

USE OF A UNIQUE SET OF TEMPERATURE-DEPENDENT BINARY INTERACTION PARAMETERS TO SIMULTANEOUSLY DESCRIBE EXCESS PROPERTIES AND FLUID-PHASE EQUILIBRIUM WITH A CUBIC EQUATION OF STATE

JAUBERT Jean-Noël, PRIVAT Romain

Université de Lorraine, École Nationale Supérieure des Industries Chimiques, Laboratoire Réactions et Génie des Procédés (UMR 7274), 1 rue Grandville, BP 20451, Nancy cedex 9, France.

ABSTRACT

PPR78 is a predictive thermodynamic model that combines the Peng–Robinson equation of state in its 1978 version and the Van Laar activity coefficient model under infinite pressure. A group contribution method is used to accurately quantify the interactions between each pair of molecules. During the last decade, the group–interaction parameters were determined in order to minimize the deviations between experimental and calculated fluid–phase equilibria on hundreds of binary systems. It is indeed acknowledged that accurate phase equilibria is the key point to design and optimize chemical processes. Excess enthalpies and excess heat capacities are however very important quantities because they are involved in the energy and exergy balances of any process. The prediction of such properties with parameters obtained from fluid–phase equilibrium data however does not give satisfactory results. It was thus decided to refit all the group–interaction parameters of the original PPR78 model taking simultaneously into account phase equilibria and excess property data. The resulting model, called *E*–PPR78 (*E* for *Enhanced*) has the same accuracy as the original PPR78 to predict phase equilibria but is able to much better describe excess enthalpies and excess heat capacities.

INTRODUCTION

Today, the synthesis design and optimization steps of chemical processes require more and more to access quasi immediately to PVT properties of a nearly infinite set of molecules in order to select the most efficient ones without having to perform costly and fastidious experiments. In that purpose, group–contribution methods can be of great interest since they allow guesstimating thermodynamic properties of a given mixture from the mere knowledge of chemical structures of molecules constituting it. Starting from these observations, the so–called PPR78 model (for Predictive Peng–Robinson 1978) is developed since 2004 [1–12]. This predictive equation of state (EoS) combines the Peng–Robinson equation in its 1978 version and the Van Laar activity coefficient model under infinite pressure. In addition a group contribution method is used to accurately quantify the interactions between each pair of molecules. Nowadays, the PPR78 model can manage complex mixtures containing alkanes, cycloalkanes, aromatic compounds, alkenes, carbon dioxide, nitrogen, hydrogen sulfide, mercaptans and hydrogen. The group–interaction parameters were determined in order to minimize the deviations between experimental and calculated fluid–phase equilibria on hundreds of binary systems. It is indeed acknowledged that accurate phase equilibria is the key point to design and optimize chemical processes. However, excess enthalpies (h^E) and excess heat capacities (c_P^E) are also very important quantities because they are involved in the energy and exergy balances of any process. Our first task was thus to check whether the PPR78 model could accurately predict such data. The obtained results were however not fully satisfactory. It was realized that while the Peng–Robinson EoS can accurately correlate vapor–liquid equilibrium (VLE) and h^E data separately, attempting to predict the values of one

property with parameters obtained from the other does not give satisfactory results. We thus decided to refit all the group–interaction parameters of the original PPR78 model taking simultaneously into account phase equilibria and excess properties data. Our goal was obviously to obtain an enhanced model having the same accuracy as the original PPR78 to predict phase equilibria but also able to accurately describe excess enthalpies and excess heat capacities.

THE PPR78 MODEL

The PPR78 model relies on the Peng–Robinson EoS [13] which for a given pure component i , can be written as:

$$\begin{aligned}
 P &= \frac{RT}{v-b_i} - \frac{a_i(T)}{v(v+b_i)+b_i(v-b_i)} \\
 \left\{ \begin{aligned}
 R &= 8.314472 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\
 X &= \frac{-1 + \sqrt[3]{6\sqrt{2} + 8} - \sqrt[3]{6\sqrt{2} - 8}}{3} \approx 0.253076587 \\
 b_i &= \Omega_b \frac{RT_{c,i}}{P_{c,i}} \\
 \Omega_b &= \frac{X}{X+3} \approx 0.0777961 \\
 a_i &= \Omega_a \frac{R^2 T_{c,i}^2}{P_{c,i}} \left[1 + m_i \left(1 - \sqrt{\frac{T}{T_{c,i}}} \right) \right]^2 \\
 \Omega_a &= \frac{8(5X+1)}{49-37X} \approx 0.4572355 \\
 &\text{if } \omega_i \leq 0.491 \\
 m_i &= 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \\
 &\text{if } \omega_i > 0.491 \\
 m_i &= 0.379642 + 1.48503\omega_i - 0.164423\omega_i^2 + 0.016666\omega_i^3
 \end{aligned} \right. \quad (1)
 \end{aligned}$$

where P is the pressure, R is the gas constant, T is the temperature, a and b are respectively the energy parameter and the covolume, v is the molar volume. $T_{c,i}$ is the critical temperature, $P_{c,i}$ is the critical pressure, and ω_i is the acentric factor of a pure component i . Extension to mixtures requires mixing rules for the energy parameter and the covolume.

- A widely employed way to extend the cubic EoS to a mixture containing p components, the mole fractions of which are x_i , is via the so-called Van der Waals one-fluid mixing rules [quadratic composition dependency for both parameters – see Eqs. (2) and (3)] and the classical combining rules, i.e. the geometric mean rule for the cross-energy [Eq. (4)] and the arithmetic mean rule for the cross covolume parameter [Eq. (5)]:

$$a = \sum_{i=1}^p \sum_{j=1}^p x_i x_j a_{ij} \quad (2)$$

$$b = \sum_{i=1}^p \sum_{j=1}^p x_i x_j b_{ij} \quad (3)$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (4)$$

$$b_{ij} = \frac{1}{2}(b_i + b_j)(1 - l_{ij}) \quad (5)$$

Doing so, two new parameters, the so-called binary interaction parameters (k_{ij} and l_{ij}) appear in the combining rules. One of them, namely k_{ij} is by far the most important one. Indeed, a non null l_{ij} is only necessary for complex polar systems and special cases. This is the reason why, phase equilibrium calculations are generally performed with $l_{ij}=0$ and the mixing rule for the covolume parameter simplifies to:

$$b = \sum_{i=1}^p x_i b_i \quad (6)$$

When used with temperature-independent k_{ij} , cubic EoS with Van der Waals one-fluid mixing rules (VdW1f) lead to very accurate results at low and high pressures for *simple* mixtures (few polar, hydrocarbons, gases). They can however not be applied with success to polar mixtures.

- In order to avoid the limitations of the VdW1f mixing rules, extension of cubic EoS to mixtures can be performed via the so-called EoS/ g^E models. Indeed, g^E models (activity-coefficient models) are applicable to low pressures and are able to correlate polar mixtures. It thus seems a good idea to combine the strengths of both approaches, i.e. the cubic EoS and the activity coefficient models and thus to have a single model suitable for phase equilibria of polar and non-polar mixtures and at both low and high pressures.

The starting point for deriving EoS/ g^E models is the equality of the excess Gibbs energies from an EoS and from an explicit activity coefficient model at a suitable reference pressure. The activity coefficient model may be chosen among the classical forms of molar excess Gibbs energy functions (Redlich-Kister, Margules, Wilson, Van Laar, NRTL, UNIQUAC, UNIFAC...). Such models are

pressure-independent (they only depend on temperature and composition) but the same quantity from an EoS depends on pressure, temperature and composition explaining why a reference pressure needs to be selected before equating the two quantities. In order to avoid confusion, we will write with a special font (G^E) the selected activity coefficient model and with a classical font (g^E) the excess Gibbs energy calculated from an EoS. The starting equation to derive EoS/ g^E models is thus:

$$\left[\frac{g^E}{RT} \right]_P = \frac{G^E}{RT} \quad (7)$$

where subscript P indicates that a reference pressure has to be chosen. The first systematic successful effort in developing such models is that of Huron and Vidal [14], who used the infinite pressure as the reference pressure. Starting from Eq. (7), Huron and Vidal (HV) obtained:

$$\begin{cases} \frac{a(T, \mathbf{x})}{b(\mathbf{x})} = \sum_{i=1}^p x_i \frac{a_i(T)}{b_i} - \frac{G^E}{C_{EoS}} \\ b(\mathbf{x}) = \sum_{i=1}^p x_i b_i \end{cases} \quad (8)$$

where $C_{EoS} = \frac{\sqrt{2}}{2} \ln(1 + \sqrt{2}) \approx 0.62$ for the Peng-Robinson EoS.

Jaubert and Privat [15–16] demonstrated that the introduction of a Van Laar-type excess Gibbs energy model:

$$\frac{G_{Van\ Laar}^E}{C_{EoS}} = \frac{1}{2} \cdot \frac{\sum_{i=1}^p \sum_{j=1}^p x_i x_j b_i b_j E_{ij}(T)}{\sum_{j=1}^p b_j x_j} \quad (9)$$

in Eq. (8) was rigorously equivalent to using VdW1f mixing rules with temperature-dependent k_{ij} . The mathematical relation between $k_{ij}(T)$ [Eq. (4)] and the interaction parameter of the Van-Laar g^E model [$E_{ij}(T)$ in Eq. (9)] is:

$$k_{ij}(T) = \frac{E_{ij}(T) - (\delta_i - \delta_j)^2}{2\delta_i \delta_j} \quad \text{with} \quad \delta_i = \frac{\sqrt{a_i}}{b_i} \quad (10)$$

The works by Jaubert and Privat thus demonstrate that the use of temperature-dependent k_{ij} in the VdW1f mixing rules can overcome the limitations encountered with a constant k_{ij} .

The previous considerations were the starting point for the development of the PPR78 model. We indeed wanted a model which could be used with commercial process simulators in which the PR EoS is systematically available but we also wanted to overcome the limitations of the constant k_{ij} VdW1f mixing rules (which, as previously explained, only apply to simple fluids). This is why, following the previous works of Abdoul et al. [17] a group contribution method (GCM) to estimate indifferently the interaction parameters $E_{ij}(T)$ in Eq. (9) or the $k_{ij}(T)$ in Eq. (4) was developed.

The following equations were considered:

$$E_{ij}(T) = -\frac{1}{2} \sum_{k=1}^{N_g} \sum_{l=1}^{N_g} (\alpha_{ik} - \alpha_{jk}) (\alpha_{il} - \alpha_{jl}) A_{kl} \cdot \left(\frac{298.15}{T/K} \right)^{\left(\frac{B_{kl} - 1}{A_{kl}} \right)} \quad (11)$$

$$k_{ij}(T) = \frac{E_{ij}(T) \left(\text{given by Eq. 11} \right) - \left(\frac{\sqrt{a_i(T)}}{b_i} - \frac{\sqrt{a_j(T)}}{b_j} \right)^2}{2 \sqrt{a_i(T) \cdot a_j(T)}} \cdot \frac{1}{b_i \cdot b_j} \quad (12)$$

Eq. (11) will be employed with the HV mixing rules and Eq. (12) with the VdW1f mixing rules. In both cases, the same results will be obtained. In Eqs. (11) and (12), T is the temperature. a_i and b_i are the attractive parameter and the covolume of pure i . N_g is the number of different groups defined by the method (for the time being, twenty-one groups are defined and $N_g = 21$). α_{ik} is the fraction of molecule i occupied by group k (occurrence of group k in molecule i divided by the total number of groups present in molecule i). $A_{kl} = A_{lk}$ and $B_{kl} = B_{lk}$ (where k and l are two different groups) are constant parameters determined during the development of the model ($A_{kk} = B_{kk} = 0$). As can be seen, to calculate the k_{ij} (or E_{ij}) parameter between two molecules i and j at a selected temperature, it is only necessary to know: the critical temperatures of both components ($T_{c,i}$, $T_{c,j}$), the critical pressures of both components ($P_{c,i}$, $P_{c,j}$), the acentric factors of each component (ω_i , ω_j) and the decomposition of each molecule into elementary groups (α_{ik} , α_{jk}). It means that no additional input data besides those required by the EoS itself is necessary. Such a model relies on the Peng–Robinson EoS as published by Peng and Robinson in 1978 [Eq. (1)]. The addition of GC method to estimate the temperature-dependent k_{ij} (or E_{ij}) makes it predictive; it was thus decided to call it PPR78 (predictive 1978, Peng Robinson EoS).

For the 21 groups, we had to estimate 420 parameters ($210A_{kl}$ and $210B_{kl}$) the values of which were determined in order to minimize the deviations between calculated and experimental vapor–liquid equilibrium data from an extended data base containing roughly 100,000 experimental data points (56,000 bubble points + 42,000 dew points + 2,000 mixture critical points).

The following objective function was minimized:

$$F = \frac{F_{obj,bubble} + F_{obj,dew} + F_{obj,crit.comp} + F_{obj,crit.pressure}}{n_{bubble} + n_{dew} + n_{crit} + n_{crit}} \quad (13)$$

with:

$$\left\{ \begin{aligned} F_{obj,bubble} &= 100 \sum_{i=1}^{n_{bubble}} 0.5 \left(\frac{|\Delta x|}{x_{1,exp}} + \frac{|\Delta x|}{x_{2,exp}} \right)_i ; |\Delta x| = |x_{1,exp} - x_{1,cal}| \\ F_{obj,dew} &= 100 \sum_{i=1}^{n_{dew}} 0.5 \left(\frac{|\Delta y|}{y_{1,exp}} + \frac{|\Delta y|}{y_{2,exp}} \right)_i ; |\Delta y| = |y_{1,exp} - y_{1,cal}| \\ F_{obj,crit.comp} &= 100 \sum_{i=1}^{n_{crit}} 0.5 \left(\frac{|\Delta x_c|}{x_{c1,exp}} + \frac{|\Delta x_c|}{x_{c2,exp}} \right)_i ; |\Delta x_c| = |x_{c1,exp} - x_{c1,cal}| \\ F_{obj,crit.pressure} &= 100 \sum_{i=1}^{n_{crit}} \left(\frac{P_{cm,exp} - P_{cm,cal}}{P_{cm,exp}} \right)_i \end{aligned} \right.$$

n_{bubble} , n_{dew} and n_{crit} are the number of bubble points, dew points and mixture critical points respectively. x_1 is the mole fraction in the liquid phase of the most volatile component and x_2 the mole fraction of the heaviest component (it is obvious that $x_2 = 1 - x_1$). Similarly, y_1 is the mole fraction in the gas phase of the most volatile component and y_2 the mole fraction of the heaviest component (it is obvious that $y_2 = 1 - y_1$). x_{c1} is the critical mole fraction of the most volatile component and x_{c2} the critical mole fraction of the heaviest component. P_{cm} is the binary critical pressure.

For all the data points included in our database, the objective function defined by Eq. (13) is only:

$$F_{obj} = 7.6 \% \quad (14)$$

The average overall deviation on the liquid phase composition is:

$$\overline{\Delta x \%} = \frac{\overline{\Delta x_1 \%} + \overline{\Delta x_2 \%}}{2} = \frac{F_{obj,bubble}}{n_{bubble}} = 7.4 \% \quad (15)$$

The average overall deviation on the gas phase composition is:

$$\overline{\Delta y \%} = \frac{\overline{\Delta y_1 \%} + \overline{\Delta y_2 \%}}{2} = \frac{F_{obj,dew}}{n_{dew}} = 8.0 \% \quad (16)$$

The average overall deviation on the critical composition is:

$$\overline{\Delta x_c \%} = \frac{\overline{\Delta x_{c1} \%} + \overline{\Delta x_{c2} \%}}{2} = \frac{F_{obj,crit.comp}}{n_{crit}} = 7.1 \% \quad (17)$$

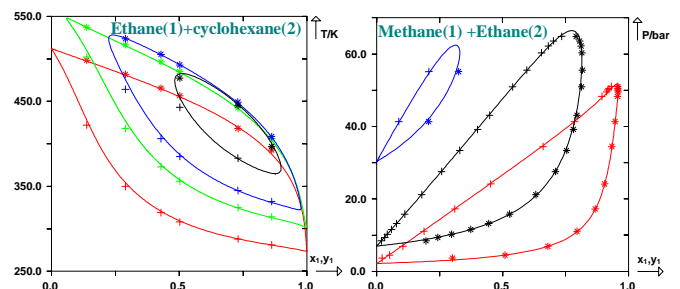
The average overall deviation on the binary critical pressure is:

$$\overline{\Delta P_c \%} = \frac{F_{obj,crit.pressure}}{n_{crit}} = 4.9 \% \quad (18)$$

We can thus assert that the PPR78 model is an accurate thermodynamic model which it is able to predict fluid–phase equilibria in any mixture containing alkanes, aromatics, naphthenes, CO₂, N₂, H₂S, H₂, mercaptans, water and alkenes.

It is today integrated in many process simulators like ProSimPlus, PRO/II, ChemSep, GEM–Selektor, EQ–COMP (and probably soon in UniSim).

Figure 1 graphically illustrates the accuracy of the PPR78 model.



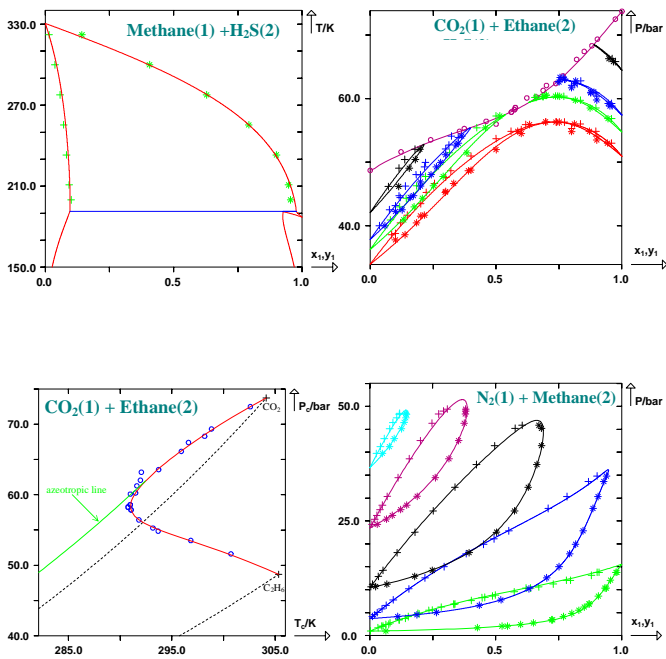


Figure 1. Illustration of the accuracy of the PPR78 model. The symbols are the experimental data points. The full lines are the predictions with the PPR78 model.

FROM THE PPR78 MODEL TO THE E -PPR78 MODEL

The PPR78 model being able to predict with accuracy fluid–phase equilibria, it was decided to test its ability to predict excess enthalpies (h^E) and excess heat capacities (c_P^E). A literature review made it possible to collect 30,000 h^E data points over 500 binary systems and 2,000 c_P^E data points over 100 binary systems.

By definition, the molar excess enthalpy h^E [see Eq. (19)] is the difference between the molar enthalpy of a solution and the sum of the molar enthalpies of the components which make it up, all at the same temperature and pressure as the solution, in their actual state weighted by their mole fractions z_i :

$$h^E(T, P, z) = h(T, P, z) - \sum_{i=1}^P z_i \cdot h_{\text{pure}i}(T, P) \quad (19)$$

For nearly ideal solutions i.e. when the molecules of a mixture are similar, h^E tends to zero and its influence on an energy balance is negligible. For such systems (e.g. mixture of n–hexane and n–heptane), high relative deviations – even higher than 200 % – are totally acceptable. In return, for highly non–ideal systems, h^E values can reach several kJ/mol and important absolute deviations can have a detrimental impact on the energy balance even if the corresponding relative deviations remain low (20 % deviation on a h^E value of 5 kJ/mol leads to a non–acceptable absolute deviation of 1 kJ/mol). For these reasons, the deviations on the excess enthalpies were neither expressed as relative nor absolute deviations but instead as a temperature difference defined by:

$$\Delta T = \left| \frac{h_{\text{cal}}^E - h_{\text{exp}}^E}{c_P} \right| \quad (20)$$

where h_{cal}^E and h_{exp}^E are respectively the calculated and the experimental h^E values. c_P is the heat capacity of the mixture.

From an engineering point of view, a deviation of 1 K is considered as acceptable. For the 30,000 experimental h^E data point collected, the PPR78 model lead to an average deviation of: $\overline{\Delta T}_{\text{PPR78}} = 2.1 \text{ K}$ which is at least twice too high.

Regarding the accuracy on the c_P^E prediction, an average deviation (on the 2,000 experimental data points) of: $\overline{\Delta c_P^E}_{\text{PPR78}} = 14.5 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ was obtained. Such a

deviation is huge and totally unacceptable. c_P^E values are indeed generally small and only a deviation smaller than $0.5 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ can be considered as acceptable. In front of such disappointing results, the group–interaction parameters [A_{kl} and B_{kl} in Eq. (11)] were fitted in order to minimize an objective function which took into account only the deviations on h^E and c_P^E . In that case, very accurate predictions could be obtained on such quantities but the deviations on VLE data were really too large. Moreover, we found unacceptable to have two sets of parameters: one for phase–equilibrium calculations and another one to perform energy balances. Indeed phase equilibrium and enthalpy calculations are frequently made together and it is thus useful to consider the applicability of a single set of parameters to both these properties. This statement was the basis to develop the E -PPR78 model in which the group–interaction parameters were determined in order to minimize an objective function which included both the deviations on the fluid–phase compositions [see Eq. (13)] and the deviations on the excess properties. The corresponding A_{kl} and B_{kl} group–interaction parameters are not yet published but can be found in the thesis by Qian [18]. The deviations obtained with such an enhanced model can be summarized as follows:

- the deviation on fluid–phase equilibria is:

$$\overline{F_{\text{obj}}}_{E\text{-PPR78}} = 7.8 \% \quad [\text{see Eq. (13)}]$$

- the deviation on h^E is:

$$\overline{\Delta T}_{E\text{-PPR78}} = 0.6 \text{ K}$$

- the deviation on c_P^E is:

$$\overline{\Delta c_P^E}_{E\text{-PPR78}} = 0.5 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

Such deviations highlight that the accuracy of the E -PPR78 model to predict fluid–phase equilibria, is the same as the one obtained with the original PPR78 model (the two objective functions: 7.6 % and 7.8 % are very close). On the other hand, the E -PPR78 model allows a much better prediction of the h^E (ΔT has been divided by a factor 3.5) and a spectacular improvement on the c_P^E prediction can be noticed.

Figure 2 graphically illustrates the accuracy of the E -PPR78 model to predict excess properties.

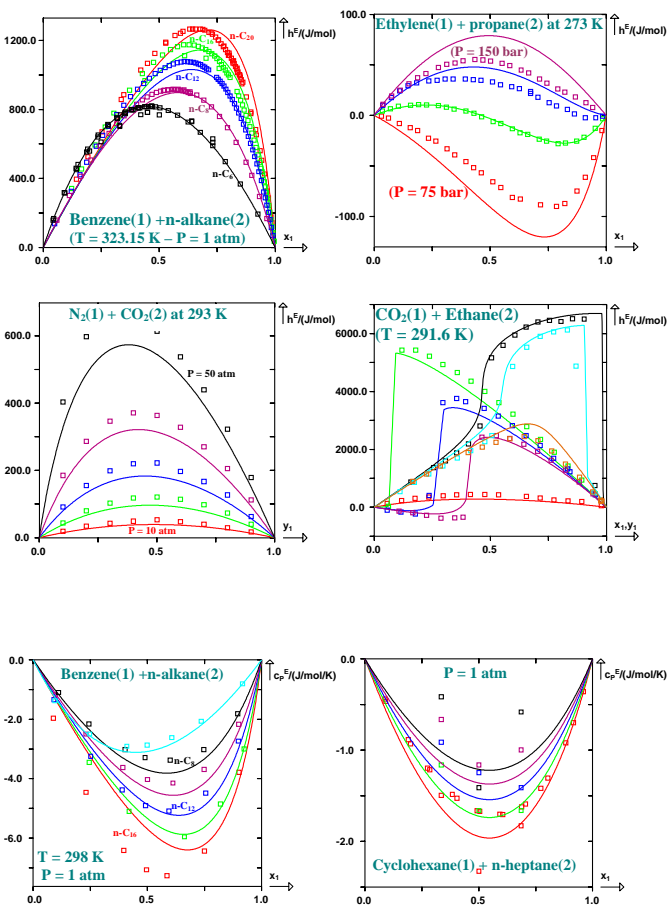


Figure 2. Illustration of the accuracy of the E-PPR78 model. The symbols are the experimental data points. The full lines are the predictions with the E-PPR78 model.

CONCLUSION

In this study, the parameters of the PPR78 model have been readjusted by considering phase equilibrium (vapor–liquid equilibrium, liquid–liquid equilibrium, mixture critical points), excess enthalpy and excess heat capacity data, in order to have a simultaneous correlation of VLE, LLE, h^E and c_p^E . The resulting model has been called E-PPR78 where E means enhanced.

Several conclusions can be made from this work:

- (1) In comparison with the original PPR78 model, by using this enhanced version, the prediction quality of VLE and LLE is retained, as well as that of mixture critical points. On the other hand, the accuracy of the predicted h^E (and c_p^E) data has been remarkably improved.
- (2) It is possible to use a cubic EoS with a unique set of temperature–dependent binary interaction parameters to represent both phase equilibrium and excess properties.
- (3) Fitting parameters only to excess properties data or only to phase–equilibrium data deteriorates the prediction of VLE data and of excess properties, respectively. Consequently, parameters must be fitted by considering

the simultaneous correlation of phase equilibrium and excess properties data.

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