

Thermodynamic Modeling of Vapor-Liquid Equilibria and Excess Properties of the Binary Systems Containing Diethers and n-Alkanes by Cubic Equation of State

Slobodan P. Šerbanović, Ivona R. Grgurić, Mirjana Lj. Kijevčanin, Aleksandar Ž. Tasić and Bojan D. Djordjević[†]

Department of Chemical Engineering, Faculty of Technology and Metallurgy,
University of Belgrade, 11120 Belgrade, Karnegijeva 4, Serbia and Montenegro
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Abstract—A comparison of the performances of two different approaches of cubic equations of state models, based on a classical van der Waals and mixing rules incorporating the G^E equation, was carried out for correlation of Vapor-Liquid Equilibria (VLE), H^E and c_p^E data alone, and simultaneous correlation of VLE+ H^E , VLE+ c_p^E , $H^E+c_p^E$ and VLE+ $H^E+c_p^E$ data for the diethers (1,4-dioxane or 1,3-dioxolane) with n-alkane systems. For all calculations the Peng-Robinson-Stryjek-Vera cubic equation of state (PRSV CEOS) was used. A family of mixing rules for the PRSV CEOS based on the Modified van der Waals one-fluid mixing rule (MvdW1) and two well-known CEOS/ G^E mixing rules (MHV1 and MHV2), was considered. The NRTL equation, as the G^E model with linear or reciprocal temperature dependent parameters, was incorporated in the CEOS/ G^E models. The results obtained by the CEOS/ G^E models exhibit significant improvement in comparison to the MvdW1 models.

Key words: Cubic Equation of State, Thermodynamic Properties, Diether, n-Alkane, Simultaneous Correlation

INTRODUCTION

Numerous cubic equations of state (CEOS) have been proposed for description of the phase behaviour and thermodynamic properties of pure components and their mixtures. Due to their simplicity and accuracy, CEOS are the most frequently used equations of state for computer-aided design of chemical processes. The success of VLE (vapor-liquid equilibria) fitting depends on the accuracy of the vapor pressures calculation of pure compounds and the functional form of mixing rules. In the past the CEOS approach has been widely applied successfully to systems containing only non-polar and slightly polar components at all conditions of practical interest. Relatively simple mixtures (i.e., hydrocarbons, hydrocarbons with inorganic gases) are performed adequately by the so-called van der Waals one fluid mixing and combining rules at low-density limit as the ideal gas law and at high-density state ("dense fluid").

However, for asymmetric non-ideal mixtures, where molecules are dissimilar in size or chemical nature, a number of alternative mixing rules have to be applied—first of all, composition-dependent and density-dependent mixing rules. The first of them in the low-density limit are inconsistent with the statistical mechanical result that the second virial coefficient must be a quadratic function of composition. To correct this problem attempts have been made to develop density-dependent mixing rules. Both rules improve the representation of phase behaviour in very complex non-ideal mixtures. A concise review of development of these two types of rules has been given by a few authors [Panagiotopoulos and Reid, 1986; Anderko, 1990; Malanowski and Anderko, 1992].

Very recently some mixing rules that combine molar Gibbs or Helmholtz free energy models (G^E or A^E) and CEOS have been successfully applied to very complex systems of diverse nature cover-

ing wide ranges of temperature and pressure. Among these theoretical and approximate models, the so-called CEOS/ G^E or CEOS/ A^E have been used for correlation and prediction of VLE, liquid-liquid equilibria (LLE) and other thermodynamic properties. These models have been widely studied and an extensive analysis of their applicability has been reviewed in several articles and monographs [Sandler, 1994; Heidemann, 1996; Sandler and Orbey, 1998, 2000; Djordjević et al., 2001]. A number of comparative studies of various cubic equation of state mixing rules have been made with no general conclusion about which models are superior to others, keeping in mind that their capabilities and weaknesses vary for different mixtures and corresponding calculations, for example Knudsen et al. [1993], Voros and Tassios [1993], Kang et al. [1995], Orbey and Sandler [1996], Valderama and Silva [2003], Grgurić et al. [2004], Kijevčanin et al. [2004]. However, very limited information exists in the relevant literature, concerning the simultaneous correlation of several thermodynamic properties with CEOS/ G^E models. The reason for this situation is certainly based on the fact that it is difficult to correlate accurately with sufficient precision VLE data at different temperatures simultaneously with molar excess enthalpy (H^E) and molar excess heat capacity (c_p^E) data, etc. A few CEOS/ G^E models have been used for correlation of the binary VLE and H^E data [Orbey and Sandler, 1996; Ohta, 1997], and binary VLE, H^E and c_p^E data [Orbey and Sandler, 1995; Djordjević et al., 1999a, b, c]. Also, the applicability of the hydrogen-bonding lattice fluid equation of state to describe simultaneous correlation of VLE, H^E and V^E data for mixtures containing associating components was investigated by Park et al. [2003].

In the present work the Peng-Robinson-Stryjek-Vera (PRSV) CEOS [Stryjek and Vera, 1986] is coupled with three different mixing rules: the modified van der Waals one-fluid [Schwartzentruber and Renon, 1989] (MvdW1), the modified Huron-Vidal first order (MHV1) [Michelsen, 1990] and second order (MHV2) [Dahl and Michelsen, 1990] were applied. These models were used for single

[†]To whom correspondence should be addressed.

E-mail: bojan@tmf.bg.ac.yu

VLE, H^E and c_p^E as well as for the simultaneous correlation of VLE+ H^E , VLE+ c_p^E , H^E + c_p^E and VLE+ H^E + c_p^E data of 1,4-dioxane or 1,3-dioxolane with n-alkanes (heptane, octane and nonane), which exhibit the distinct W-shape of the c_p^E -x curves. Various data sources for mixtures studied here are available from literature [Tassios and van Winkle, 1967; Calvo et al., 1998; Wu and Sandler, 1989; Brocos et al., 1998].

Systems of solvent pairs which include diethers (1,4-dioxane, 1,3-dioxolane) and n-alkanes are frequently present in industrial practice. Also, the importance of diethers, bearing in mind their toxicity and danger, is particularly emphasized in many situations where they are used as solvent agents or stabilizers. Thermodynamic information about those mixtures is needed for rational design of chemical processes or to replace such mixtures by those which ensure greater safety.

Excess properties such as H^E or c_p^E and VLE behaviour of the diether+n-alkane mixtures, point to their very complex structure and, hence on the difficulty in their modeling by various approaches.

EQUATION OF STATE AND MIXING RULES

For pure components we have chosen to use the PRSV CEOS, in the form of

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

For pure compound it follows

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

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

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

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

where k_{ij} is the pure compound adjustable parameter [Stryjek and Vera, 1986].

For the purpose of evaluating the parameter a of binary mixtures the PRSV CEOS was coupled with three different mixing rules: MvdW1, MHV1 and MHV2.

1. Mixing Rule MvdW1

The mixture parameter a of the modified van der Waals one-fluid mixing rule (MvdW1), which includes a composition-dependent term, is given by

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

where $k_{ij} = k_{ji}$ and $l_{ij} = -l_{ji}$.

2. Mixing Rule MHV1 and MHV2

The Modified Huron-Vidal first order (MHV1) mixing rule is as follows:

$$\varepsilon = \sum_i x_i \varepsilon_i + \frac{1}{q_1} \left[\frac{G_y^E}{RT} + \sum_i x_i \ln \left(\frac{b_i}{b} \right) \right] \quad (7)$$

where q_1 is a numerical constant dependent on the CEOS (for the PRSV CEOS, $q_1 = -0.53$), while ε stands for the dimensionless parameter: $\varepsilon = a/bRT$.

The Modified Huron-Vidal second order mixing rule (MHV2) is given by

$$q_1 \left(\varepsilon - \sum_i x_i \varepsilon_i \right) + q_2 \left(\varepsilon^2 - \sum_i x_i \varepsilon_i^2 \right) = \frac{G_y^E}{RT} + \sum_i x_i \ln \left(\frac{b_i}{b} \right) \quad (8)$$

where for the PRSV CEOS: $q_1 = -0.4347$ and $q_2 = -0.003654$.

The NRTL equation [Renon and Prausnitz, 1968] has the form

$$\frac{G_y^E}{RT} = \sum_i x_i \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_k x_k G_{ki}} \quad (9)$$

Table 1. Mixing rules for CEOS and CEOS/ G^E models investigated here

Model	Temperature dependency of parameters	Equations
MvdW1-1	$(k_{ij} \text{ and } l_{ij})^a$	(6), (11), (12)
MvdW1-2	$(k_{ij} \text{ and } l_{ij})^b$	(6), (11), (13)
MHV1-1	$\alpha_{12}=0.3$	$(a_{12} \text{ and } a_{21})^a$
MHV1-3a	α_{12} optimized ^c	$(a_{12} \text{ and } a_{21})^a$
MHV1-3	Linear form ^d for α_{12}	$(a_{12} \text{ and } a_{21})^a$
MHV2-1	$\alpha_{12}=0.3$	$(a_{12} \text{ and } a_{21})^a$
MHV2-3a	α_{12} optimized ^c	$(a_{12} \text{ and } a_{21})^a$
MHV2-3	Linear form ^d for α_{12}	$(a_{12} \text{ and } a_{21})^a$
MHV1-2	$\alpha_{12}=0.3$	$(a_{12} \text{ and } a_{21})^b$
MHV1-4a	α_{12} optimized ^c	$(a_{12} \text{ and } a_{21})^b$
MHV1-4	Reciprocal form ^f for α_{12}	$(a_{12} \text{ and } a_{21})^b$
MHV2-2	$\alpha_{12}=0.3$	$(a_{12} \text{ and } a_{21})^b$
MHV2-4a	α_{12} optimized ^c	$(a_{12} \text{ and } a_{21})^b$
MHV2-4	Reciprocal form ^f for α_{12}	$(a_{12} \text{ and } a_{21})^b$

^aLinear form.

^bReciprocal form.

^c $\alpha_{12} = \alpha_{12,0}$; ^d $\alpha_{12} = \alpha_{12,0} + \alpha_{12,1}T$; ^e $\alpha'_{12} = \alpha'_{12,0}$; ^f $\alpha'_{12} = \alpha'_{12,0} + \frac{\alpha'_{12,1}}{T}$

where for a binary system

$$G_{12} = \exp(-\alpha_{12}\tau_{12}), G_{21} = \exp(-\alpha_{12}\tau_{21}), \tau_{12} = a_{12}/T, \tau_{21} = a_{21}/T \quad (10)$$

where $a_{12} = g_{12} - g_{22}$ and $a_{21} = g_{21} - g_{11}$.

In all CEOS and CEOS/ G^E models the parameter b is determined by the linear mixing rule

$$b = \sum_i x_i b_i \quad (11)$$

For the interaction parameters of the mixing rules, mentioned above, two temperature dependent forms were used:

$$Y_{ij} = Y_{ij,0} + Y_{ij,1}T \quad (\text{the linear temperature dependence}) \quad (12)$$

$$Y'_{ij} = Y_{ij,0} + \frac{Y_{ij,1}}{T} \quad (\text{the reciprocal temperature dependence}) \quad (13)$$

where Y_{ij} or Y'_{ij} stands for k_{ij} , l_{ij} , α_{12} , a_{12} or a_{21} .

The non-randomness parameter α_{12} is treated in three ways as: (i) the value recommended by Renon and Prausnitz: $\alpha_{12} = 0.3$, (ii) optimal temperature independent value between 0 and 1, and (iii) temperature dependent value in the same range of the values.

All mixing rules mentioned above are systematized in Table 1.

DATA REDUCTION PROCEDURE

The calculated pressure and the vapor mole fraction of component i for each data point of isothermal VLE are evaluated by the bubble point calculation, equating the fugacity of vapor and liquid phase for each component. The expression for the fugacity f_i of the component i (or the fugacity coefficient ϕ_i) needed for the VLE calculation is

$$\ln \frac{f_i}{x_i P} = \ln \phi_i = \frac{1}{RT} \int_{\infty}^V \left[\frac{RT}{V} - n \left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} \right] dV - \ln \frac{PV}{RT} \quad (14)$$

The general equation for the H^E calculation is given as

$$H^E = \sum_i x_i (H_i^* - H_i) - (H^* - H) \quad (15)$$

where $(H_i^* - H_i)$ and $(H^* - H)$ are the residual enthalpies for pure component and mixture, respectively. These residual terms can be calculated from a CEOS, using the expression

$$(H^* - H)_{\text{pure or mix}} = RT - PV + \int_{\infty}^V \left[P - T \left(\frac{\partial P}{\partial T} \right) \right] dV \quad (16)$$

In order to obtain c_p^E we used a relationship between c_p^E and H^E

$$c_p^E = \left(\frac{\partial H^E}{\partial T} \right)_{P,x} \quad (17)$$

All coefficients in the expressions for temperature-dependent parameters of the CEOS and CEOS/ G^E models were generated by minimizing the following objective function OF [Djordjević et al., 1999a]:

$$\text{OF} = \text{OF}_1 + \text{OF}_2 + \text{OF}_3 = \frac{1}{k} \sum_{i=1}^k \left(\frac{P_{\text{exp}} - P_{\text{cal}}}{P_{\text{exp}}} \right)_i^2 + \frac{1}{m} \sum_{i=1}^m \left(\frac{H_{\text{exp}}^E - H_{\text{cal}}^E}{H_{\text{exp}}^E} \right)_i^2 + \frac{1}{n} \sum_{i=1}^n \left(\frac{c_{p,\text{exp}}^E - c_{p,\text{cal}}^E}{c_{p,\text{exp}}^E} \right)_i^2 \rightarrow \min \quad (18)$$

For the minimization of the OF, the Hooke and Jeeves tech-

nique [Hooke and Jeeves, 1961] was used.

The results of VLE, H^E and c_p^E data calculation are assessed by the following deviations. Average absolute deviation $D(Z)$:

$$D(Z) = \frac{1}{n} \sum_{i=1}^n |Z_{\text{exp}} - Z_{\text{cal}}|_i \quad (19)$$

where Z stands for y . Percentage average absolute deviation $PD(Z)$:

$$PD(Z) = \frac{100}{n} \sum_{i=1}^n \frac{|Z_{\text{exp}} - Z_{\text{cal}}|}{(Z_{\text{exp}})_{\max i}} \quad (20)$$

where Z stands for P or H^E or c_p^E .

RESULTS AND DISCUSSION

For the purpose of fitting of VLE, H^E and c_p^E data alone, and simultaneous fitting of VLE+ H^E , VLE+ c_p^E , H^E + c_p^E and VLE+ H^E + c_p^E , data we selected the diether+n-alkane systems for which VLE, H^E and c_p^E data are available in the literature as given in Table 2. All calculations were performed by the CEOS and CEOS/ G^E models listed in Table 1. The results obtained for simultaneous correlation by the CEOS/ G^E models with the constant non-randomness parameter α_{12} are very poor and therefore were not further considered. Also, the correlating results reached by the CEOS/ G^E models having linear temperature-dependent parameters, in most cases, are inferior to the models with reciprocal temperature-dependent parameters, so they were excluded from the tables of results. The MvdW1-1 and MvdW1-2 models work almost identically, so henceforth only the MvdW1-1 model will be considered. Numerical values of the optimized coefficients, existing in the CEOS and CEOS/ G^E models used for correlation of c_p^E , as well as of diverse combinations of VLE, H^E and c_p^E data, are summarized in Tables A.1, A.2 and A.3

Table 2. Binary systems and thermodynamic properties being used

Property	No. of experimental points	T [K]	Ref.
1,4-dioxane+heptane			
VLE	12	353.15	a
H^E	17	298.15	b
c_p^E	12	298.15	b
1,4-dioxane+octane			
VLE	8	353.15	a
H^E	17	298.15	b
c_p^E	12	298.15	b
1,4-dioxane+nonane			
VLE	7	353.15	a
H^E	16	298.15	b
c_p^E	12	298.15	b
1,3-dioxolane+heptane			
VLE	21	313.15	c
VLE	19	343.15	c
H^E	17	298.15	d
c_p^E	12	298.15	d

^a[Tassios and van Winkle, 1967].

^b[Calvo et al., 1998].

^c[Wu and Sandler, 1989].

^d[Brocos et al., 1998].

of the Appendix.

1. Correlation of VLE Data

Fitting of VLE data of the 1,4-dioxane+n-alkane systems at 353.15 K, using the objective function $OF=OF_1$ for the determination of optimized parameters, was performed by the simple CEOS/ G^E models with two temperature-dependent parameters (four adjusted coefficients and recommended value for $\alpha_{12}=0.3$) and the MvdW1-1 model. The obtained results of all models were outstanding with errors in PD(P) below 1%, and the deviation D(y) within experimental accuracy. Therefore, the CEOS/ G^E models with a larger number of the adjusted coefficients are not needed. The VLE data for the 1,3-dioxolane+heptane system, which exhibits azeotropes at 313.15 K and 343.15 K, were correlated inside this temperature range. As in the case of the 1,4-dioxane+n-alkane systems, the same models gave excellent results, with the exception of the MvdW1-1 model which gave deviations PD(P) larger than 1%.

2. Correlation of H^E Data

Correlation of the H^E data using the chosen CEOS and CEOS/ G^E models with $OF=OF_2$ was carried out for all 1,4-dioxane+n-alkane systems. Overall H^E results obtained by the simplest MHV1-2 and MHV2-2, as well as the MvdW1-1 models, are exceptional and almost within experimental accuracy, having errors below 1%. The results obtained by the same models for the 1,3-dioxolane+heptane system at 298.15 K are even better than those for the 1,4-dioxane+n-alkane systems with the errors less than 0.5%.

3. Correlation of c_p^E Data

Correlation of c_p^E data for the 1,4-dioxane+n-alkane and 1,3-dioxolane+heptane systems at 298.15 K with $OF=OF_3$ was performed using all types of the models chosen. The following observations can be made for the CEOS/ G^E models: (i) the simplest MHV1-2 and MHV2-2 models gave satisfactory results with errors below 2% for 1,4-dioxane+n-alkane systems and below 1% for the 1,3-dioxolane+heptane system (Table 3); (ii) models with optimized or temperature-dependent non-randomness parameter α_{12} , in most cases gave slightly better correlation compared to models with $\alpha_{12}=0.3$. An exception was obtained for the systems of 1,4-dioxane+heptane and +octane, where the MHV2-2a model is superior over the MHV2-2 model (in Table 3 given in brackets). Correlated c_p^E results achieved with the MvdW1-1 model for all systems are unsatisfactory with errors considerably higher than those obtained by CEOS/ G^E models as presented in Table 3.

Table 3. PD(c_p^E) from correlation of c_p^E obtained for investigated systems by various models

System	MHV1-2	MHV2-2	MvdW1-1
1,4-dioxane+heptane	1.63	2.01 (1.41) ^a	4.26
1,4-dioxane+octane	1.51	1.81 (1.38) ^b	2.38
1,4-dioxane+nonane	1.63	1.77	1.99
1,3-dioxolane+heptane	0.99	0.84	1.79

^{a,b}Values in brackets obtained by MHV2-2a models with the following parameters:

^a $\alpha'_{12,0}=0.467282E-1$; $\alpha'_{12,0}=0.255415E+4$ K; $\alpha'_{12,1}=0.547353E+6$ K²; $\alpha'_{21,0}=-0.522962E+4$ K; $\alpha'_{21,1}=0.203266E+6$ K².

^b $\alpha'_{12,0}=0.153976E-1$; $\alpha'_{12,0}=0.914628E+4$ K; $\alpha'_{12,1}=-0.563247E+6$ K²; $\alpha'_{21,0}=-0.640996E+4$ K; $\alpha'_{21,1}=0.657379E+6$ K².

4. Simultaneous Correlation of VLE+ H^E Data

A unique set of optimized coefficients of all models was generated from VLE+ H^E data by using the objective function $OF=OF_1+OF_2$. For all systems it could be noticed that the temperature dependence of parameters in the CEOS/ G^E models is practically of no influence on the values of errors. For the systems of 1,4-dioxane with n-alkanes, the MHV1 and MHV2 models with five optimized coefficients perform comparably, with slightly lower accuracy in PD(H^E), compared to the corresponding models with six coefficients. As can be seen from Table 4, the errors obtained with the MvdW1-1 model are considerably larger in D(y) than those of the CEOS/ G^E models. For the system 1,3-dioxolane+heptane, all CEOS/ G^E models achieved higher errors in PD(P) and D(y) and similar error is reached in PD(H^E) as in the case of the 1,4-dioxane+n-alkane sys-

Table 4. Calculated results for simultaneous correlation of VLE, H^E and c_p^E binary data

Property	Deviation	MHV1-4a	MHV1-4	MHV2-4	MvdW1-1
1,4-dioxane+heptane					
VLE+ H^E	PD(P)	0.43	0.47	0.48	0.46
	D(y)	0.0064	0.0061	0.0062	0.0154
	PD(H^E)	0.64	0.40	0.40	1.56
VLE+ c_p^E	PD(P)	0.45	0.44	0.41	6.52
	D(y)	0.0070	0.0070	0.0055	0.0259
	PD(c_p^E)	1.71	1.73	1.36	34.56
$H^E+c_p^E$	PD(H^E)	2.67	2.57	2.50	12.62
	PD(c_p^E)	1.94	1.77	1.52	32.82
1,4-dioxane+octane					
VLE+ H^E	PD(P)	0.44	0.34	0.35	0.84
	D(y)	0.0029	0.0031	0.0031	0.0106
	PD(H^E)	0.97	0.62	0.62	1.50
VLE+ c_p^E	PD(P)	0.47	0.57	0.55	1.71
	D(y)	0.0032	0.0038	0.0039	0.0173
	PD(c_p^E)	2.46	1.75	1.69	38.90
$H^E+c_p^E$	PD(H^E)	2.74	1.74	1.74	6.17
	PD(c_p^E)	2.98	1.79	1.76	29.26
1,4-dioxane+nonane					
VLE+ H^E	PD(P)	0.53	0.53	0.58	1.19
	D(y)	0.0051	0.0052	0.0052	0.0105
	PD(H^E)	0.83	0.58	0.58	1.28
VLE+ c_p^E	PD(P)	0.79	0.79	0.83	4.33
	D(y)	0.0043	0.0043	0.0067	0.0244
	PD(c_p^E)	1.94	1.92	1.81	29.13
$H^E+c_p^E$	PD(H^E)	2.25	1.74	1.79	8.68
	PD(c_p^E)	2.81	1.78	1.73	25.49
1,3-dioxolane+heptane					
VLE+ H^E	PD(P)	1.47	1.47	1.51	1.76
	D(y)	0.0124	0.0124	0.0125	0.0195
	PD(H^E)	0.82	0.80	0.79	0.79
VLE+ c_p^E	PD(P)	2.94	1.55	1.65	1.74
	D(y)	0.0168	0.0117	0.0122	0.0269
	PD(c_p^E)	2.51	1.97	1.95	29.84
$H^E+c_p^E$	PD(H^E)	2.89	2.16	2.15	2.30
	PD(c_p^E)	3.47	1.82	1.81	20.73

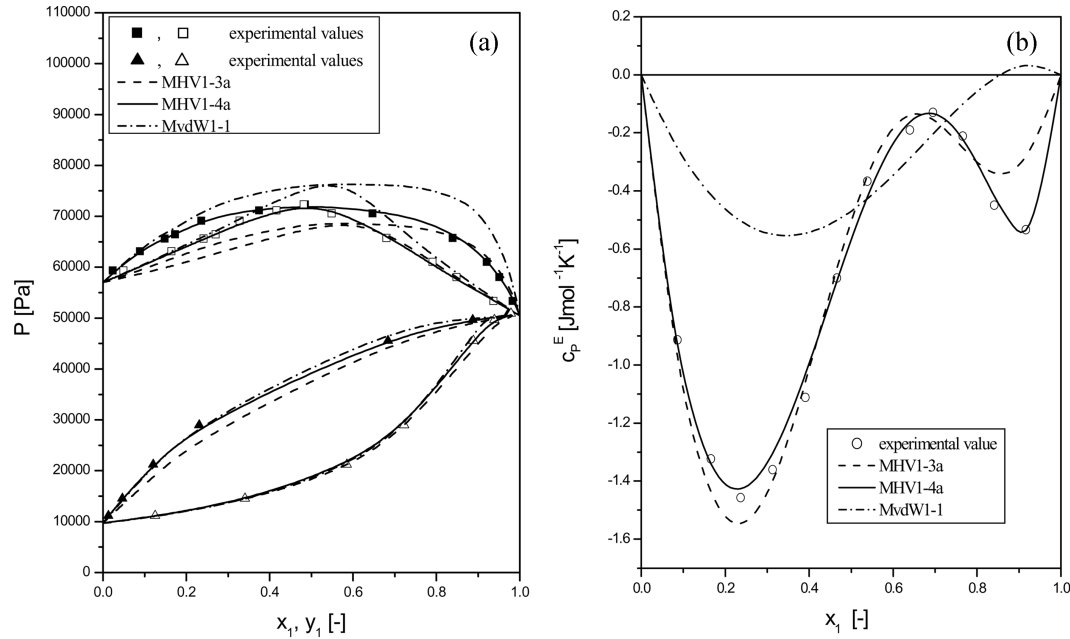


Fig. 1. Simultaneous correlation of VLE data at 353.15 K and c_p^E data at 298.15 K. The points are experimental data: a) ■, □- VLE at 353.15 K for the system 1,4-dioxane (1)+heptane (2) [Tassios and van Winkle, 1967], ▲, △- VLE at 353.15 K for the system 1,4-dioxane (1)+nonane (2) [Tassios and van Winkle, 1967]; b) ○- c_p^E at 298.15 K for the system 1,4-dioxane (1)+nonane (2) [Calvo et al., 1998].

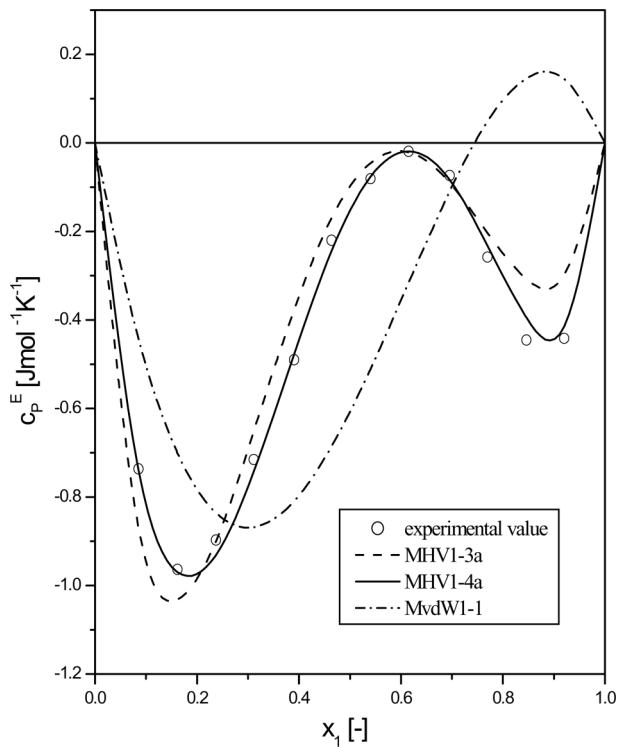


Fig. 2. Correlation of c_p^E data at 298.15 K with parameters of the models generated from the $H^E + c_p^E$ data for the system 1,4-dioxane (1)+heptane (2). The points ○ are experimental data [Calvo et al., 1998].

tems. For the MvdW1-1 model all deviations gave slightly better agreement with experimental data.

5. Simultaneous Correlation of VLE+ c_p^E Data

The simultaneous correlation of VLE+ c_p^E data was carried out by employing a single set of the optimized coefficients generated from the VLE+ c_p^E data of these properties using the objective function $OF=OF_1+OF_3$. As can be seen from Table 4, significant im-

Table 5. Calculated results for simultaneous correlation of VLE + $H^E + c_p^E$ binary data

Deviation	MHV1-4a	MHV1-4	MHV2-4
1,4-dioxane+heptane			
PD(P)	0.49	0.44	0.53
D(y)	0.0069	0.0053	0.0041
PD(H^E)	2.68	2.76	2.49
PD(c_p^E)	1.94	1.89	1.42
1,4-dioxane+octane			
PD(P)	0.33	0.33	1.16
D(y)	0.0032	0.0032	0.0035
PD(H^E)	2.97	2.96	3.01
PD(c_p^E)	3.43	3.42	3.56
1,4-dioxane+nonane			
PD(P)	2.56	2.25	0.34
D(y)	0.0144	0.0131	0.0058
PD(H^E)	3.52	3.53	3.89
PD(c_p^E)	3.61	3.61	3.53
1,3-dioxolane+heptane			
PD(P)	3.58	2.18	2.74
D(y)	0.0124	0.0132	0.0168
PD(H^E)	2.86	2.60	2.67
PD(c_p^E)	3.86	3.79	3.85

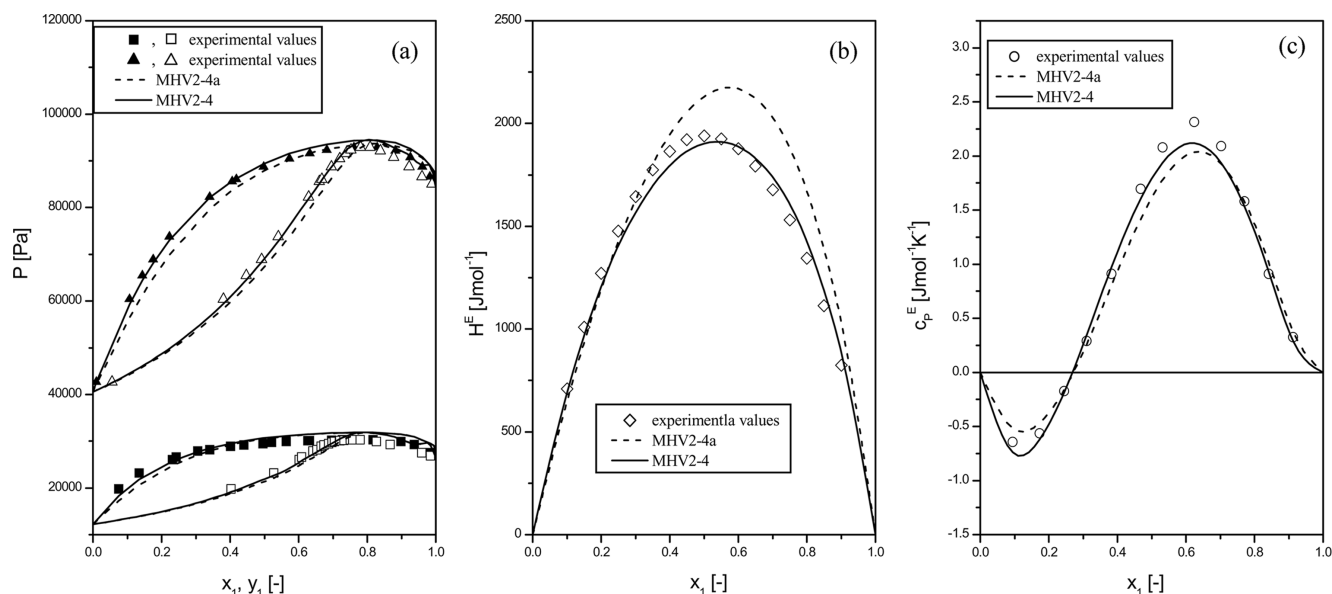


Fig. 3. Simultaneous correlation of the VLE+ H^E + c_p^E data of the system 1,3-dioxolane (1)+heptane (2). The points are experimental data: a) ■, □- VLE at 313.15 K [Wu and Sandler, 1989], ▲, △-VLE at 343.15 K [Wu and Sandler, 1989], b) ◇- H^E at 298.15 K [Brocos et al., 1998], c) ○- c_p^E at 298.15 K [Brocos et al., 1998].

provement is not achieved when the α_{12} is treated as a temperature-dependent parameter (comparison of the MHV1-4a to the MHV1-4 models); an exception is the 1,3-dioxolane+heptane system where the improvement is evident especially in calculating of the P and y. Both models with all temperature-dependent parameters (the MHV1-4 and MHV2-4), work similarly and very satisfactory. The MvdW1-1 model behaves qualitatively in a different way compared to the CEOS/ G^E models and works very poorly with very large errors in $PD(c_p^E)$ as summarized in Table 4. Fig. 1a and 1b represent the results of VLE and c_p^E fitting for the systems: 1,4-dioxane+heptane and 1,4-dioxane+nonane. As already mentioned, the linear CEOS/ G^E models are apparently inferior in comparison to the reciprocal CEOS/ G^E models, as is obviously shown in these Figures. The MHV1-3a as well as the MvdW1-1 model fail to indicate the position of the azeotrope and shape of VLE curves, as shown in Fig. 1a. In the case of c_p^E correlation, the MvdW1-1 model is not able to follow the W-shape of c_p^E - x_1 relationship in the whole composition range, while the MHV1-3a model gives a poor description in the region of two minima (Fig. 1b). On the contrary, the lines representing the MHV1-4a model are in a very good agreement with experimental values.

6. Simultaneous Correlation of H^E + c_p^E Data

Optimized coefficients of all models were generated from the simultaneous correlation of H^E + c_p^E data using the objective function $OF=OF_2+OF_3$. As can be seen from Table 4, the simultaneous fitting was successfully carried out with the MHV1-4 and MHV2-4 models, while the MvdW1-1 model gave very unsatisfactory fit of c_p^E data. The results of the simpler MHV2-4a model are absolutely inferior to the MHV2-4 model, while the quality of the fit obtained with the similar MHV1-4a model appeared to be better, but also relatively poor with the exception of the 1,4-dioxane+heptane system. Fig. 2 shows a comparison of c_p^E correlation using various models for the 1,4-dioxane+heptane system at 298.15 K. It is clear that the MHV1-4a model agrees most closely with the experimental data points and obviously dominates in comparison to the linear

MHV1-3a model. The fit obtained by the MvdW1-1 model does not follow the W-shape of the c_p^E experimental points, causing very large deviation in $PD(c_p^E)$.

7. Simultaneous Correlation of VLE+ H^E + c_p^E Data

Simultaneous fitting of binary VLE+ H^E + c_p^E data for the 1,4-dioxane+n-alkane and 1,3-dioxolane+heptane systems was performed with all models shown in Table 1, but only the acceptable results are listed in Table 5. As it was expected from the simultaneous cor-

Table A.1. Optimized coefficients for correlation of c_p^E binary data by CEOS and CEOS/ G^E models

	MHV1-2 ^a	MHV2-2 ^a	MvdW1-1
System	$a'_{12,0}$ [K]	$a'_{12,0}$ [K]	$k_{12,0}$ [-]
	$a'_{12,1}$ [K ²]	$a'_{12,1}$ [K ²]	$k_{12,1}$ [K ⁻¹]
	$a'_{21,0}$ [K]	$a'_{21,0}$ [K]	$l_{21,0}$ [-]
	$a'_{21,1}$ [K ²]	$a'_{21,1}$ [K ²]	$l_{21,1}$ [K ⁻¹]
1,4-dioxane +heptane	0.413866E+3	0.725320E+1	0.439190E+0
	0.434687E+5	0.124662E+6	0.205597E-3
	-0.252025E+3	-0.603685E+3	-0.385163E-1
	0.118846E+6	0.197579E+6	0.981973E-4
1,4-dioxane +octane	0.414791E+4	0.450791E+4	0.449896E+0
	-0.101645E+7	-0.109322E+7	0.236603E-3
	-0.320965E+4	-0.343277E+4	-0.454860E-1
	0.705880E+6	0.735710E+6	0.686508E-4
1,4-dioxane +nonane	0.428915E+4	0.242914E+3	0.484173E+0
	-0.104954E+7	0.111761E+6	0.271021E-3
	-0.326369E+4	-0.974098E+3	-0.811408E-1
	0.715880E+6	0.259765E+6	0.269580E-4
1,3-dioxolane +heptane	0.466088E+4	0.495241E+4	0.479247E+0
	-0.115487E+7	-0.121623E+7	0.247383E-3
	-0.354293E+4	-0.370728E+4	-0.894866E-1
	0.780806E+6	0.798333E+6	0.937006E-4

^a $\alpha_{12}=0.3$.

relation which includes c_p^E data, the MvdW1-1 model cannot be used for the simultaneous correlation of VLE+ H^E + c_p^E data. For all systems the results obtained with the MHV1-4 and MHV2-4 models are comparable and acceptable. For the 1,4-dioxane+octane system, both MHV1 models are superior to the MHV2-4 model in VLE correlation, while the MHV2-4 model correlates VLE data much better in the case of the 1,4-dioxane+nonane system. Performance of the MHV1-4a model is quite satisfactory, while on the contrary, similar MHV2-4a model with the same number of optimized pa-

rameters works very poorly. In addition, it can be observed that the errors of the CEOS/ G^E models in PD(H^E) and PD(c_p^E) mostly increase when the chain of n-alkane molecule increases. Fig. 3 shows superior behavior for the MHV2-4 compared to the MHV2-4a model as expressed most clearly in the H^E - x_1 diagram.

CONCLUSION

Correlation of VLE and H^E data for the diether+n-alkane sys-

Table A.2. Optimized coefficients for simultaneous correlation of VLE, H^E and c_p^E binary data by CEOS and CEOS/ G^E models

Property	MHV1-4a	MHV1-4	MHV2-4	MvdW1-1	MHV1-4a	MHV1-4	MHV2-4	MvdW1-1
	$\alpha'_{12,1}$ [K]	$\alpha'_{12,0}$ [-]	$\alpha'_{12,0}$ [-]	$k_{12,0}$ [-]	$\alpha'_{12,1}$ [K]	$\alpha'_{12,0}$ [-]	$\alpha'_{12,0}$ [-]	$k_{12,0}$ [-]
	$a'_{12,0}$ [K]	$\alpha'_{12,1}$ [K]	$\alpha'_{12,1}$ [K]	$k_{12,1}$ [K ⁻¹]	$a'_{12,0}$ [K]	$\alpha'_{12,1}$ [K]	$\alpha'_{12,1}$ [K]	$k_{12,1}$ [K ⁻¹]
	$a'_{12,1}$ [K ²]	$a'_{12,0}$ [K]	$a'_{12,0}$ [K]	$l_{21,0}$ [-]	$a'_{12,1}$ [K ²]	$a'_{12,0}$ [K]	$a'_{12,0}$ [K]	$l_{21,0}$ [-]
	$a'_{21,0}$ [K]	$a'_{12,1}$ [K ²]	$a'_{12,1}$ [K ²]	$l_{21,1}$ [K ⁻¹]	$a'_{21,0}$ [K]	$a'_{12,1}$ [K ²]	$a'_{12,1}$ [K ²]	$l_{21,1}$ [K ⁻¹]
	$a'_{21,1}$ [K ²]	$a'_{21,0}$ [K]	$a'_{21,0}$ [K]		$a'_{21,1}$ [K ²]	$a'_{21,0}$ [K]	$a'_{21,0}$ [K]	
		$a'_{21,1}$ [K ²]	$a'_{21,1}$ [K ²]			$a'_{21,1}$ [K ²]	$a'_{21,1}$ [K ²]	
1,4-dioxane+heptane				1,4-dioxane+nonane				
VLE+ H^E	0.403400E+0	-0.179120E+1	-0.161147E+1	0.499102E-1	0.386963E+0	-0.191179E+1	-0.175827E+1	0.325794E-1
	0.344773E+3	0.658600E+3	0.594358E+3	-0.322036E-4	0.555786E+3	0.710112E+3	0.652364E+3	-0.849723E-4
	0.189820E+5	0.276092E+4	0.286683E+4	-0.850111E-2	-0.154551E+5	0.322346E+4	0.329078E+4	-0.168332E-1
	-0.302544E+3	-0.646923E+6	-0.664632E+6	0.564239E-4	-0.519862E+3	-0.761327E+6	-0.770381E+6	0.466440E-4
	0.140104E+6	-0.221751E+4	-0.243018E+4		0.179391E+6	-0.235084E+4	-0.260542E+4	
		0.634660E+6	0.693978E+6			0.649285E+6	0.726602E+6	
VLE+ c_p^E	0.375959E+0	0.345932E+0	0.101101E+1	0.191223E-1	0.378957E+0	0.348884E+0	-0.168841E+1	0.475024E-1
	0.292660E+3	0.578650E+1	-0.149374E+3	-0.169221E-4	0.464326E+3	0.605565E+1	0.625389E+3	-0.183903E-4
	0.468433E+5	0.302687E+3	-0.703647E+2	0.149496E-1	0.377420E+5	0.486178E+3	0.404182E+4	-0.168332E-1
	-0.234968E+3	0.447787E+5	0.155784E+6	0.499814E-4	-0.401657E+3	0.330462E+5	-0.111096E+7	0.428361E-4
	0.107835E+6	-0.249367E+3	-0.206492E+3		0.128993E+6	-0.419953E+3	-0.169485E+4	
		0.110759E+6	0.127175E+6			0.132522E+6	0.449061E+6	
H^E + c_p^E	0.371265E+0	0.635445E+0	0.931861E+0	0.662860E-	0.141668E+0	-0.628502E+1	-0.945019E+1	0.572055E-1
	0.247725E+3	-0.605144E+2	-0.131404E+3	-0.109965E-4	0.508786E+4	0.212337E+4	0.308400E+4	-0.295709E-4
	0.510117E+5	0.278983E+3	-0.832217E+2	-0.151426E-2	-0.117614E+7	0.316198E+4	0.358948E+4	-0.619438E-1
	-0.211351E+3	0.635918E+5	0.143124E+6	0.108463E-3	-0.362746E+4	-0.899382E+6	-0.103149E+7	0.395253E-4
	0.108790E+6	-0.566233E+2	-0.261758E+3		0.777079E+6	-0.251984E+4	-0.291110E+4	
		0.880224E+5	0.131075E+6			0.712835E+6	0.833510E+6	
1,4-dioxane+octane				1,3-dioxolane+heptane				
VLE+ H^E	0.391497E+0	-0.223273E+1	-0.206091E+1	0.423478E-1	0.413786E+0	0.475306E+0	0.843014E+0	0.505347E-1
	0.463643E+3	0.818431E+3	0.755575E+3	-0.501775E-4	-0.126300E+3	-0.141725E+2	-0.116167E+3	-0.680386E-4
	-0.640014E+3	0.304763E+4	0.313903E+4	-0.110024E-1	0.127598E+6	-0.116026E+3	-0.208758E+3	-0.284759E-1
	-0.412705E+3	-0.721863E+6	-0.737951E+6	0.593494E-4	0.187052E+2	0.126013E+6	0.160963E+6	0.940402E-5
	0.158605E+6	-0.225833E+4	-0.246812E+4		0.792174E+5	0.871568E+1	-0.102343E+3	
		0.630435E+6	0.690388E+6			0.823587E+5	0.121662E+6	
VLE+ c_p^E	0.376711E+0	0.228091E+1	0.228320E+1	0.465972E-1	0.432020E+0	0.256117E+1	0.257266E+1	0.505215E-1
	0.337554E+3	-0.596934E+3	-0.602258E+3	-0.732692E-5	0.343464E+3	-0.667433E+3	-0.672082E+3	0.384647E-4
	0.477076E+5	0.670517E+3	0.623082E+3	-0.110420E-1	0.437334E+5	0.671425E+3	0.627606E+3	-0.224981E-1
	-0.317758E+3	-0.110464E+6	-0.927961E+5	0.143575E-4	-0.266227E+3	-0.107036E+6	-0.919458E+5	0.672068E-4
	0.122054E+6	0.185508E+2	0.677946E+0		0.121555E+6	0.282622E+3	0.270336E+3	
		0.439332E+5	0.500607E+5			-0.183574E+5	-0.136303E+5	
H^E + c_p^E	0.929682E-1	-0.150492E+2	-0.200726E+2	0.599930E-1	0.360067E+0	-0.114553E+2	-0.170328E+2	0.747593E-1
	0.639866E+4	0.4764109E+4	0.627353E+4	-0.190068E-4	0.384362E+3	0.362874E+4	0.531653E+4	0.535356E-4
	-0.146768E+7	0.378065E+4	0.421881E+4	-0.454921E-1	0.420539E+5	0.471832E+4	0.505273E+4	-0.140304E-1
	-0.470098E+4	-0.109861E+7	-0.123182E+7	0.685024E-4	-0.241852E+3	-0.137069E+7	-0.147609E+7	0.741894E-4
	0.100630E+7	-0.319644E+4	-0.3609298E+4		0.128097E+6	-0.391026E+4	-0.425938E+4	
		0.926944E+6	0.105227E+7			0.113373E+7	0.124262E+7	

tems alone, can be performed by the MHV1 and MHV2 models with two temperature-dependent parameters and a constant value of non-randomness parameter α_{12} . Correct description of the binary c_p^E data for the 1,4-dioxane+n-alkane systems, exhibiting a W-shaped form, requires two temperature-dependent parameters as well as the optimized value of the parameter α_{12} (MHV1-4a and MHV2-4a). Correlation of c_p^E data for the system 1,3-dioxolane+heptane can be successfully carried out by the MHV1-2 and MHV2-2 models. All CEOS/ G^E models with two temperature-dependent parameters, and with the optimized α_{12} parameter can be recommended for simultaneous correlation of VLE+ H^E and VLE+ c_p^E data of the diether+n-alkane systems. On the other hand, the CEOS/ G^E models, which include the temperature dependences of all parameters, work very well in simultaneous fitting of $H^E+c_p^E$ data of the same systems. In simultaneous correlation of VLE+ c_p^E and $H^E+c_p^E$ data, the MvdW1-1 model gives unsatisfactory results and cannot be recommended for these applications.

Simultaneous correlation of VLE+ $H^E+c_p^E$ data of the diether+n-

alkane systems by the MHV1-4a, MHV1-4 and MHV2-4 models leads to very similar results. Great flexibility of the CEOS/ G^E models with temperature-dependent parameters allows a more realistic description of the thermodynamic properties of the complex systems, because such an approach has a significant influence on the simultaneous correlation.

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APPENDIX A

In Tables A.1, A.2 and A.3 are summarized the numerical values of the optimized coefficients, existing in the CEOS and CEOS/ G^E models used for correlation of c_p^E , as well as of diverse combinations of VLE, H^E and c_p^E data.

NOMENCLATURE

- a : equation of state parameter [$\text{Pacm}^6\text{mol}^{-2}$]
 A^E : molar excess Helmholtz free energy [Jmol^{-1}]
 a_{ij} : temperature-dependent binary interaction parameters in CEOS/ G^E models [K]
b : equation of state parameter [$\text{cm}^3\text{mol}^{-1}$]
 c_p^E : molar excess heat capacity [$\text{Jmol}^{-1}\text{K}^{-1}$]
f : fugacity [Pa]
 G^E : molar excess Gibbs free energy [Jmol^{-1}]
 G_γ^E : molar excess Gibbs free energy from liquid activity coefficient model [Jmol^{-1}]
 G_{ji}, G_{ki} : coefficients of the NRTL model in Eq. (9)
H : molar enthalpy [Jmol^{-1}]
 H^E : molar excess enthalpy [Jmol^{-1}]
k, m, n : number of experimental data points [-]
 k_{ij}, l_{ij} : temperature dependent binary interaction parameters in MvdW1 mixing rule [-]
 n_i : number of moles of component i [mol]
P : pressure [Pa]
R : gas constant [$\text{Jmol}^{-1}\text{K}^{-1}$]
T : absolute temperature [K]
V : molar volume [$\text{cm}^3\text{mol}^{-1}$]
 x_i : liquid phase mole fraction of component i [-]
 y_i : vapor phase mole fraction of component i [-]

Greek Letters

- α_{12} : NRTL excess free energy non-randomness parameter [-]
 ϕ : fugacity coefficient [-]
 τ_{ji} : NRTL excess free energy model binary interaction parameter [-]
 ω : acentric factor [-]

Subscripts

- i, j, k : components
c : critical property
cal : calculated property

Table A.3. Optimized coefficients for simultaneous correlation of VLE+ $H^E+c_p^E$ binary data

MHV1-4a	MHV1-4	MHV2-4
$\alpha'_{12,1}$ [K]	$\alpha'_{12,0}$ [-]	$\alpha'_{12,0}$ [-]
$a'_{12,0}$ [K]	$\alpha'_{12,1}$ [K]	$\alpha'_{12,1}$ [K]
$a'_{12,1}$ [K ²]	$a'_{12,0}$ [K]	$a'_{12,0}$ [K]
$a'_{21,0}$ [K]	$a'_{12,1}$ [K ²]	$a'_{12,1}$ [K ²]
$a'_{21,1}$ [K ²]	$a'_{21,0}$ [K]	$a'_{21,0}$ [K]
	$a'_{21,1}$ [K ²]	$a'_{21,1}$ [K ²]
1,4-dioxane+heptane		
0.371693E+0	0.342154E+0	0.965310E+0
0.247262E+3	0.677696E+1	-0.140656E+3
0.510545E+5	0.249764E+3	-0.660322E+2
-0.211560E+3	0.495224E+5	0.150128E+6
0.108794E+6	-0.226932E+3	-0.221580E+3
	0.111331E+6	0.130647E+6
1,4-dioxane+octane		
0.376446E+0	0.375155E+0	0.104678E+1
0.277431E+3	0.335673E+0	-0.160775E+3
0.531061E+5	0.276764E+3	-0.120468E+3
-0.295202E+3	0.530700E+5	0.172899E+6
0.123458E+6	-0.295734E+3	-0.295588E+3
	0.123596E+6	0.145170E+6
1,4-dioxane+nonane		
0.356894E+0	0.326419E+0	0.105404E+1
0.378137E+3	0.701743E+1	-0.168708E+3
0.467838E+5	0.387330E+3	-0.169358E+3
-0.373070E+3	0.432502E+5	0.207430E+6
0.136853E+6	-0.392669E+3	-0.364264E+3
	0.140622E+6	0.160045E+6
1,3-dioxolane+heptane		
0.394087E+0	0.153598E+0	0.796571E+0
0.296569E+3	0.536387E+2	-0.101009E+3
0.482157E+5	0.314346E+3	0.256728E+2
-0.234032E+3	0.370463E+5	0.134926E+6
0.126971E+6	-0.349858E+3	-0.357009E+3
	0.147631E+6	0.162918E+6

exp : experimental property
 max : maximum value of experimental property
 mix : mixture property
 pure : property of pure substance
 r : reduced property
 ij, 12, 21 : components of binary system
 ∞ : infinite pressure condition

Superscript

* : reference molar enthalpy of the ideal gas

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