

Application of the MvdW1 and HVOS-NRTL mixing rules to the simultaneous correlation of excess enthalpies and W-shaped excess heat capacities data of 1,3-dioxolane + *n*-alkane systems*

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The Peng-Robinson-Stryjek-Vera (PRSV) equation of state (EOS) coupled with a modified two parameter van der Waals one-fluid mixing rule (MvdW1) and the Huron-Vidal-Orbey-Sandler mixing rule incorporating the NRTL equation as a G^E model was used for the correlation of excess enthalpy (H^E), excess heat capacity (C_p^E) and the simultaneous correlation of both properties. All calculations with temperature dependent parameters of EOS models were applied to 1,3-dioxolane+*n*-alkane systems. The correlation of the H^E and C_p^E data alone with four coefficients and the $H^E+C_p^E$ data with six coefficients of the temperature dependent parameters of the HVOS-NRTL models could be considered as very satisfactory.

Keywords: equation of state, mixing rule, excess properties, 1,3-dioxolane, *n*-alkane.

In recent years various types of mixing rules have been successfully proposed for the representation of vapor-liquid equilibrium (VLE) and other thermodynamic properties using cubic equations of state (EOS). In particular, multi-parameter mixing rules which incorporate the excess free energy into the equation of state (EOS/ G^E) have been applied as a new proposal for the simultaneous description of binary VLE+ H^E data,^{1,2} binary VLE, H^E and C_p^E data,³ and $H^E+C_p^E$ data with unusual W-shaped concentration dependencies of C_p^E for the 1,4-dioxane+*n*-alkane systems.^{4,5}

In this note EOS models based on the Peng-Robinson-Stryjek-Vera (PRSV) equation of state⁶ coupled with two different types of mixing rules, *i.e.*, a modified van der Waals one-fluid (MvdW1) rule proposed by many authors⁷⁻¹⁰ and the Huron-Vidal-Orbey-Sandler¹¹ (HVOS) rule were examined to fit individually and simultaneously the H^E and C_p^E data of the 1,3-dioxolane+*n*-alkane (heptane, octane, nonane and decane) systems,¹² which exhibit much more accentuated W-shape behavior of the C_p^E-x curves than the corresponding 1,4-dioxane+*n*-alkane systems.

* Dedicated to Professor John M. Prausnitz on the occasion of his 70th birthday

PURE-COMPONENT PRSV EOS

For the EOS models to be considered here, the Peng-Robinson-Stryjek-Vera equation of state is taken as follows:

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

where

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

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

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

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

where k_{1i} is the adjustable parameter of the pure compound.⁶

MIXING RULES

The modified van der Waals one fluid (MvdW1) mixing rule

The mixture energy parameter a , which includes a composition-dependent term, is given by:

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

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

Two temperature dependent functions for k_{ij} and l_{ij} , which appear in Eq (6), were used:

— the linear form

$$k_{12} = c_1 + c_2 T \quad (7)$$

$$l_{12} = c_3 + c_4 T \quad (8)$$

— the reciprocal form

$$k_{12} = c_1' + c_2'/T \quad (9)$$

$$l_{12} = c_3' + c_4'/T \quad (10)$$

More details about various equivalent forms of this mixing rule can be found in the original literature.^{7-10,13}

The Huron-Vidal-Orbey-Sandler (HVOS) mixing rule

Orbey and Sandler¹¹ obtained the HVOS mixing rule

$$\frac{a}{bRT} = \frac{A_g^{E\infty}}{CRT} + \frac{1}{C} \sum_i x_i \ln \frac{b}{b_i} + \sum_i x_i \frac{a_i}{b_i RT} \quad (11)$$

where the excess Helmholtz energy, A_g^E , is given at the infinite pressure reference state, at which the liquid activity coefficient model and the EOS model are equated $A_g^E = A_{EOS}^E$. In this mixing rule, the excess Helmholtz energy is used instead of the excess Gibbs energy. The excess Helmholtz energy from a cubic EOS (A_{EOS}^E) is nearly insensitive to pressure, also at low pressures G_g^E and A_g^E are practically equal:

$$G^E(T, x, P = \text{low}) = A^E(T, x, P = \text{low}) = A^E(T, x, P = \infty) \quad (12)$$

NRTL equation for the HVOS model

The non-random, two-liquid (NRTL) equation of Renon and Prausnitz¹⁴ was chosen bearing in mind the very good results obtained when this equation coupled with MHV1 mixing rule was applied to correlate the $H^E + C_p^E$ data for 1,4-dioxane+n-alkane mixtures.⁴

The NRTL equation is

$$\frac{G^E}{RT} = \sum_i x_i \frac{j}{k} \frac{x_j G_{ji} \tau_{ji}}{x_k G_{ki}} \quad (13)$$

where for binary systems it follows

$$G_{12} = \exp(-a_{12} \tau_{12}), \quad G_{21} = \exp(-a_{12} \tau_{21}), \quad \tau_{12} = (g_{12} - g_{22})/RT, \quad \tau_{21} = (g_{21} - g_{11})/RT \quad (14)$$

with the linear functions of temperature for a_{12} , $(g_{12} - g_{22})$ and $(g_{21} - g_{11})$:

$$a_{12} = c_5 + c_6 T \quad (15)$$

$$g_{12} - g_{22} = c_7 + c_8 T \quad (16)$$

$$g_{21} - g_{11} = c_9 + c_{10} T \quad (17)$$

and with the reciprocal temperature dependence of the same parameters:

$$a_{12} = c_5' + c_6'/T \quad (18)$$

$$g_{12} - g_{22} = c_7' + c_8'/T \quad (19)$$

$$g_{21} - g_{11} = c_9' + c_{10}'/T \quad (20)$$

In all HVOS-NRTL models, the size parameter b is determined by the conventional linear mixing rule

$$b = \sum_i x_i b_i \quad (21)$$

In this way the mixing rules summarized in Table I were obtained.

TABLE I. Investigated EOS models

Model	Temperature dependencies of parameters
MvdW1-1	Linear form for l_{ij} and m_{ij}
MvdW1-2	Reciprocal form for l_{ij} and m_{ij}
HVOS-NRTL-1	Linear form for $(g_{12} - g_{22})$ and $(g_{21} - g_{11})$, $a_{12} = \text{const}$
HVOS-NRTL-2	Reciprocal form for $(g_{12} - g_{22})$ and $(g_{21} - g_{11})$, $a_{12} = \text{const}$
HVOS-NRTL-3	Linear form for $(g_{12} - g_{22})$, $(g_{21} - g_{11})$, and a_{12}
HVOS-NRTL-4	Reciprocal form for $(g_{12} - g_{22})$, $(g_{21} - g_{11})$ and a_{12}

REPRESENTATION OF EOS MODELS

The general expression for the excess enthalpy calculations is written as

$$H^E = \sum_i x_i (H_i^* - H_i) - (H^* - H) \quad (22)$$

where $(H_i^* - H_i)$ and $(H^* - H)$ are the residual enthalpies for the pure component i and the mixtures, respectively. These residual enthalpies can be obtained from an EOS, using the well-known thermodynamic formula

$$(H^* - H)_{\text{pure or mix}} = RT - Pn + \int_{P^0}^P \frac{1}{T} \left(\frac{\partial P}{\partial T} \right)_n - T \int_{P^0}^P \frac{1}{T^2} \left(\frac{\partial P}{\partial T} \right)_n dT \quad (23)$$

For the C_p^E calculation we used the basic relationship between C_p^E and H^E

$$C_p^E = \frac{1}{T} \left(\frac{\partial H^E}{\partial T} \right)_{p,x} \quad (24)$$

Inclusion of the EOS model with the temperature dependent interaction parameters from Table I, in the general Eqs. (22) to (24) gave the EOS models used here.

All coefficients in the functions for the temperature dependent parameters of the EOS models were adjusted from corresponding fits of H^E , C_p^E or $H^E + C_p^E$ by minimizing the following objective function

$$OF = OF_1 + OF_2 = \frac{1}{n} \sum_{i=1}^n \frac{(H_{\text{exp}}^E - H_{\text{cal}}^E)^2}{H_{\text{exp}}^E} + \frac{1}{k} \sum_{i=1}^k \frac{(C_{p\text{exp}}^E - C_{p\text{cal}}^E)^2}{C_{p\text{exp}}^E} \quad \text{fi min} \quad (25)$$

where n and k are the number of the experimental H^E and C_p^E data points, respectively. For the minimization of the objective function, the Hooke and Jeeves¹⁵ technique was used.

RESULTS AND DISCUSSION

The systems examined in this work consisted of an n -alkane (hexane, octane, nonane and decane) and diether (1,3-dioxolane). These systems show a W-shape concentration dependence of C_p^E . It has been described¹⁶ that the W-shape results from two C_p^E contributions, a positive non-random contribution, associated with extremely large H^E and G^E values, and a negative contribution with parabolic concentration dependence. Details of this phenomenon are explained in the literature.^{16,17}

In this paper it will be shown how the EOS models are able to describe well the H^E , C_p^E and $H^E+C_p^E$ data for these types of systems, bearing in mind that the W-shape behavior of the C_p^E curves is much more accentuated with 1,3-dioxolane¹² than with 1,4-dioxane.¹⁸ In our recent work,⁵ we successfully used EOS/ G^E models to describe 1,4-dioxane+ n -alkane systems.

Correlation of the H^E data

All the EOS models gave extremely good fits of the H^E data for all the investigated systems at 25 °C. In all cases the percent deviations were considerably below 1% and very similar to the results obtained from the Redlich-Kister (RK) equation using values of the parameters reported in the literature.¹² The conclusion is illustrated in the best way in Fig. 1 where the HVOS-NRTL-2 model was used.

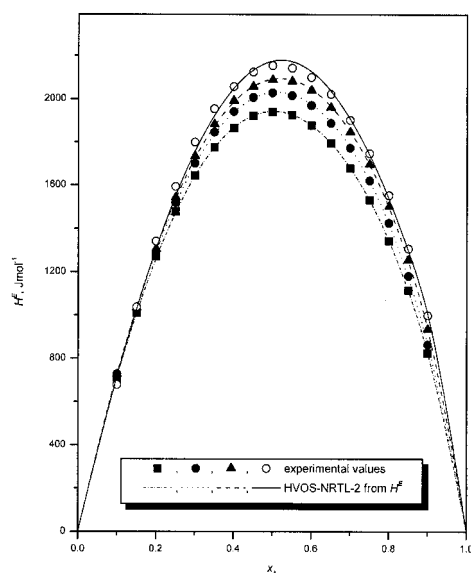


Fig. 1. Experimental and calculated excess enthalpy for the 1,3-dioxolane(1)+ n -alkane(2) systems at 25 °C. Experimental H^E values of the binary systems for 1,3-dioxolane with: ■— heptane, ●— octane, ▲— nonane, ○— decane, Brocos *et al.*¹² The various types of lines indicate the HVOS-NRTL-2 model for the corresponding systems.

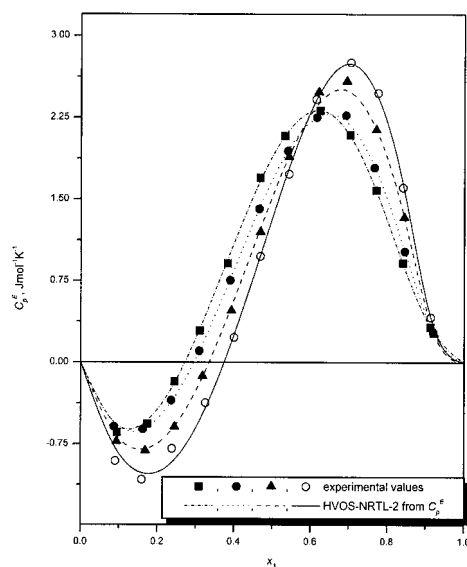


Fig. 2. Experimental and calculated excess heat capacity for the 1,3-dioxolane(1)+ n -alkane(2) systems at 25 °C. Experimental C_p^E values of the binary systems for 1,3-dioxolane with: ■— heptane, ●— octane, ▲— nonane, ○— decane, Brocos *et al.*¹² The various types of lines indicate the HVOS-NRTL-2 model for the corresponding systems.

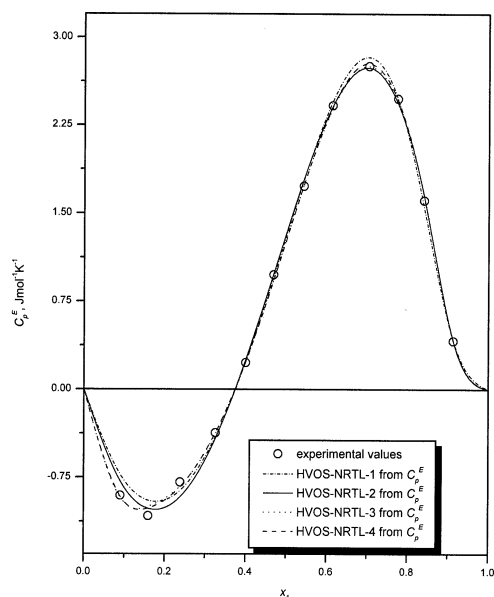


Fig. 3. Experimental and calculated excess heat capacity for the 1,3-dioxolane(1)+*n*-decane(2) system at 25 °C. ○ – experimental values, Brocos *et al.*¹² The various types of lines are specified in the legend.

Correlation of the C_p^E data

The correlation of the C_p^E data obtained for the investigated systems at 25 °C by all the EOS models can be considered as very satisfactory. In all cases the errors obtained with the HVOS-NRTL-3 and 4 models were below 1%, for the HVOS-NRTL-1 and 2 models close to 1.5%, while the MvdW1 and 2 models mostly result in errors below 3%.

The HVOS-NRTL-2 model with the reciprocal temperature dependence of the parameters gives better results than the linear HVOS-NRTL-1. The same conclusion is valid for the HVOS-NRTL-3 and 4 models.

Using the HVOS-NRTL-1 model, the error mostly decreases when the number of open chain *n*-alkane molecules increases, while the opposite tendency was observed with the HVOS-NRTL-2 model. The HVOS-NRTL-3 and 4 models show a similar trend having somewhat larger deviations when the number of open chain *n*-alkane molecules increases. The RK function with the parameters taken from literature¹² behaved in a similar manner to the HVOS-NRTL-3 and 4 models. Besides the fact that the best correlations were obtained using the HVOS-NRTL-3 and 4 models, it can be concluded that the C_p^E data of all system can be fitted quite accurately using the HVOS-NRTL-1 and 2 models without generating two additional coefficients for the non-randomness parameter a_{12} needed in the HVOS-NRTL-3 and 4 models.

Figure 2 shows the results obtained for all systems using the HVOS-NRTL-2 model. The correlations carried out by all HVOS-NRTL models for the system

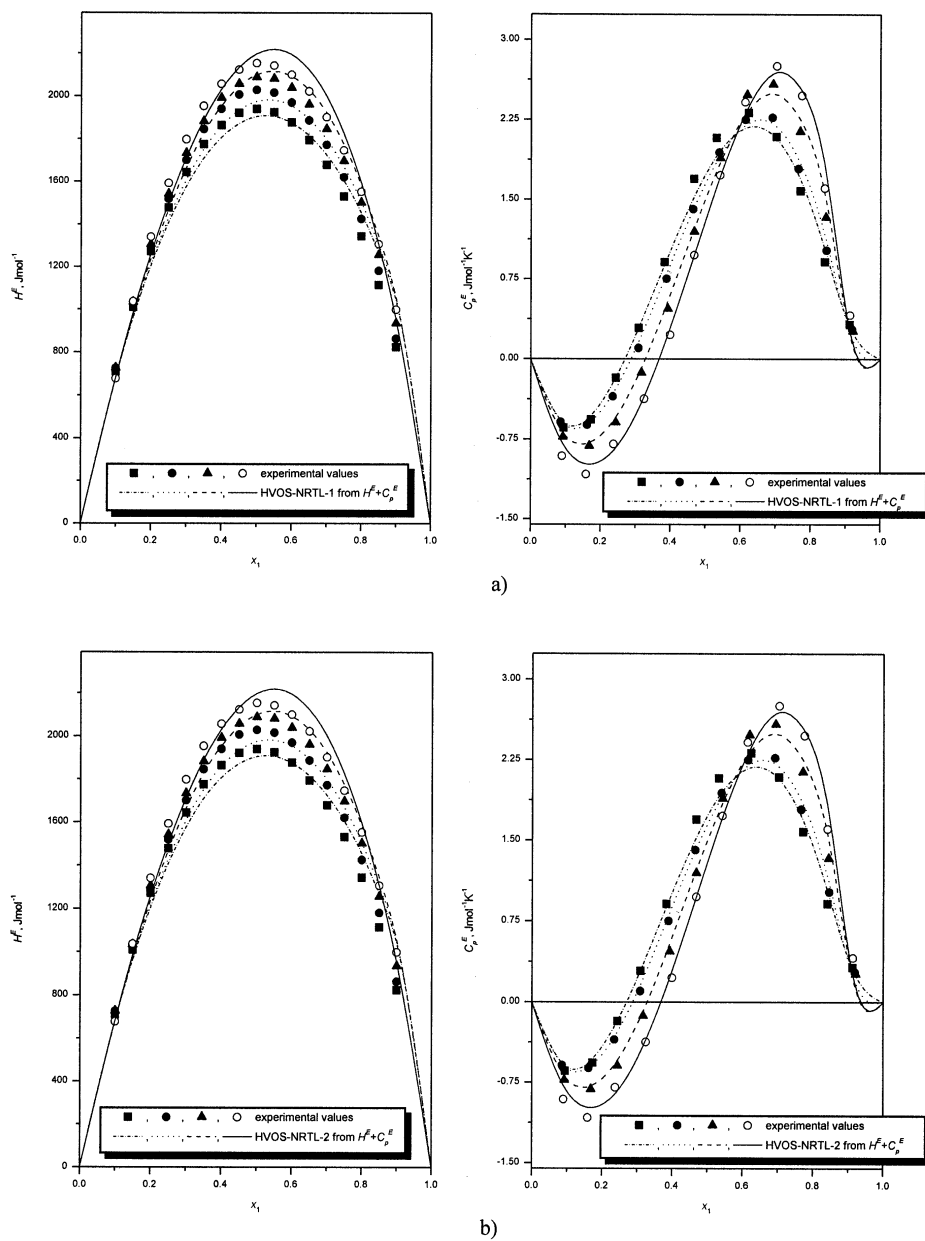
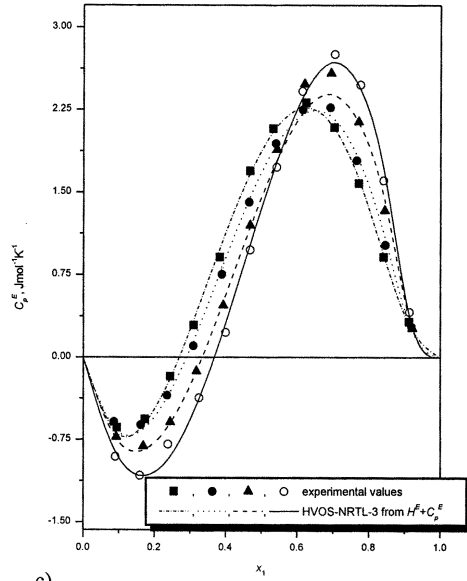
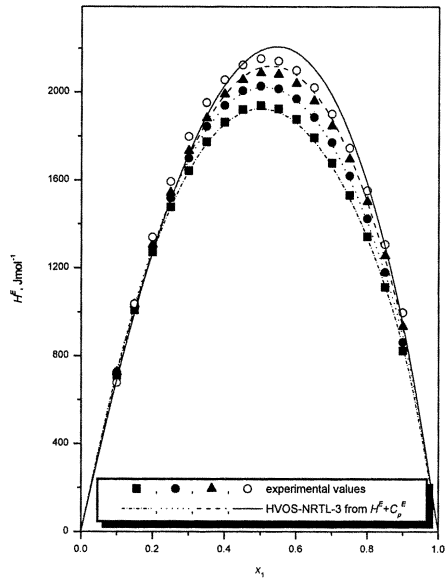
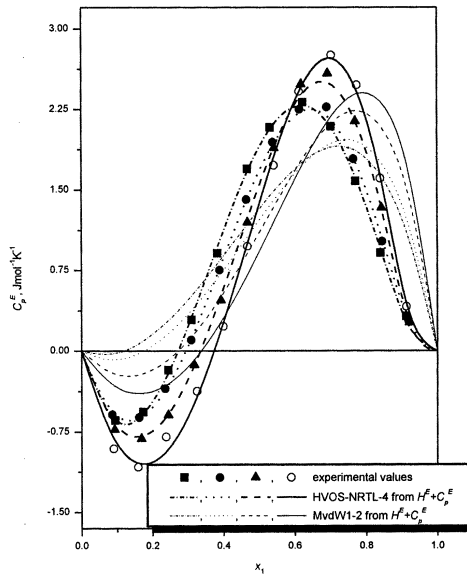
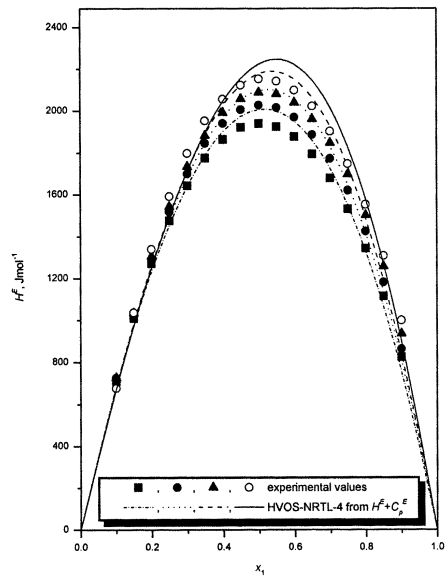


Fig. 4. Experimental and calculated results for the 1,3-dioxolane(1)+*n*-alkane(2) systems at 25 °C. Experimental H^E and C_p^E values of the binary systems for 1,3-dioxolane with: ■— heptane, ●— octane, ▲— nonane, ○— decane, Brocos *et al.*¹² The EOS models with a unique set of parameters generated from the $H^E+C_p^E$ data: a) HVOS-NRTL-1, b) HVOS-NRTL-2, c) HVOS-NRTL-3, d) HVOS-NRTL-4 and MvdW1-2.



c)



d)

1,3-dioxolane+decane are presented in Fig. 3, from which it can be seen that the data could be correlated well by all the models.

Simultaneous correlation of the $H^E + C_p^E$ data

The simultaneous correlation of the $H^E + C_p^E$ data at 25 °C using a single set of optimized coefficients of the EOS parameters can be successfully carried out by all HVOS-NRTL models (Fig. 4). The HVOS-NRTL-3 and 4 models gave clear improvements in the fit of both excess properties when compared to the HVOS-NRTL-1 and 2. Further, it can be noticed that the HVOS-NRTL-2 model mostly works better than the HVOS-NRTL-1 for fitting the C_p^E data, while the opposite is true for the H^E data. A similar conclusion could be reached when comparing the HVOS-NRTL-3 and 4 models. Somewhat better C_p^E fits were obtained using the HVOS-NRTL-4 model, while the HVOS-NRTL-3 model worked better with the H^E data. In addition, the HVOS-NRTL-1 and 2 show the opposite trend for the correlation of the H^E and C_p^E data as a function of the number of open chain n -alkane molecules. Namely, the HVOS-NRTL-1 gives deviations which decrease for H^E and increase for C_p^E , when the number of n -alkane molecules increases. The HVOS-NRTL-2 model behaves in the opposite way. On the contrary, both the HVOS-NRTL-3 and 4 models lead to similar correlations, *i. e.*, when the number of n -alkane molecules increases, the errors of H^E and C_p^E also increase.

The results obtained using the MvdW1-1 and 2 models are satisfactory for H^E but very poor for C_p^E . The deviations in C_p^E are very high (see Fig. 4d), and also, the fit by these models is not able to follow adequately the W-shape of the experimental C_p^E points. For these reasons the MvdW1 model cannot be recommended for the simultaneous correlation of those systems.

CONCLUSION

The Peng-Robinson-Stryjek-Vera (PRSV) equation of state coupled with the Huron-Vidal-Orbey-Sandler (HVOS) mixing rule can be recommended for the correlation of the H^E , C_p^E and $H^E + C_p^E$ data of the 1,3-dioxolane+ n -alkane mixtures with W-shaped excess heat capacities. The NRTL equation represents a very convenient choice for the G^E model incorporated in the HVOS mixing rule.

LIST OF SYMBOLS

- A^E – excess Helmholtz energy
- a – equation of state energy parameter
- b – equation of state size parameter
- C – numerical constant of the HVOS mixing rule dependent on the EOS (for the PRSV EOS, $C = -0.62323$)
- c – coefficients in the temperature dependent equations
- C_p^E – excess heat capacity
- G_{ji} – coefficients of the NRTL model, defined by Eq. (14)
- G_{ki} – coefficients of the NRTL model, defined by Eq. (14)
- G^E – excess Gibbs energy

g_{ij} – NRTL model parameter
 H – molar enthalpy
 H^E – excess enthalpy
 k, n – number of experimental data points
 k_{0i} – parameter defined by Eq. (5)
 k_{1i} – pure component adjustable parameter
 k_{ij} – MvdW1 model parameter
 l_{ij} – MvdW1 model parameter
 OF – objective function
 P – pressure
 R – gas constant
 T – absolute temperature
 v – molar volume
 x_i – liquid phase mole fraction of component i

Greek letters

a_{12} – non-randomness parameter
 τ_{ij} – NRTL binary interaction parameter
 w – acentric factor

Subscripts

i, j, k – components
 cal – calculated property
 exp – experimental property
 mix – mixture property
 pure – property of pure substance
 r – reduced property
 $ij, 12, 21$ – components of binary system
 ∞ – infinite pressure conditions

Superscripts

* – reference molar enthalpy of the ideal gas

ИЗВОД

ПРИМЕНА MvdW1 И HVOS-NRTL ПРАВИЛА МЕШАЊА НА СИМУЛТАНО КОРЕЛИСАЊЕ
 ДОПУНСКИХ ЕНТАЛПИЈА И ДОПУНСКИХ ТОПЛОТНИХ КАПАЦИТЕТА W-ОБЛИКА
 СИСТЕМА 1,3-ДИОКСОЛАН_n-АЛКАНИ

БОЈАН Д. ЂОРЂЕВИЋ, МИРЈАНА Љ. КИЈЕВЧАНИН, АЛЕКСАНДАР Ж. ТАСИЋ
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Peng-Robinson-Stryjek-Vera (PRSV) једначина стања (EOS) са правилима мешања:
 модификовано двопараметарско van der Waals један-флуид (MvdW1) и Huron-Vidal-Orbey-
 Sandler (HVOS) у који је уведена NRTL једначина као G^E модел, је коришћена за корели-

сање допунске енталпије (H^E), допунског топлотног капацитета (C_p^E) и симултано корелисање обе особине. Сва израчунавања са температурно зависним параметрима EOS модела су примењена на системе 1,3-диоксолан+n-алкани. Корелисање посебно H^E и C_p^E података са четири коефицијента и $H^E+C_p^E$ података са шест коефицијената температурно зависних параметара HVOS-NRTL модела, може се сматрати задовољавајућим.

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