Simultaneous correlation of the excess enthalpy and W-shaped excess heat capacity of 1,4-dioxane+*n*-alkane systems by PRSV-HVOS CEOS

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Abstract: In this work the Peng-Robinson-Stryjek-Vera (PRSV) equation of state coupled with the Huron-Vidal-Orbey-Sandler (HVOS) rule was tested for the correlation of the excess enthalpy (H^E) and the excess heat capacity (c_p^E) alone and simultaneously. The HVOS mixing rule incorporates the NRTL equation as the G^E model. All calculations were performed using the linear and reciprocal forms of the temperature dependent parameters of the models. For all the evaluations the 1,4-dioxane+*n*-alkane systems were chosen having in mind the unusually W-shaped concentration dependence of c_p^E for these systems. The correlation of the H^E and c_p^E data alone for all the investigated systems using four coefficients and for the simultaneous correlation of $H^E+c_p^E$ data using six coefficients of the temperature dependent parameters of the PRSV-HVOS models could be considered as being very satisfactory.

Keywords: thermodynamics, *n*-alkane, 1,4-dioxane, excess properties, CEOS.

INTRODUCTION

The simultaneous representation of two or more thermodynamic properties is of particular interest for the realistic description of the thermodynamic behavior of phase equilibria and of liquid solutions.

During the last several decades, the simultaneous correlation of vaporl–iquid equilibria (VLE) and excess enthalpy (H^E) data has been studied by well known models (G^E models: NRTL, Wilson, UNIQUAC, group contribution methods: ASOG, UNIFAC and by various empirical equations).

In recent years, several cubic equations of state with G^E equation (CEOS/G^E) models have been applied as a new proposal for the simultaneous correlation of binary VLE, H^E and c_p^E data.[1–5]

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In the present work, the Peng-Robinson-Stryjek-Vera[6] (PRSV) CEOS, coupled with the Huron-Vidal-Orbey-Sandler (HVOS) rule, was used for single H^E and c_p^E and the simultaneous correlation of $H^E + c_p^E$ data of the 1,4-dioxane+n-alkane (heptane, octane, nonane and decane) systems, the $c_p^E - x$ curves of which show a particular W-shape. For the purpose of comparison, the two well known polynomials used for H^E calculation are also included in this work.

PURE-COMPONENT EQUATION OF STATE

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

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

where

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

$$b_i = 0.077796 \frac{RT_{ci}}{P_{ci}} \tag{3}$$

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

$$k_{0i} = 0.378893 + 1.48971\omega_i - 0.1713848\omega_i^2 + 0.0196544\omega_i^3 \tag{5}$$

and k_{1i} is the adjustable parameter of the pure compound.[6]

THE HURON-VIDAL-ORBEY-SANDLER (HVOS) MIXING RULE

In the Huron-Vidal-Orbey-Sandler (HVOS) mixing rule, the mixture parameters are given by

$$\frac{a}{bRT} = \frac{A_\gamma^E}{CRT} + \frac{1}{C} \sum_i x_i \ln \frac{b}{b_i} + \sum_i x_i \frac{a_i}{b_i RT} \tag{6}$$

where A_γ^E is the molar excess Helmholtz energy at infinite reference pressure at which the liquid activity coefficient model and the CEOS model are equated ($A_\gamma^E = A_{CEOS}^E$). In the HVOS mixing rule, the molar excess Helmholtz energy A^E is used instead of the molar excess Gibbs free energy G^E. Namely, since A^E from a CEOS is nearly insensitive to pressure and that at low pressures G_γ^E and A_γ^E are practically equal, the HVOS mixing rule includes the following approximation as proposed by the authors[7]

$$A^E(T, P \to \infty, x_i) = A^E(T, P_{low}, x_i) = G^E(T, P_{low}, x_i) - P_{low}V^E(T, P_{low}, x_i) \approx$$
$$\approx G^E(T, P_{low}, x_i) \tag{7}$$

where P_{low} represents any low pressure.

NRTL EQUATION FOR PRSV–HVOS MODELS

Bearing in mind that the W-shape of the $c_p^E - x$ curves is a consequence of the non-randomness in the mixture, we have chosen the non-random two-liquid (NRTL) equation,[8] which is based on a "local composition" concept, as this model as very flexible and suitable for the assigned purposes. The NRTL equation is

$$\frac{G^E}{RT} = \sum_i x_i \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_k x_k G_{ki}} \tag{8}$$

where for a binary system

$$G_{12} = \exp(-\alpha_{12}\tau_{12}); \ G_{21} = \exp(-\alpha_{12}\tau_{21}); \ \tau_{12} = (g_{12} - g_{22})/RT; \\ \tau_{21} = (g_{21} - g_{11})/RT \tag{9}$$

In all PRSV–HVOS models, the parameter b is determined by the linear mixing rule

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

For the interaction parameters of the NRTL equation, we used two temperature dependent forms:

– the linear temperature dependence

$$Y_{ij} = c_{ij,0} + c_{ij,1}T \tag{11}$$

where Y_{ij} stands for $g_{12} - g_{22}$, $g_{21} - g_{11}$ or α_{12}.

– the reciprocal tempeature dependence

$$Y_{ij}' = c_{ij,0}' + \frac{c_{ij,1}'}{T} \tag{12}$$

where Y_{ij}' stands for $g_{12} - g_{22}$, $g_{21} - g_{11}$ or α_{12}.

Thus, the mixing rules shown in Table I were obtained.

REPRESENTATION OF CEOS MODELS

The general equation for the excess enthalpy calculation is given as

$$H^E = \sum_i x_i (H_i^* - H_i) - (H^* - H) \tag{13}$$

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

$$(H^* - H)_{\text{pure or mix}} = RT - PV + \int_\infty^V \left[P - T\left(\frac{\partial P}{\partial T}\right)_V \right] dV \tag{14}$$

In order to obtain the excess heat capacity, the following relationship between c_p^E and H^E was used

$$c_p^{\mathrm{E}} = \left(\frac{\partial H^{\mathrm{E}}}{\partial T} \right)_{P,x} \tag{15}$$

Inclusion of the CEOS models with the temperature dependent parameters from Table I in the general Eqs. (13) to (15) gave the PRSV–HVOS models used in this work.

TABLE I. Investigated PRSV–HVOS models

Model	Number of coefficients	Temperature dependencies of the parameters
HVOS-1	4	Linear form for $g_{12} - g_{22}$ and $g_{21} - g_{11}$ (Eq. (11)), $\alpha_{12} = const$
HVOS-2	4	Reciprocal form for $g_{12} - g_{22}$ and $g_{21} - g_{11}$ (Eq. (12)), $\alpha_{12} = const$
HVOS-3	6	Linear form for $g_{12} - g_{22}$, $g_{21} - g_{11}$ and α_{12} (Eq. (11))
HVOS-4	6	Reciprocal form for $g_{12} - g_{22}$, $g_{21} - g_{11}$ and α_{12} (Eq. (12))

All the coefficients in the expression for the temperature dependent parameters of these models were generated from the corresponding fits of H^{E}, c_p^{E} or $H^{\mathrm{E}} + c_p^{\mathrm{E}}$ by minimizing the following objective function

$$OF = OF_1 + OF_2 = \frac{1}{n} \sum_{i=1}^{n} \left(\frac{H_{\exp}^{\mathrm{E}} - H_{\mathrm{cal}}^{\mathrm{E}}}{H_{\exp}^{\mathrm{E}}} \right)_i^2 + \frac{1}{k} \sum_{i=1}^{k} \left(\frac{c_{p\,\exp}^{\mathrm{E}} - c_{p\,\mathrm{cal}}^{\mathrm{E}}}{c_{p\,\exp}^{\mathrm{E}}} \right)_i^2 \rightarrow \min \tag{16}$$

In Eq. (16), n and k are the number of the experimental H^{E} and c_p^{E} data points, respectively. The correlating results of the H^{E} and c_p^{E} data were assessed by the percentage average absolute deviation $PD(Z)$

$$PD(Z) = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{Z_{\exp} - Z_{\mathrm{cal}}}{(Z_{\exp})_{\max}} \right|_i \tag{17}$$

where Z stands for H^{E} or c_p^{E}.

RESULTS AND DISCUSSION

The coefficients of the temperature dependent interaction parameters for each of the PRSV-HVOS CEOS models were estimated from the unique source of the experimental H^{E} and c_p^{E} data of the 1,4-dioxane+n-alkane systems at 298.15 K.[9] The results obtained for each fit are given separately.

Correlation of the H^{E} *data*

The correlation of H^{E} data using the chosen PRSV-HVOS models were performed for four binary systems[9] of the 1,4-dioxane with alkanes (heptane, octane, nonane and decane). For comparison the polynomials I and II (see Appendix) with temperature dependant parameters were also used to calculate the property of H^{E}. The overall H^{E} results obtained by all the investigated models with the temperature dependent parameters can be considered as extremely
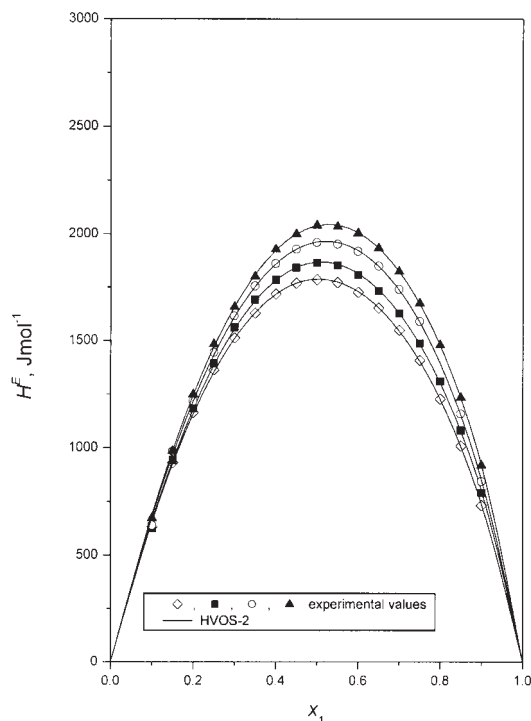
Fig. 1. The correlation of the H^E data of the systems 1,4-dioxane (1)+*n*-alkane (2) at 298.15 K with the HVOS model. The points represent the experimental data of the systems[9] with: ◇– heptane, ■ – octane, ○– nonane, ▲– decane.

good. In all cases the errors are considerably below 1 %. Also, we tried to use the CEOS models without the terms which include the temperature dependent parameters. However, high errors were always obtained. This indicates that the correlation of H^E data by the PRSV–HVOS CEOS as CEOS/G^E models needs the temperature dependent parameters with four optimized coefficients and a constant value of the non-randomness parameter α_{12}. Fig. 1, where the HVOS-2 model was used, illustrates this conclusion in the best way.

Correlation of the c_p^E *data*

Correlation of the c_p^E data for the four binary systems[9] available at 298.15 K was realized by all CEOS models. The obtained results given in Table II for the PRSV–HVOS models can be regarded mostly as very good. The deviations for the HVOS-2 and HVOS-4 model mostly decrease when the open chain of the *n*-alkane molecules is increased (see Fig. 2). The HVOS-1 model shows a similar trend having somewhat larger deviations except for the system 1,4-dioxane+decane where the error is larger and could be treated as an unexpected result. Also, it can be concluded that both polynomials gave very poor results. It is evident that the complex interaction causing the W-chaped curve of c_p^E data is the main reason, which eliminates the use of power series of those types to be used for the correlation of c_p^E data. This fact is clearly demonstrated by Figs. 3 and 4 were the deviations of the polynomial II from the experimental points
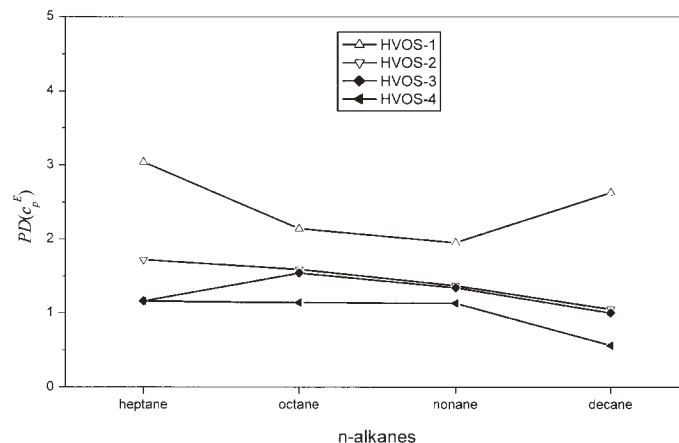
Fig. 2. The percentage average absolute deviation $PD(c_p^E)$ between the HVOS models and the experimental points of the systems 1,4-dioxane+n-alkane[9] at 298.15 K.

are very high. On the other hand, the PRSV-HVOS-4 CEOS model plotted in the same Figures provides an excellent c_p^E correlation.

These good fits of the c_p^E data, obtained by all the HVOS models, could be considered as a consequence of the local composition behavior of the NRTL equation and of its
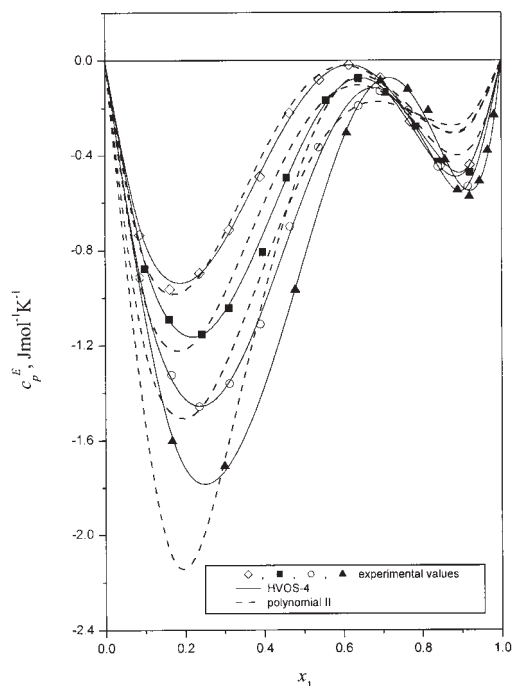

Fig. 3. The correlation of the c_p^E data of the systems 1,4-dioxane (1)+n-alkane (2) at 298.15 K with the HVOS-4 (solid line) and polynomial II (dashed line) models. The points represent the experimental data of the systems[9] with: ◇ – heptane, ■ – octane, ○ – nonane, ▲ – decane.

high flexibility to correlate very successfully two visible minima separated by a maximum.

It can be concluded that the HVOS-2 model reproduce the c_p^E data of all systems quite accurately without adjusting the two additional coefficients needed in the HVOS-3 and 4 models of both mixing rules.

TABLE II. The correlation of the c_p^E data

System	HVOS-1 $PD(c_p^E)$	HVOS-2 $PD(c_p^E)$	HVOS-3 $PD(c_p^E)$	HVOS-4 $PD(c_p^E)$	Polynomial I[a] $PD(c_p^E)$	Polynomial II[b] $PD(c_p^E)$
1,4-Dioxane (1) + heptane (2)	3.04	1.72	1.16	1.16	6.18	5.20
1,4-Dioxane (1) + octane (2)	2.14	1.59	1.54	1.14	7.91	7.81
1,4-Dioxane (1) + nonane (2)	1.95	1.37	1.34	1.13	7.80	7.60
1,4-Dioxane (1) + decane (2)	2.63	1.05	1.00	0.56	10.11	9.99

[a] Number of coefficients used in this work $N = 12$; [b] Number of coefficients used in this work $N = 16$
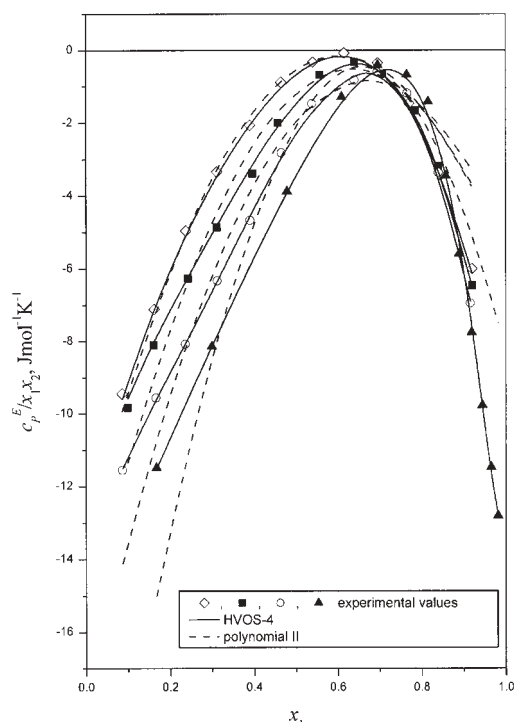

Fig. 4. c_p^E/x_1x_2 correlation of the systems 1,4-dioxane (1)+*n*-alkanes (2) at 298.15 K with the HVOS-4 (solid line) and polynomial II (dashed line) models. The points represent the experimental data of the systems[9] with: ◇ – heptane, ■ – octane, ○ – nonane, ▲ – decane.

TABLE III. Simultaneous correlation of the H^E and c_p^E data

System	Polynomial I[a]		Polynomial II[b]		HVOS-1		HVOS-2		HVOS-3		HVOS-4	
	$PD(H^E)$	$PD(c_p^E)$	$PD(H^E)$	$PD(c_p^E)$	$PD(H^E)$	$PD(c_p^E)$	$PD(H^E)$	$PD(c_p^E)$	$PD(H^E)$	$PD(c_p^E)$	$PD(H^E)$	$PD(c_p^E)$
1,4-Dioxane (1) + heptane (2)	1.92	7.92	0.79	6.92	3.42	3.04	3.20	1.90	1.72	2.38	1.80	2.31
1,4-Dioxane (1) + octane (2)	1.11	9.21	1.17	8.90	3.42	2.05	3.50	3.00	1.87	1.65	1.75	1.61
1,4-Dioxane (1) + nonane (2)	1.17	10.05	1.09	8.85	2.89	3.17	4.63	1.35	1.77	1.79	1.78	1.76
1,4-Dioxane (1) + decane (2)	1.21	12.84	1.00	12.40	2.79	2.96	4.20	1.71	1.96	1.30	2.14	1.32

[a] Number of coefficients used in this work $N = 12$; [b] Number of coefficients used in this work $N = 16$
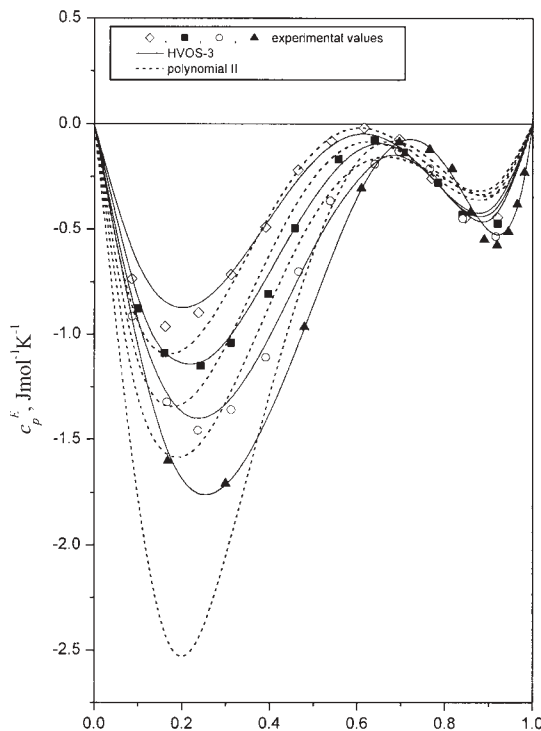
Fig. 5. c_p^E correlation from the simultaneous $H^E + c_p^E$ data of the systems 1,4-dioxane (1)+*n*-alkanes (2) at 298.15 K with the HVOS-3 (solid line) and polinomial II (dashed line) models. The points represent the experimental data of the systems[9] with: ◇ – heptane, ■ – octane, ○ – nonane, ▲ – decane.

Simultaneous correlation of the $H^E + c_p^E$ *data*

The estimate values of the unique set of optimized coefficients of all HVOS models ($OF = OF_1 + OF_2$), generated from the simultaneous correlation of the $H^E + c_p^E$ data, were used to obtain the results given in Table III.

As can be seen from Table III and Fig. 5, the simultaneous fitting of the $H^E + c_p^E$ data is very successfully carried out by the HVOS-3 and 4 models, which mostly gave a significant improvement when compared to the HVOS-2 and particularly to the HVOS-1. Further, the deviations in c_p^E by the HVOS-3 and HVOS-4 mostly decrease, whereas those in H^E data have a nearly uniform quality, when the open chain of the *n*-alkane molecules increases.

Furthermore, the mutually close values of the variances of the HVOS-3 and 4 models confirm the fact that the six coefficients of these models were needed for the simultaneous fit. The quality of the fit appeared to be nearly the same in both of the models.

The results obtained by the polynomial I and II were unsatisfactory bearing in mind the very high deviations in c_p^E. The fits by these models were not able to follow the W-shape of the c_p^E experimental points (for polynomial I, for example, see Fig. 5).

In our opinion, the main advantage of using the HVOS-3 and 4 models is, in addition to the very accurate simultaneous correlation of $H^E + c_p^E$ data, a better insight into the investigated type of systems, bearing in mind, also, their high capability and flexibility to fit simultaneously several thermodynamic properties, allowing a correct description of the real behavior of the 1,4-dioxane+n-alkane mixtures.

We are aware that in this way the suggestions given by Renon[10] for the extensive application of the local composition models (here the inclusion of the NRTL into the HVOS mixing rule) to all properties: H^E, G^E, LLE, VLE (here H^E and c_p^E) could be still valid.

CONCLUSIONS

The use of the Peng–Robinson–Stryjek–Vera (PRSV) equation of state coupled with the CEOS/G^E mixing rule (Huron–Vidal–Orbey–Sandler (HVOS)) was suggested for the correlation of H^E, c_p^E and $H^E + c_p^E$ data of the 1,4-dioxane+n-alkane mixtures. For the G^E model in NRTL equation represents a very convenient choice.

The HVOS models, using the temperature dependent parameters with four optimized coefficients, gave mostly very satisfactory results for the fit of the H^E and c_p^E data alone, while for the successful simultaneous correlation of the $H^E + c_p^E$ data, six optimized coefficient should be used. The polynomial type of equations used for the correlation of the $H^E + c_p^E$ data gave unsatisfactory results.

LIST OF SYMBOLS

A^E – Molar excess Helmholtz free energy
a – Equation of state energy parameter
b – Equation of state size parameter
C – Numerical constant of the HVOS mixing rule dependent on CEOS (for the PRSV CEOS, C = –0.62323)
c_p^E – Molar excess heat capacity
G^E – Molar excess Gibbs energy
g – NRTL model parameter
H – Molar enthalpy
H^E – Molar excess enthalpy
k, n – Number of experimental data points
OF – Objective function
P – Pressure
R – Gas constant
T – Absolute temperature
V – Molar volume
x – Liquid phase mole fraction
Greek letters
α – NRTL excess free energy non-randomness parameter
τ – NRTL excess free energy model binary interaction parameter
ω – Acentric factor
Subscripts
1, 2, i, j, k – Components
c – Critical property

cal – Calculated property
exp – Experimental property
mix – Mixture property
pure – Property of pure substance
r – Reduced property
Superscripts
* – Reference molar enthalpy of the ideal gas

ИЗВОД

СИМУЛТАНО КОРЕЛИСАЊЕ ДОПУНСКЕ ЕНТАЛПИЈЕ И ДОПУНСКОГ ТОПЛОТНОГ КАПАЦИТЕТА СА W-ОБЛИКОМ ЕКСПЕРИМЕНТАЛНИХ ТАЧАКА КОД СИСТЕМА 1,4-ДИОКСАН+*n*-АЛКАНИ ПОМОЋУ PRSV-HVOS CEOS

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У овом раду је помоћу Peng–Robinson–Stryjek–Vera (PRSV) једначине стања и Huron–Vidal–Orbey–Sandler (HVOS) правила мешања извршено појединачно и симултано корелисање допунске енталпије (H^E) и допунског топлотног капацитета (c_p^E). У HVOS правило мешања је као G^E модел укључена NRTL једначина. За сва израчунавања су изабрани системи 1,4-диоксана са *n*-алканима, узимајући у обзир веома сложену зависност c_p^E од састава W-облика, присутног код ових система. Помоћу HVOS модела са четири оптимизована коефицијента су код свих испитиваних система добијени веома задовољавајући резултати корелисања H^E и c_p^E података појединачно. За симултано корелисање $H^E + c_p^E$ података морају се користити HVOS модели са шест оптимизованих коефицијената.

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<center>APPENDIX</center>

The experimental H^E and c_p^E data were correlated by two types of polynomial equations, signed as Polynomial I and Polyunomial II, with temperature dependent parameters

Polynomial I

$$H^E = x_1 x_2 \sum_{i=0}^{3} a_i^{H^E} Q_i \tag{A1}$$

$$c_p^E = x_1 x_2 \sum_{i=0}^{3} a_i^{c_p^E} Q_i \tag{A2}$$

where

$$Q_i = (x_1 - x_2)^i \tag{A3}$$

$$a_i^{H^E} = a_{i,1} + a_{i,2}\left(\frac{T}{T_0}\right)^{-1} + a_{i,3}\left(\frac{T}{T_0}\right)^{-2} \tag{A4}$$

$$a_i^{c_p^E} = \left(-a_{i,2}\left(\frac{T}{T_0}\right)^{-2} + 2a_{i,3}\left(\frac{T}{T_0}\right)^{-3}\right)/T_0 \tag{A5}$$

Polynomial II

$$\frac{H^E}{RT_0} = -x_1 x_2 \sum_{i=0}^{3} a_i^{H^E} Q_i \tag{A6}$$

$$\frac{c_p^E}{R} = -x_1 x_2 \sum_{i=0}^{3} a_i^{c_p^E} Q_i \tag{A7}$$

where parameter Q_i is determined by the following expressions

for:
$$\begin{aligned} i=0 &\quad Q_0 = 1 \\ i=1 &\quad Q_i = (x_1 - x_2) \\ i\geq 2 &\quad Q_i = [(2i-1)(x_1-x_2)Q_{i-1} - (i-1)Q_{i-2}]/i \end{aligned} \tag{A8}$$

and

$$a_i^{H^E} = a_{i,1}\left(\frac{T}{T_0}\right) + a_{i,2}\left(\frac{T}{T_0}\right)^2 + 2a_{i,3}\left(\frac{T}{T_0}\right)^3 - a_{i,4} \tag{A9}$$

$$a_i^{c_p^E} = a_{i,1} + 2a_{i,2}\left(\frac{T}{T_0}\right) + 6a_{i,3}\left(\frac{T}{T_0}\right)^2 \tag{A10}$$

The coefficients $a_{i,k}$ in Eqs. (A4), (A5), (A9) and (A10) are temperature independent parameters of the H^E and c_p^E and T_0 is a reference temperature.