*

Bearing in mind the exceptional flexibility of the NRTL model and its capability to correlate composition dependences of experimentally measured excess properties of non-specific shape (W-shaped curves), this equation was chosen as an activity coefficient model for the calculation of the excess Gibbs energy (G^{E}). The NRTL equation[16] can be expressed by the equation:

$$\frac{G^{\mathrm{E}}}{RT} = \sum_i x_i \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_k x_k G_{ki}} \tag{18}$$

where, for binary systems

$$G_{12} = \exp(-\alpha_{12}\tau_{12}); \; G_{21} = \exp(-\alpha_{12}\tau_{21}); \; \tau_{12} = (g_{12} - g_{22})/RT; \\ \tau_{21} = (g_{21} - g_{11})/RT \tag{19}$$

$$\alpha_{12} = c_1 \tag{20}$$

$$g_{12} - g_{22} = c_2 \tag{21}$$

$$g_{21} - g_{11} = c_3 \tag{22}$$

The binary interaction parameters were treated as temperature independent quantities since our preliminary investigation showed that treating these parameters as temperature dependent does not improve the results of the correlation. The CEOS models obtained on this basis are systematized in Table I.

TABLE I. The CEOS and CEOS/G^E models used in the present work

Model	Equations
vdW1	(6), (7), (10), (11)
MvdW1-1	(6), (8), (9)
MvdW1-2	(6), (9), (10), (12) $m_{ij}' = 0$, $k_{ij}' \neq 0$, $l_{ij}' \neq 0$
MvdW1-3	(6), (9), (10), (12) $l_{ij}' = 0$, $k_{ij}' \neq 0$, $m_{ij}' \neq 0$
MvdW1-4	(6), (9), (10), (12), $k_{ij}' \neq 0$, $l_{ij}' \neq 0$, $m_{ij}' \neq 0$
TCBT-1	(6), (7), (10), (11), (13)–(22) $\alpha_{12} = 0.3$, $k_{ij} = 0$, $m_{ij} = 0$
TCBT-2	(6), (7), (10), (11), (13)–(22) $\alpha_{12} = 0.3$, $k_{ij} \neq 0$, $m_{ij} = 0$
TCBT-3	(6), (7), (10), (11), (13)–(22) $\alpha_{12} = 0.3$, $k_{ij} \neq 0$, $m_{ij} \neq 0$
TCBT-4	(6), (7), (10), (11), (13) – (22) $k_{ij} = 0$, $m_{ij} = 0$
TCBT-5	(6), (7), (10), (11), (13) – (22) $k_{ij} \neq 0$, $m_{ij} \neq 0$

PRESENTATION OF THE CEOS AND CEOS/G^E MODELS

The general equation for the excess volume calculation is given by

$$V^E = V - \sum_i x_i V_i \tag{23}$$

where: V_i – represents the molar volume of the pure component i, and V – denotes the molar volume of the mixture.

The binary interaction parameters can be determined by minimization of the following objective function

$$OF = \frac{1}{n} \sum_{i=1}^{n} \left(\frac{V^E_{\exp} - V^E_{\text{cal}}}{V^E_{\exp}} \right)_i^2 \rightarrow \min \tag{24}$$

where n stands for the number of experimental data points.

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

$$PD(V^E) = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{V^E_{\exp} - V^E_{\text{cal}}}{(V^E_{\exp})_{\max}} \right| \tag{25}$$

RESULTS AND DISCUSSION

By applying the CEOS and CEOS/G^E models which are systematized in Table I, correlation of the composition dependences of V^E data for the binaries methanol (1) + acetonitrile (2) and ethanol (1) + acetontrile (2) was performed. These data sets were determined experimentally at 298.15 K and reported in the first part of our investigation.[13] All the correlation results are summarized in Table II of the present work.

TABLE II. Correlation of the V^E data by vdW and TCBT models for the alcohol (1) + acetonitrile (2) systems at 298.15 K

Model	Number of parameters	Methanol (1)+acetonitrile (2)	Ethanol (1)+acetonitrile (2)
		$PD(V^E)$	$PD(V^E)$
vdW1	2	17.57	20.25
MvdW1-1	2	4.79	12.59
MvdW1-2	2	7.63	5.46
MvdW1-3	2	16.98	10.86
MvdW1-4	3	2.54	3.19
TCBT-1	2	2.48	10.75
TCBT-2	3	1.87	3.08
TCBT-3	4	1.75	2.63
TCBT-4[a]	3	2.41	7.44
TCBT-5[b]	5	1.74	2.49

[a] Methanol (1)+acetonitrile (2): α_{12} =0.037; ethanol (1)+acetonitrile (2): α_{12} =0.043; [b] methanol (1) + acetonitrile (2): α_{12} =0.065; ethanol (1)+acetonitrile (2): α_{12} =0.137

Methanol (1)+acetonitrile (2) system. For this system very small negative V^E values are characteristic over the entire composition range. It can be seen from Table II that particularly unreliable results with errors over 15 % were obtained when the two parameter vdW1 and MvdW1-3 models were used. The obtained results indicate the large influence of the way in which the interaction parameters are incorporated in the vdW two parameter models. Namely, when the parameter m_{ij} or m_{ij}' was replaced by the interaction parameter l_{ij}' (MvdW1-1 and MvdW1-2), somewhat better results with the corresponding errors amounting to 7.63 % and 4.79 %, respectively, were obtained. To obtain acceptable result with the vdW models, application of the three parameters MvdW1-4 model is necessary.

The deviations presented in Table II show that the models TCBT-2, TCBT-3 and TCBT-5 result in very satisfactory correlations with the corresponding errors being less than 1.90 %. On the other hand, the TCBT-1 and TCBT-4 models gave results slightly better than those obtained by the MvdW1-4 model.

Comparison of the results obtained by the various TCBT models lead to several conclusions: *i*) successful correlations can be obtained by means of the three parameter TCBT-2 model, whereas a further increase in the number of parameters (TCBT-3 and TCBT-5) does not improve the results significantly, *ii*) similar to the case of the vdW models, the choice of the op-

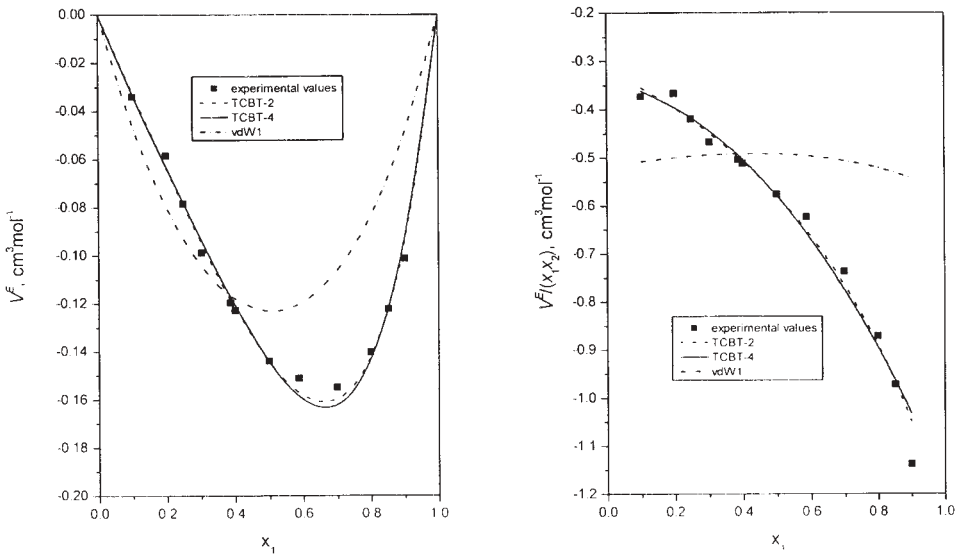

Fig. 1. Experimental[13] and calculated V^E for the methanol (1) + acetonitrile (2) system at 298.15 K given in following diagrams: a) $V^E - x_1$; b) $V^E/(x_1\,x_2) - x_1$. The symbols and the various types of lines are reported in the legend.

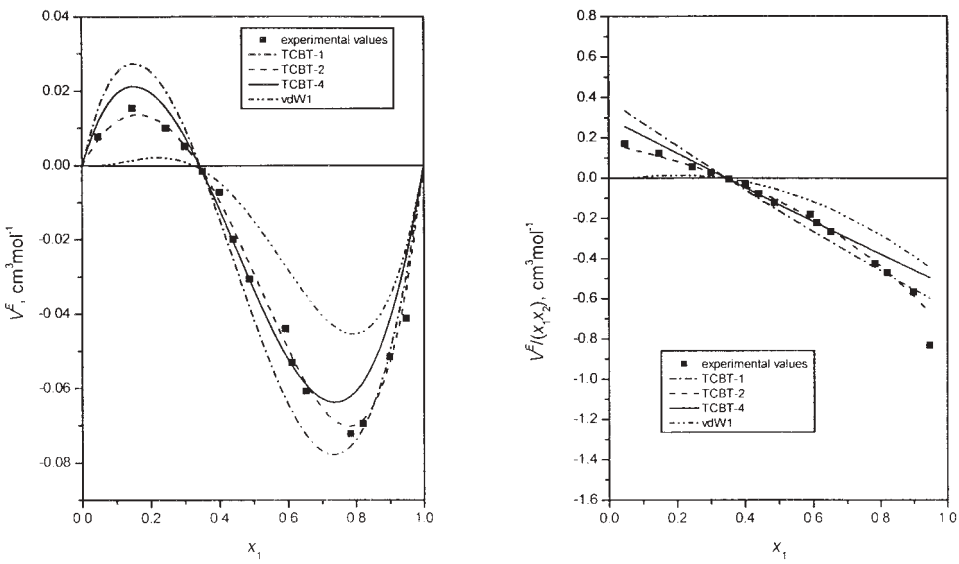

Fig. 2. Experimental[13] and calculated V^E for the ethanol (1) + acetonitrile (2) system at 298.15 K given in following diagrams: a) $V^E - x_1$; b) $V^E/(x_1\,x_2) - x_1$. The symbols and the various types of lines are reported in the legend.

timized parameters was crucial; namely comparison of the TCBT-2 and TCBT-4 models shows that incorporation of one parameter of the van der Waals fluid leads to better results than if the parameter α_{12} was incorporated with its optimal value, *iii*) the presence of the optimal values of parameter α_{12} has a negligible effect on the improvement of the results (comparison of the errors corresponding to the models TCBT-1 and TCBT-4, as well as those obtained by the TCBT-3 and TCBT-5 models); hence, correlation of the V^E data can be carried out by the models which use a constant value of the parameter α_{12} = 0.3 (for example, the TCBT-2 model), *iv*) the three parameter TCBT-2 model gave better results in comparison to those generated by the three parameter MvdW1-4 model.

The correlation results obtained by means of the vdW1, TCBT-2 and TCBT-4 models are presented in Figs. 1a and 1b. The large deviation of the correlation based on the two parameters vdW1 model from the experimental data points is a consequence of the inability of the mentioned model to follow the non-symmetric behavior of the V^E–x_1 relationship over the entire composition range.

Ethanol (1)+acetonitrile (2) system. For this system the W-shape of the V^E–x_1 curve is characteristic; in addition, these V^E values are rather small. It can be seen from Table II that the correlation based on the two parameter vdW models gave pure results, *i.e.*, that the W-shape of the V^E–x_1 curve, which is a consequence of the specific interactions between the molecules,[13] cannot be adequately represented by the above mentioned models. Some improvement was obtained when the MvdW1-4 model was employed.

On the basis of the results from Table II, which correspond to the TCBT models, the following conclusions can be drawn: *i*) the models which do not include the parameters of the vdW fluids (TCBT-1 and TCBT-4) are not suitable for correlation of the V^E data, *ii*) comparison of the results obtained by the TCBT-2 and TCBT-3 models shows that the use of both binary interaction parameters of the vdW fluid is not necessary, *iii*) the optimized values for the α_{12} parameter do not lead to a substantial improvement of the correlation and, hence, a constant value α_{12} = 0.3 should be used.

Figures 2a and 2b show that the two parameter models vdW1 and TCBT-1, as well as the TCBT-4 model work inadequately, being unable to follow the variation of V^E with composition, which exhibits a maximum and a minimum value.

CONCLUSION

Correlatioin of the composition dependences of the experimental excess molar volume data for the systems methanol (1) + acetonitrile (2) and ethanol (1) + acetonitrile (2) at 298.15 K and atmospheric pressure by the TCBT models, which incorporate the binary interaction parameters of the vdW fluid, as well as by the MvdW1-4 models lead to exceptionally good results. Also, it appeared that the use of the temperature dependent parameters of the models was not necessary.

LIST OF SYMBOLS

A^E – Excess molar Hemlholtz free enrgy
a – Equation of state energy parameter
b – Equation of state size parameter
G^E – Excess molar Gibbs energy
g – NRTL model parameter
k, m, k', l', m' – Interaction parameters
n – Number of experimental data points
OF – Objective function
P – Pressure
R – Gas constant
T – Absolute temperature
V – Molar volume
V^E – Excess molar volume
x – Liquid phase mole fraction
z – Compressibility factor

Greek letters
α – NRTL excess free energy non-randomness parameter
τ – NRTL excess free energy model binary interaction parameter
ω – Acentric factor

Subscripts
i, j, k – Components
c – Critical property
cal – Calculated property
exp – Experimental property
r – Reduced property
vdW – Van der Waals fluid
max – Maximal value

Supersripts
* – Reduced values

ИЗВОД

ДОПУНСКА МОЛАРНА ЗАПРЕМИНА СИСТЕМА АЦЕТОНИТРИЛ + АЛКОХОЛ НА 298.15 K. II ДЕО. КОРЕЛИСАЊЕ ПОМОЋУ КУБНЕ ЈЕДНАЧИНЕ СТАЊА

ИВОНА Р. ГРГУРИЋ, МИРЈАНА Љ. КИЈЕВЧАНИН, БОЈАН Д. ЂОРЂЕВИЋ, АЛЕКСАНДАР Ж ТАСИЋ и СЛОБОДАН П. ШЕРБАНОВИЋ

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Допунска моларна запремина V^E бинарних течних смеша ацетонитрил + метанол и ацетонитрил + етанол, експериментално одређена у претходном делу рада, корелисана је помоћу PRSV једначине са vdW и TCBT правилима мешања. Добијени резултати показују да је број и положај интеракционих параметара у разматраним моделима од велике важности за задовољавајуће корелисање V^E података.

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