

REVIEW

## Mixing rules for excess free energy models

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### 1. INTRODUCTION

Cubic equations of state (CEOS) have been the frequent subject of active research since van der Waals<sup>1</sup> presented his equation in 1873. Numerous CEOS have been proposed for the phase behavior 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 accuracy of VLE calculations depends on the accuracy of the vapor pressure calculations of pure compounds and the functional form of the mixing rules. In the past the CEOS approach has been applied successfully to systems containing only non-polar and slightly polar components for all conditions of practical interest. In cases of relatively simple mixtures (*i.e.*, hydrocarbons, hydrocarbons with inorganic gases) the so-called van der Waals one fluid mixing and combining rules perform adequately at the low-density limit as the ideal gas law and at the high-density state ("dense fluid").

The general form of a two-parameter cubic equations of state (CEOS) used in this review is as follows

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$$p = \frac{RT}{v-b} - \frac{a}{(v-ub)(v-wb)} \quad (1)$$

The constants  $u$  and  $w$  are EOS dependent.

CEOS can describe pure components reasonably well. Remarkable success in the development of a generalized temperature and acentric factor dependent function of the attractive term of CEOS energetic parameters  $a$  has been achieved by many authors for example<sup>2-10</sup>. Alternatively, Xu and Sandler<sup>11</sup> gave polynomial expressions for both the energy and covolumen parameters of the PR EOS which are specific for each fluid. However, for asymmetric non-ideal mixtures where the molecules are dissimilar in size or chemical nature, a number of alternative mixing rules must be applied, first of all composition-dependent and density-dependent mixing rules. The first of them are inconsistent at the low-density limit 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 behavior in very complex non-ideal mixtures. Concise reviews of the development of these two types of rules have been given by a few authors.<sup>12-14</sup>

Very recently some mixing rules combining free energy models ( $G^E$  or  $A^E$ ) and equations of state (EOS) have been successfully applied to very complex systems of diversified nature covering wide ranges of temperature and pressure. Among of these models the so-called EOS/ $G^E$  or EOS/ $A^E$  have been used for the correlation and prediction of vapor-liquid (VLE), liquid-liquid (LLE) equilibria and other thermodynamic properties. These models have been widely studied and an extensive analysis of their applicability has been reviewed in several excellent articles and monographs.<sup>12-16</sup>

In this review, some recent advances in describing phase equilibria and excess properties using CEOS/ $G^E$  models will be briefly considered.

The starting point for equating excess free energy from activity coefficient models and from equation of state models is the relationship

$$G_{\text{CEOS}}^E = RT \ln \frac{f_i}{f_i^0} \quad (2)$$

where  $f_i$  and  $f_i^0$  are the fugacity coefficients of the mixture and of the pure component  $i$ , both determined from the CEOS at the pressure and temperature of the system. Thus, one has

$$\frac{G_{\text{CEOS}}^E}{RT} = \int_v^v \frac{z-1}{z} dv - \sum_i x_i \int_v^{v_i} \frac{z_i-1}{z_i} dv \quad (3)$$

or equivalently, for the excess Helmholtz free energy

$$\frac{A_{\text{CEOS}}^E}{RT} = \sum_i x_i \ln \frac{z}{z_i} - \int_v^v \frac{z-1}{z} dv + \sum_i x_i \int_v^{v_i} \frac{z_i-1}{z_i} dv \quad (4)$$

For the two-parameter CEOS, the mentioned equations become

$$\frac{G_{\text{CEOS}}^{\text{E}}}{RT} = z \left[ x_i z_i \left( x_i \ln \frac{z}{z_i} \right) + x_i \ln \frac{v}{v_i} \right] \ln \frac{b}{b_i} + C \frac{a}{bRT} - x_i \frac{a_i}{b_i RT} C_i \quad (5)$$

and

$$\frac{A_{\text{CEOS}}^{\text{E}}}{RT} = x_i \ln \frac{z}{z_i} + x_i \ln \frac{v}{v_i} \ln \frac{b}{b_i} + C \frac{a}{bRT} - x_i \frac{a_i}{b_i RT} C_i \quad (6)$$

where  $C$  is a molar volume dependent function specific to the CEOS chosen. Depending of the CEOS model, different values of the  $C$  parameter are obtained.

A functional relation between the  $a$  and  $b$  parameters of the CEOS can be given in the approximated form

$$\frac{a}{bRT} = f(a_i, b_i, x_i, G^{\text{E}} \text{ or } A^{\text{E}}) \quad (7)$$

where  $G^{\text{E}}$  and  $A^{\text{E}}$  are molar  $G^{\text{E}}$  and  $A^{\text{E}}$  obtained from a liquid activity coefficient model. For a detailed explanation of the condition under which  $G_{\text{CEOS}}^{\text{E}}$  or  $A_{\text{CEOS}}^{\text{E}}$  can be equated to those from an activity coefficient model see below.

## 2. HURON-VIDAL MIXING RULE (HV)

Vidal<sup>17</sup> and then later Huron and Vidal<sup>18</sup> derived the first reasonably successful linking of a CEOS and activity coefficient models. They inserted zero reduce volume,  $v = b$  and  $v_i = b_i$  for the reference volumes and infinitive pressure as the reference pressure, at which the liquid activity coefficient and the CEOS model are equated. In their work, an assumption for the parameter  $b$  (mixing rule introduced by van der Waals) is made

$$b = \sum x_i b_i \quad (8)$$

which implies

$$\lim_{p \rightarrow 0} (pV^{\text{E}}) = 0 \quad (9)$$

In their approach (the HV model),  $G^{\text{E}}$  is assumed to be independent of pressure and Eq. (10) is used

$$G^{\text{E}}(T, p, x_i) = G_{\text{CEOS}}^{\text{E}}(T, p, x_i) \quad (10)$$

Bearing in mind Eq. (9) and the relation  $G^{\text{E}} = A^{\text{E}} + pV^{\text{E}}$ , one obtains  $G^{\text{E}} = A^{\text{E}}$ . On the basis of this relevant fact, and Eqs. (5) and (6), the resulting HV mixing rule for parameter  $a$  is

$$\frac{a}{b} = \sum x_i \frac{a_i}{b_i} \frac{G^{\text{E}}}{C^*} \quad (11)$$

where  $C = C^* = C_i$ . The mixing rule (11) does not satisfy the low density boundary condition

$$B(T, x_i) = \sum_{i,j} x_i x_j B_{ij} - \sum_{i,j} x_i x_j \frac{b_{ij}}{RT} + b \frac{a}{RT} \quad (12)$$

A number of authors<sup>16–40</sup> demonstrated the validity of this mixing rule, Eqs. (8) and (9) coupled with various CEOS (RK, SRK, VdW, PRSV, volume-shifted PR, PT) and activity coefficient models (van Laar, Redlich Kister, NRTL, UNIQUAC, UNIFAC, ASOG) to correlate and predict VLE and other thermodynamic properties of complex chemical systems. Among them, Tochigi *et al.*<sup>27</sup> and Soave *et al.*<sup>35</sup> investigated a SRK group contribution method to predict high pressure VLE and the infinite pressure activity coefficient, respectively.

The poor predictive performance of this model is analyzed in detail and explained by Orbey and Sandler.<sup>16</sup> They concluded that  $G^E$  model parameters obtained by the – method at low pressure (for example DECHEMA Chemistry Data Series) could not be used with EOS/ $G^E$  models. Namely, a main shortcoming of the HV model is the use of the pressure dependent  $G^E$  in the EOS rather than  $A^E$  which is practically pressure independent.

Some modifications of the HV mixing rule were developed and applied in several works.<sup>21,27,38</sup>

### 3. MHV1, MHV2 MIXING RULES

More recent mixing rules are based on less restrictive assumptions than those used for the HV mixing rule. Mollerup<sup>41</sup> used the condition that  $V^E = 0$ , but based his approach on the zero pressure limit in a manner similar to the HV model at infinite pressure. Gupte *et al.*<sup>42</sup> used Eqs. (5) and (7) at the experimental pressure to establish the UNIWAALS model. Some restrictions of this model were eliminated by Gani *et al.*<sup>43</sup> by reformulating the computational aspects of the resultant model in a more consistent way.

In the VLE calculations of Novenario *et al.*,<sup>44</sup> the liquid volume was set to be a constant factor  $K(=v/b)$  multiplied by the excluded volume  $b$  at the standard state where  $G^E = G_{\text{EOS}}^E$ . Using this method, the calculations of a zero pressure liquid volume, as part of any EOS calculations, is not needed. The authors showed that  $K = 1.15$  is suitable for the PR EOS but for each EOS  $K$  must be separately determined.

Michelsen<sup>45</sup> proposed the Huron-Vidal approach of matching  $G^E$  using a reference pressure of zero.

Applying the condition for a reference pressure  $p = 0$  to Eq. (5), one obtains

$$\frac{G_{0,\text{CEOS}}^E}{RT} = \sum_i x_i \ln \frac{v_0}{b} - 1 - \sum_i \ln \frac{v_{0i}}{b_i} - 1 - \sum_j x_j \frac{b}{b_i} - \frac{a}{bRT} C_0 \quad (13)$$

where subscript 0 indicates the reference pressure of zero. Eq. (13) can be given in the Michelsen form when rewritten as

$$q(\rho) = x_i q(\rho_i) \frac{G_0^E}{RT} - x_i \ln \frac{b}{b_i} \quad (14)$$

where  $\rho = a/bRT$  is the function

$$q(\rho) = \ln \frac{a - b}{b} - C_0 \quad (15)$$

The zero pressure liquid volume  $v_0$  is determined by solving the CEOS as part of a VLE calculation. However, a problem can arise at temperatures at which there is no liquid root of the EOS. For this reason, Michelsen arbitrarily chose a cut-off value of  $\rho$  for which a liquid root exists.

In the first case, with smaller values of  $\rho$ , a linear extrapolation was used

$$q(\rho) = q_0 + q_1 \rho \quad (16)$$

then Eq. (14) becomes

$$\frac{a}{RT} - \frac{G_0^E}{C_0 RT} - \frac{1}{C_0} - x_i \ln \frac{b}{b_i} - x_i \rho_i \quad (17)$$

or

$$x_i \rho_i = \frac{1}{q_1} \frac{G_0^E}{RT} - x_i \ln \frac{b}{b_i} \quad (18)$$

where  $q_1$  is a numerical constant dependent of the EOS. Eqs. (8) and (18) are known as the Modified Huron-Vidal First Order mixing rule (MHV1). Michelsen sets  $q_1 = -0.593$ .

In the second approximation, Dahl and Michelsen<sup>46</sup> used the second-order polynomial

$$q(\rho) = q_0 + q_1 \rho + q_2 \rho^2 \quad (19)$$

where the parameters must be chosen to give continuity of the auxiliary function  $q(\rho)$  and its derivatives. In this way Eq. (14) becomes

$$q_1 \left( x_i \rho_i \right) - q_2 \left( \rho_i^2 - x_i \frac{\rho_i^2}{i} \right) - \frac{G_0^E}{RT} - x_i \ln \frac{b}{b_i} \quad (20)$$

Eq. (20) is known as the Modified Huron-Vidal Second Order mixing rule (MHV2). For the interval  $10 < \rho < 13$ , Dahl and Michelsen<sup>46</sup> suggest values of  $q_1 = -0.478$  and  $q_2 = -0.0047$  when the RK EOS was used. Huang and Sandler<sup>47</sup> proposed values of  $q_1 = -0.4347$  and  $q_2 = -0.003654$  for the PR EOS. When  $q_2$  is set as zero, MHV2 (Eq. (20)) reduces to MHV1 (Eq. (18)). Soave<sup>48a</sup> gave a more accurate expression for  $\rho$  comparable to those from Eq. (19) for the range  $\rho = 8 - 18$ . The results obtained in this way remain accurate up to  $\rho = 21$ .

The MHV2 mixing rule is in fact more complex than the HV approach, but  $G^E$  models obtained by fitting low-pressure data may be used directly by means of the parameters reported in the DECHEMA Chemistry Data Series.

The MHV1 and MHV2 mixing rules have been widely applied to correlations or/and predictions of diverse thermodynamic properties (VLE, LLE, VLLE, LLLLE, gas solubility, VLE of gas/large alkane systems, excess enthalpy, excess heat capacity, activity coefficients at infinite dilution, *etc.*).<sup>14–16,33–40,46–67</sup>

Heidemann and Kokal<sup>68</sup> gave an extrapolation procedure using zero pressure as the standard state. Their rule is also based on Eq. (13). They proposed a zero pressure limit for pure components above the limiting  $a/bRT$  value, below which the root does not appear. When there is not a zero pressure solution for the liquid volume, the reduced density  $\rho_i$  is extrapolated as

$$\rho_i = \frac{b_i}{v_i} + p_0 \left[ 1 - \frac{a_i}{b_i RT} \right]^2 + \frac{a_i}{b_i RT} \left[ \frac{a_i}{b_i RT} \right]^3 \quad (21)$$

where the coefficients  $b_i$  and  $a_i$  insure that  $\rho_i$  and its derivative contain a function of  $(a_i/b_i RT)$ . Heidemann and Kokal set the mixed phase standard state pressure by demanding that

$$z = \sum x_i z_i = 0 \quad (22)$$

To find  $\rho_i$  and the  $(a/bRT)$  parameters of a mixture, Eq. (22) is solved with the condition of equality of  $G^E = G_{EOS}^E$ . In this case, the  $a$  parameter is not density dependent in contrast to the UNIWAALS model.

Tochigi *et al.*,<sup>38</sup> using the procedure of Wong and Sandler,<sup>69</sup> proposed an extension of the MHV1 mixing rule consistent with the second virial coefficient condition.

The resulting zero pressure mixing rule is

$$\frac{a}{RT} = b + \sum x_i \frac{a_i}{b_i} \frac{1}{q_1} \frac{G_{0,i}^E}{RT} + \sum x_i \ln \frac{b}{b_i} \quad (23)$$

$$b = \frac{B}{1 + \frac{a}{RT}} + \frac{\sum x_i b_i \frac{a_i}{RT}}{1 + \sum x_i \frac{a_i}{b_i RT} \frac{1}{q_1} \frac{G_{0,i}^E}{RT} + \sum x_i \ln \frac{b}{b_i}} \quad (24)$$

This model coupled with the SRK and PRSV EOS has been applied to the prediction of binary and ternary systems.<sup>38</sup> Using the same model, Eqs. (23) and (24), with low pressure ASOG parameters, high pressure VLE have been predicted.<sup>70</sup> Michelsen<sup>56</sup> proposed an extension of the MHV2 mixing rule to incorporate mixtures containing components of widely differing volatilities, such as the hexane-hexadecane and acetone-water mixture.

The work of Boukouvalas *et al.*<sup>50</sup> demonstrated that the PRSK model (SRK EOS + MHV1) performs rather poorly for VLE prediction of gaseous higher alkane mixtures. Zhong and Masuoka<sup>58</sup> used a modified MHV1 mixing rule in order to improve its accuracy as follows

$$\frac{a}{bRT} = \sum x_i \frac{a_i}{b_i RT} \frac{1}{q_1} \frac{G^E(1-f)}{RT} + \sum x_i \ln \frac{b}{b_i} \quad (25)$$

The parameter  $f$  corrects for inadequacies of both the UNIFAC and MHV1 for highly asymmetric systems (CO<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> with alkane systems). In later works<sup>59,62</sup> this method was extended to other gases (C<sub>2</sub>H<sub>4</sub>, CO and H<sub>2</sub>).

Zhong and Masuoka<sup>65</sup> modified the MHV1 mixing rule in order that it gives almost identical  $H^E$  predictions to those obtained from the incorporated modified UNIFAC model and which are much better than those obtained from the MHV1 mixing rule.

This model is expressed as follows

$$\frac{a}{bRT} = x_i \frac{a_i}{b_i RT} - \frac{1}{q_1} \frac{G^E}{RT} - x_i \ln \frac{b}{b_i} \quad (26)$$

Parameter  $a$  is calculated for binary system by solving the equation  $H_{\text{SRK}}^E = H_{\text{mod}}^E \text{UNIFAC}$  (at  $p=0.1013$  MPa,  $x_1=x_2=0.5$  and the system temperature  $T$ ). The modified MHV1 mixing rule shows significantly improved predictions over the MHV1 mixing rule.

Some comparisons of the  $c_p^E$  correlations of the acetone(1)+dodecane(2) system at 288 K by means of the approximate MHV1 and MHV2 models coupled with the PRSV EOS follow. To make these comparisons, the same activity coefficient model (NRTL) was used in all cases. Also, for each of the EOS/ $G^E$  models, the  $c_p^E$  data were fitted with three different NRTL equations: (i) two temperature independent parameters  $\tau_{12}$  and  $\tau_{21}$  and  $\alpha = 0.3$  (MHV1-NRTL2 and MHV2-NRTL2 model), (ii) two linear temperature dependent parameters  $\tau_{12}$  and  $\tau_{21}$  and  $\alpha = 0.3$  (MHV1-NRTL4 and MHV2-NRTL4 model), (iii) three linear temperature dependent parameters  $\tau_{12}$ ,  $\tau_{21}$  and  $\alpha$ . (MHV1 – NRTL6 and MHV2 – NRTL6 model). From Fig. 1 it can be seen that the performance of these six models is quite different. The results indicate that only the models with three temperature dependent interaction parameters (the six optimized coefficients generated from  $c_p^E$  data) are very good for correlation. The best results were obtained with the MHV1-NRTL6 model.

#### 4. WONG-SANDLER MIXING RULE (WS)

Wong and Sandler proposed<sup>69</sup> a new mixing rule which is based on the desired EOS behavior at both low and high densities without being density dependent and of equating free energies at infinite pressure. Namely, Wong and Sandler equate the Helmholtz free energy at infinite pressure from the CEOS with that acquired from any activity coefficient model. In this way the theoretically correct WS mixing rule satisfies the quadratic composition dependence of the second virial coefficient model at high density. On the contrary, the HV, MHV1, MHV2 mixing rules do not satisfy this boundary condition. By means of the WS mixing rule, the  $a$  and  $b$  mixing parameters are obtained from the relations

$$a = RT \frac{QD}{1 - D} \quad (27)$$

$$b = \frac{Q}{1 - D} \quad (28)$$

where the quantities  $Q$  and  $D$  are given by

$$Q = \sum_{i,j} x_i x_j \frac{a_{ij}}{RT} b_{ij} \quad (29)$$

$$D = \sum_i x_i \frac{a_i}{b_i RT} \frac{G^E}{CRT} \quad (30)$$

where  $C$  is a constant that depends on the CEOS (for example, for PR EOS,  $C = (1+2^{1/2})/2^{1/2}$ ).

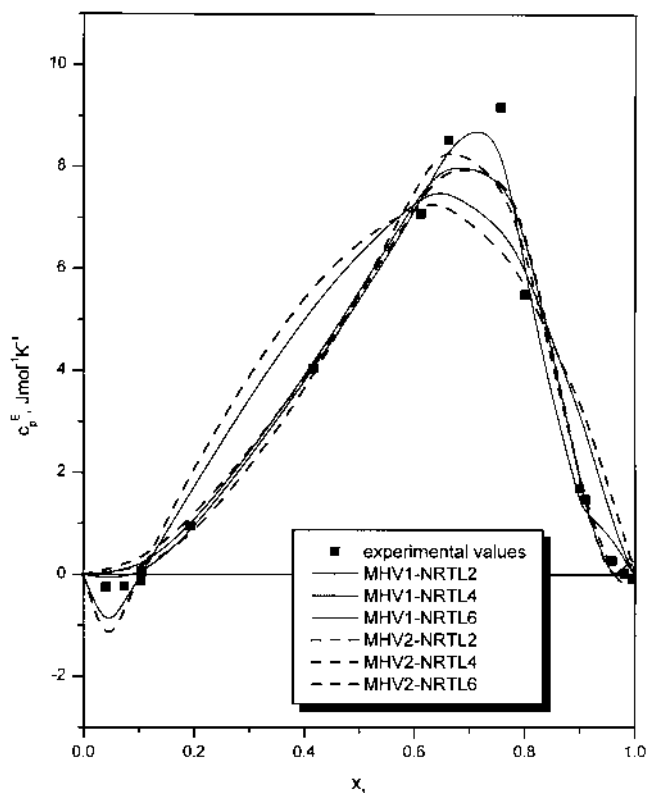


Fig. 1.  $c_p^E$  Correlation of the system acetone (1)+dodecane (2) at 288 K, with the MHV1-NRTL and the MHV2-NRTL models combined with the PRSV EOS. The solid lines represent results calculated with the following MHV1-NRTL parameters: NRTL2:  $\tau_{12} = (0.108549 \cdot 10^4)/RT$ ,  $\tau_{21} = (0.878439 \cdot 10^4)/RT$ ,  $\alpha_{12} = 0.3$ ; NRTL4:  $\tau_{12} = (0.245528 \cdot 10^4 - 3.40724T)/RT$ ,  $\tau_{21} = (-0.543588 \cdot 10^3 - 6.96601T)/RT$ ,  $\alpha_{12} = 0.3$ ; NRTL6:  $\tau_{12} = (0.17327 \cdot 10^3 + 0.114689T)/RT$ ,  $\tau_{21} = (0.58515 \cdot 10^4 - 8.81454T)/RT$ ,  $\alpha_{12} = 0.0405539 - 0.566460 \cdot 10^{-3}T$ . The dashed lines represent results calculated by the MHV2-NRTL parameters: NRTL2:  $\tau_{12} = (0.553106 \cdot 10^3)/RT$ ,  $\tau_{21} = (0.8233416 \cdot 10^4)/RT$ ,  $\alpha_{12} = 0.3$ ; NRTL4:  $\tau_{12} = (0.197987 \cdot 10^4 - 7.29184T)/RT$ ,  $\tau_{21} = (0.364533 \cdot 10^3 + 2.09463T)/RT$ ,  $\alpha_{12} = 0.3$ ; NRTL6:  $\tau_{12} = (-0.423086 \cdot 10^4 + 3.70220T)/RT$ ,  $\tau_{21} = (0.288382 \cdot 10^4 + 3.38331T)/RT$ ,  $\alpha_{12} = -0.0439628 - 0.509917 \cdot 10^{-4}T$ . The points are experimental data of Saint-Victor and Patterson.<sup>111</sup>



The  $a$  and  $b$  parameters of the mixture come from the condition that

$$\begin{aligned} A_{\text{EOS}}^{\text{E}}(T, p, x_i) &= A^{\text{E}}(T, p, x_i) = \\ &= A^{\text{E}}(T, p = \text{low}, x_i) = G^{\text{E}}(T, p = \text{low}, x_i) \end{aligned} \quad (31)$$

The parameters in the WS mixing rule are those of an activity coefficient model  $A^{\text{E}}$  and the binary interaction parameter  $k_{ij}$

$$b \frac{a}{RT} \quad \frac{b \frac{a}{RT} \quad b \frac{a}{RT}}{2} \quad (1 - k_{ij}) \quad (32)$$

Additionally, the second virial coefficient binary interaction parameter  $k_{ij}$  has to be regressed in various ways.<sup>16,47,69–75</sup> But, it is important to say that the parameter  $k_{ij}$  is not an independent or freely adjustable parameter. In the reformulated WS model, the  $k_{ij}$  parameter can be eliminated as shown by Orbey and Sandler.<sup>75</sup> The WS mixing rule gives very good correlations of VLE, LLE, VLLE, excess properties, gas solubility, volumetric properties, *etc.*<sup>48,53,60,69–82</sup>

The mismatch's, limitations and correction of the WS mixing rule are considered in a few works.<sup>53,83–85</sup>

Fig. 2 shows the predictions of  $H^{\text{E}}$  for the ternary system acetonitrile (1) + ethanol (2) + benzene (3) at 298.15 K obtained from the PRSV-WS-NRTL model using the linear temperature dependent parameters of the NRTL equation ( $k_{ij} = 0.32$ ) generated from the corresponding binary  $H^{\text{E}}$  data. It is evident that the magnitudes of the deviations of the predicted values given by the excess enthalpy surface from the experimental points are very small (the average percentage deviation is 1.71 %). Namely, this Figure indicates that the predicted excess enthalpies agree well with the experimental values.

##### 5. LCVM MIXING RULE

Boukouvalas *et al.*<sup>50</sup> proposed a new purely empirical mixing rule (LCVM) as a linear combination of the MHV1 and the HV mixing rules

$$(\text{LCVM}) = (\text{HV}) + (1 - \alpha) (\text{MHV1}) \quad (33)$$

where  $V = a/bRT$  and  $(\text{MHV1} = a/bRT)_{\text{MHV1}}$ , given by the equations for the HV and the MHV1 mixing rules, were introduced above. The recommended value of  $\alpha$  is 0.36 for the original UNIFAC and 0.65 to 0.75 for the modified UNIFAC. Thus, one obtains

$$(\text{LCVM}) \quad \frac{a}{bRT} \quad \frac{1}{C} \quad \frac{G^{\text{E}}}{C(\text{MHV1}) \quad RT} \quad (34)$$

It should be emphasized that  $G^{\text{E}}$  of the HV mixing rule is evaluated at infinite pressure while  $G^{\text{E}}$  of the MHV1 mixing rule is evaluated at zero pressure. This mixing rule gave good predictions for VLE for non-polar and polar systems similar and dissimilar in size at low and high pressure. The LCVM is better than the others (MHV2 and PSRK)

when the size of the molecules is significantly different. The quality of the results of the LCVM are similar to those obtained by the modified MHV1.<sup>58,59</sup> In the work of Orbey and Sandler,<sup>39</sup> a comparison is made of the PSRK, MHV1, MHV2, HVOS and LCVM mixing rules for mixtures of molecules differing largely in size. The results obtained show that the MHV2 model was the least accurate. Further applications of this model are considered in several articles of Tzouvaras<sup>86</sup> and Tassios and coworkers.<sup>87-89</sup>

#### 6. HURON-VIDAL-ORBAY-SANDLER MIXING RULE (HVOS)

Orbey and Sandler<sup>52</sup> developed an approximate but rigorous model by assuming that for all fluids there is a universal linear algebraic function  $u$  that relates the liquid molar volumes and their close packed hard-core volumes such as  $u = v/b$ . At infinite pressure, both for the pure liquid and for the mixtures,  $u$  has a unique value

$$A_{\text{EOS}}^{\text{E}} = x_i \ln \frac{b}{b_i} - \frac{a}{bRT} C(ub) - x_i \frac{a_i}{b_i RT} C(ub_i) \quad (35)$$

At all conditions one can take  $u = 1$ ,  $C(ub) = C(ub_i)$ , thus the resulting equation is

$$\frac{A_{\text{EOS}}^{\text{E}}}{RT} = \frac{G^{\text{E}}}{RT} = x_i \ln \frac{b}{b_i} - C \frac{a}{bRT} - x_i \frac{a_i}{b_i} \quad (36)$$

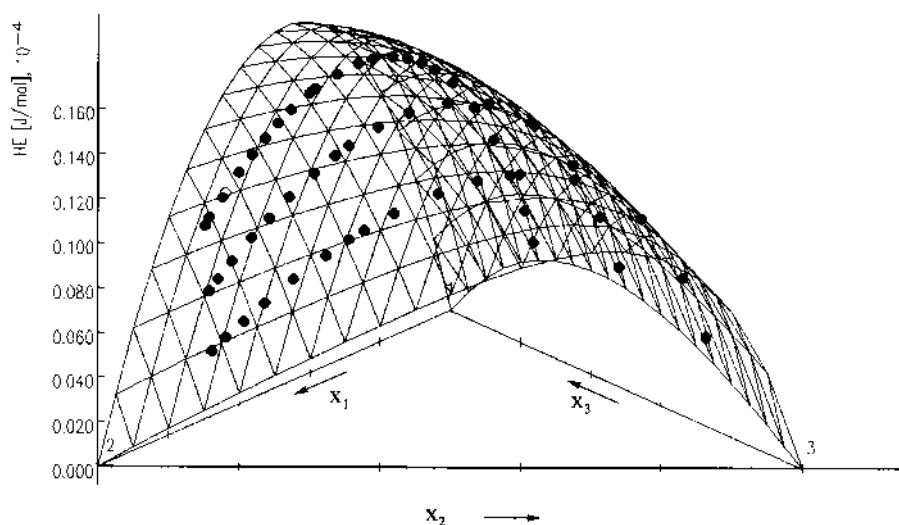


Fig. 2.  $H$  Prediction of the system acetonitrile(1)+ethanol(2)+benzene(3) at 298 K, with the WS-NRTL-PRSV model. The surface is obtained by the following binary parameters:  $\tau_{12} = (0.633398 - 10^{-6} 0.614310T)/RT$ ,  $\tau_{13} = (0.321367 - 10^{-6} 7.25368T)/RT$ ,  $\tau_{23} = (0.321355 - 10^{-6} 2.62969T)/RT$ ,  $\tau_{12}^* = (-0.252335 - 10^{-6} 3.46543T)/RT$ ,  $\tau_{13}^* = (0.331820 - 10^{-6} 0.197586 - 10T)/RT$ ,  $\tau_{23}^* = (0.715713 - 10^{-6} 8.79139T)/RT$ ;  $\alpha_{12} = 0.3$ ;  $\alpha_{13} = 0.3$ ,  $\alpha_{23} = 0.47$ ;  $k_{12} = 0.163$ ,  $k_{13} = 0.119$ ,  $k_{23} = 0.390$ . The points are experimental data of Nagata and Tamura.<sup>53</sup>

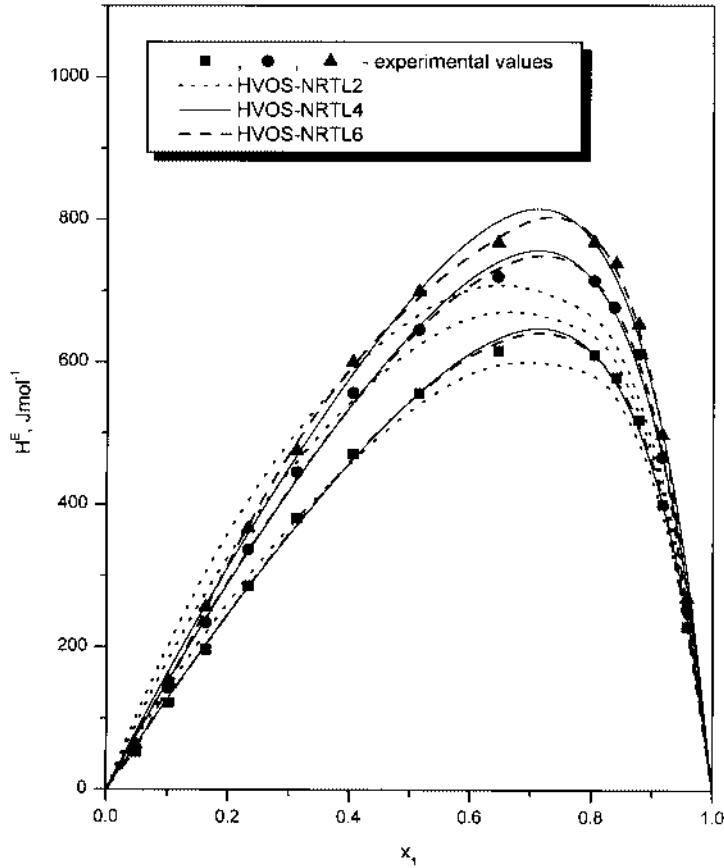


Fig. 3.  $H^E$  Correlation of the system benzene(1)+methanol(2) at 293, 303 and 308 K, with the HVOS-NRTL models and the PRSV EOS. The dotted lines represent the results of the HVOS-NRTL2 model at  $T=293$  K:  $_{12} = (0.562918 \cdot 10^4)/RT$ ,  $_{21} = (0.100044 \cdot 10^4)/RT$ ;  $T=303$  K:  $_{12} = (0.593072 \cdot 10^4)/RT$ ,  $_{21} = (0.139647 \cdot 10^4)/RT$ ;  $T=308$  K:  $_{12} = (0.604896 \cdot 10^4)/RT$ ,  $_{21} = (0.157280 \cdot 10^4)/RT$ . The solid lines denote the results of the HVOS-NRTL4 model at  $T=293$  K:  $_{12} = (0.526860 \cdot 10^4 + 0.904239T)/RT$ ,  $_{21} = (0.109694 \cdot 10^4 - 5.86245T)/RT$ ;  $T=303$  K:  $_{12} = (0.657128 \cdot 10^4 - 3.69231T)/RT$ ,  $_{21} = (0.108614 \cdot 10^4 - 3.66729T)/RT$ ;  $T=308$  K:  $_{12} = (0.731127 \cdot 10^4 - 6.14529T)/RT$ ,  $_{21} = (0.103547 \cdot 10^4 - 2.14626T)/RT$ ; In cases of the HVOS-NRTL2 and the HVOS-NRTL4 models  $_{12} = 0.47$ . The dashed lines are from the HVOS-NRTL6 model at  $T=293$  K:  $_{12} = (-1.01464 \cdot 10^4 + 0.181202 \cdot 10^3 T)/RT$ ,  $_{21} = (0.125727 \cdot 10^4 - 0.190720 \cdot 10^2 T)/RT$ ,  $_{12} = 0.1838758 - 0.422773 \cdot 10^{-4} T$ ;  $T=303$  K:  $_{12} = (-0.849092 \cdot 10^4 + 0.120972 \cdot 10^3 T)/RT$ ,  $_{21} = (0.468376 \cdot 10^3 - 5.09688T)/RT$ ,  $_{12} = 0.25760 - 0.330466 \cdot 10^{-4} T$ ;  $T=308$  K:  $_{12} = (0.607207 \cdot 10^4 - 0.401049 \cdot 10^2 T)/RT$ ,  $_{21} = (0.172028 \cdot 10^3 - 0.918426 \cdot 10^2 T)/RT$ ,  $_{12} = 0.0914807 + 0.759089 \cdot 10^{-4} T$ . The points are experimental data of Battler and Rowley<sup>113</sup>:  $\blacksquare$  – 293 K;  $\bullet$  – 303 K;  $\blacktriangle$  – 308 K.

In the HVOS model, Eqs. (8) and (36) are used to obtain the CEOS parameters  $a$  and  $b$ . Orbey and Sandler<sup>16</sup> investigated the performance of the HVOS model to corre-

late and predict VLE. They showed that the behavior of all approximate models (MHV1, MHV2, LCVI and HVOS) were similar and comparable in most cases. Application of the HVOS mixing rule to correlate  $c_p^E$ ,  $c_p^E + H^E$ , VLE +  $c_p^E$ , VLE +  $H^E$  and VLE +  $H^E + c_p^E$  have been further presented in several articles.<sup>90–93</sup> The correct representation of binary VLE +  $H^E + c_p^E$  data by their simultaneous fitting requires reliable temperature dependent EOS/ $G^E$  models.

$H^E$  Calculations using the HVOS mixing rule to incorporate the NRTL equation in the PRSV EOS are presented in Fig. 3. Comparison is made with experimental data of the benzene(1) + methanol(2) system at three temperatures 293, 303 and 308 K. It can be seen that the HVOS-NRTL models with two and three temperature dependent interaction parameters are comparable whereas there is slight inaccuracy of the performance of the HVOS-NRTL4 model along the highest temperature isotherm. In all cases, the HVOS-NRTL2 model with no temperature dependent parameters was inferior to the other ones.

The performance of the linear PRSV HVOS-NRTL and TC-NRTL models in the simultaneous fitting of  $H^E + c_p^E$  data for *N,N*-dimethylformamide(1)+tetrahydrofuran(2) system at 298 K is shown in Fig. 4. Single sets of coefficients of linear temperature dependent parameters were generated from  $H^E + c_p^E$  data. As it can be seen from Fig. 4, very good results are obtained with both the HVOS-NRTL and TC-NRTL models.

#### 7. PREDICTIVE CEOS/ $G^E$ MODELS. PSRK MODEL

The CEOS/ $G^E$  models mentioned above are not predictive because the binary interaction parameters used in those mixing rules of  $G^E$  models must be adjusted from corresponding experimental data. However, some of them by using any group contribution method, like UNIFAC or ASOG, can be used to predict VLE, LLE, excess property, *etc.* Such group contribution methods coupled with a CEOS are very capable because it makes the CEOS/ $G^E$  approach completely predictive and suitable for use at high pressure at temperatures at which activity coefficient methods, bearing in mind the supercritical components of mixtures, are not applicable.

The rigorous HV and WS models and approximate models, such as the MHV1, MHV2, LCVI and HVOS models, have been used as predictive models in many works, as can be seen from the aforementioned and other references.<sup>14–16,34,35,38–40, 55–64,68–77,94,95</sup> A low pressure reference state (zero pressure or atmospheric pressure) has a great advantage over the infinite pressure reference state because the existing parameters of the group contributions methods can be used.

The purely predictive PSRK group contribution EOS based on the SRK EOS and UNIFAC method was suggested by Holderbaum and Gmehling.<sup>96</sup> The PSRK is given as

$$\frac{a(T)}{b} = x_i \frac{a_i(T)}{b_i} - \frac{G^E}{RT} - x_i \ln(b / b_i) \quad (37)$$

$$0.64663$$

using the linear mixing rule (7) for the parameter  $b$ . Eq. (37) contains the following assumptions: (i) the excess volume is neglected, (ii) the ratio  $u = v/b = v_i/b = 1.1$  for a large

number of components at the normal boiling point. The PSRK mixing rule can also be used to introduce other  $G_0^E$  into the SRK EOS. This mixing rule requires only pure component data and the parameters of the chosen  $G^E$  model. The PSRK mixing rule is identical to the MHV1 mixing rule except for the choice of value for  $q_1 = 0.63$ .

A comparison with other group contribution EOS, such as MHV2-UNIFAC,<sup>14</sup> UNIWAALS,<sup>42,43</sup> GCEOS<sup>97</sup> and models mentioned above, shows some very important advantages.<sup>96,98</sup> Also, the PSRK model provides reliable results for VLE and gas solubility of a large number of symmetric and highly asymmetric systems over large pressure and temperature ranges.<sup>98–102</sup> Finally, the parameter matrix for the PSRK model is much larger than that for all other group contribution EOS using a larger range of applicability for the PSRK model compared to the other ones.

#### 8. TWU *et al.* MIXING RULES

Twu and coworkers introduced a new class of mixing rules with van der Waals one-fluid mixing rule and second virial coefficient constraint.<sup>103–107</sup> These mixing rules were applied to VLE of various asymmetric, highly non-ideal complex systems.

Twu and Coon<sup>103</sup> treated the ideal solution reference used by Wong and Sandler<sup>69</sup> as only one of many choices that can be used for the reference. They chose a vdW fluid as the reference. In this way, the excess Helmholtz free energy  $A_{nR}^E$  represents the non-random portion of the  $A^E$  given with respect to a vdW fluid instead of an ideal solution.

For the CEOS  $a$  and  $b$  parameters of mixture, Twu and Coon (TC) developed the following mixing rules at infinite pressure

$$b^* = \frac{b_{vdW}^* a_{vdW}^*}{1 \frac{a_{vdW}^*}{b_{vdW}^*} \frac{1}{C_1} \frac{A_{nR}^E}{RT}} \quad (38)$$

$$a^* = b^* \frac{a_{vdW}^*}{b_{vdW}^*} \frac{1}{C_1} \frac{A_{nR}^E}{RT} \quad (39)$$

The  $C_1$  constant is characteristic to the EOS used. The  $a_{vdW}$  and  $b_{vdW}$  parameters are determined from the vdW mixing rules, while  $a^*$  and  $b^*$  are defined as

$$a^* = pa/R^2T^2 \quad b^* = pb/RT \quad (40)$$

When  $A_{nR}^E$  is zero, the TC mixing rule reduces to the vdW one-fluid mixing rule.

Twu, Coon and Bluck<sup>104</sup> (TCB) extended the TC mixing rule from infinite pressure to zero pressure in order to incorporate the UNIFAC group contribution method into the CEOS for high pressure VLE predictions.

The TCB mixing rule in terms of  $A_0^E$  at zero pressure is given as

$$b^* = \frac{b_{vdW}^* a_{vdW}^*}{1 \frac{a_{vdW}^*}{b_{vdW}^*} \frac{1}{C_{v0}} \frac{A_0^E}{RT} \frac{A_{0vdW}^E}{RT} \ln \frac{b_{vdW}}{b}} \quad (41)$$

$$a^* = b^* \frac{a_{\text{vdW}}^*}{b_{\text{vdW}}^*} \frac{1}{C_{\text{v}0}} \frac{A_0^{\text{E}}}{RT} \frac{A_{0\text{vdW}}^{\text{E}}}{RT} \ln \frac{b_{\text{vdW}}}{b} \quad (42)$$

where  $C_{\text{v}0}$  is a zero pressure function defined as

$$C_{\text{v}0} = \frac{1}{w} \ln \frac{v_0^*}{v_0} \frac{w}{u} \quad (43)$$

where  $w$  and  $u$  are CEOS dependent constants (Eq. (1)).

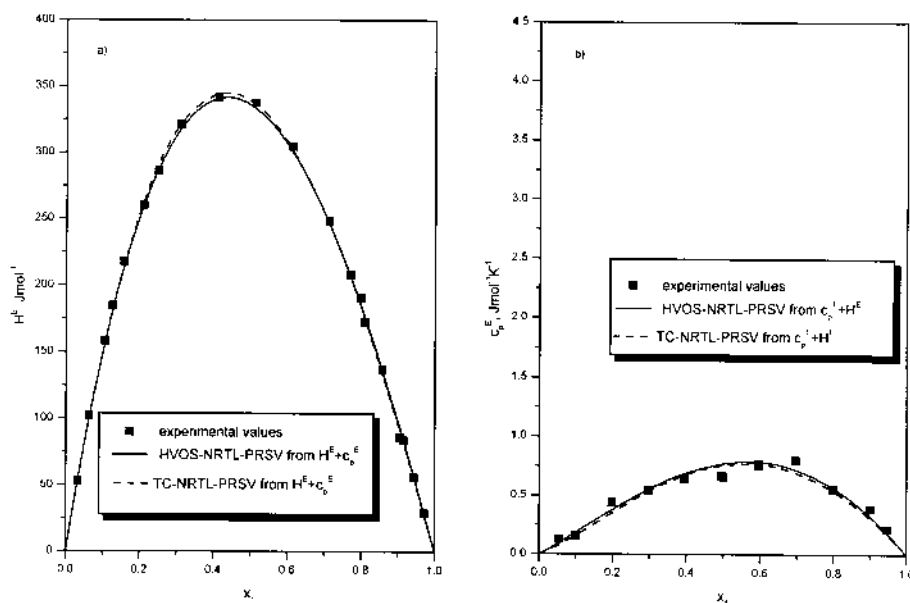


Fig. 4. Simultaneous correlation of  $H + c_i$  data of the system  $N,N$ -dimethylformamide(1)+tetrahydrofuran(2) at 298 K. The lines are correlations obtained by the unique set of parameters (a)  $H$  from  $H + c_i$ ; (b)  $c_i$  from  $H + c_i$ . The solid lines represent the results calculated with the HVOS-NRTL-PRSV model parameters  $\tau_{12} = (-0.685303 - 10 + 3.91997T)/RT$ ,  $\tau_{21} = (0.214124 - 10 - 1.62296T)/RT$ ,  $\tau_{11} = 0.281004 - 0.299352 - 10T$ . The dashed line denote the results using the TC-NRTL-PRSV model parameters  $\tau_{12} = (-0.188181 - 10 - 0.319688T)/RT$ ,  $\tau_{21} = (0.774147 - 10 - 0.206451 - 10T)/RT$ ,  $\tau_{11} = -1.55120 + 0.576814 - 10T$ . The points are experimental data of Conti *et al.*.

The reduced liquid volume at zero pressure  $v_0^*(=v_0/b)$  can be calculated for both the mixture and the pure components from the CEOS using the vdW mixing rule for its  $a$  and  $b$  parameters. Bearing in mind that  $A_0^{\text{E}}$  is at zero pressure,  $G^{\text{E}}$  models such as the NRTL or the UNIFAC can be directly incorporated into  $A_0^{\text{E}}$ . The same authors<sup>105</sup> applied the TCB mixing rule to predict high pressure VLE using infinite dilution activity coefficients at low temperature. They compared the TCB mixing rule incorporating the Wilson activity model with other models such as MHV1 and WS. The TCB model gave

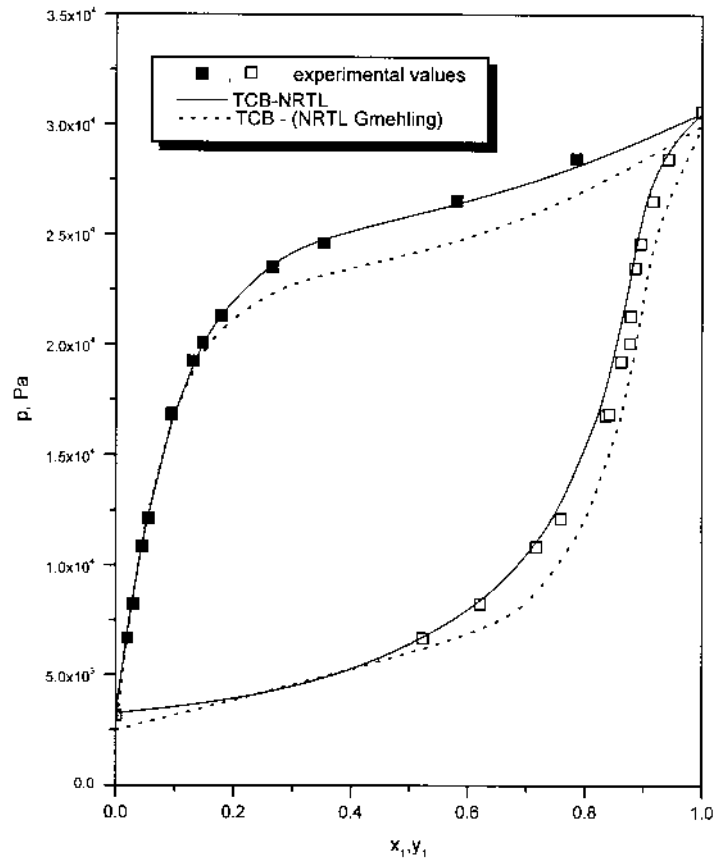


Fig. 5. VLE Correlation and prediction of the system acetone(1)+water(2) at 298 K, with the TCB-NRTL model and the PRSV EOS. The solid lines denote the results using the TCB-NRTL model parameters:  $\ln \gamma_1^\infty = -0.127173 \cdot 10^4/RT$ ,  $\ln \gamma_2^\infty = 0.382969 \cdot 10^4/RT$ ,  $\ln \gamma_1^E = 0.240917$ . The dashed line denote the predicted results using the Gmehling *et al.*<sup>115</sup> NRTL parameters. The points are experimental data.<sup>115</sup>

consistent results of the predictions over wide ranges of pressure and temperature using only information on the infinite dilution activity coefficients.

Twu *et al.*<sup>106</sup> simplified the TCB zero pressure mixing rule. Namely, the authors treated the density dependent function  $C_{v0}$ , Eq. (43), as constant assuming that the zero pressure liquid volume of the vdW fluid ( $v_{0vdW}^*$ ) has the selected value  $v_{0vdW}^* = r$ . An optimum value of  $r = 1.18$  was recommended for the TCB( $r$ ) mixing rule. The authors showed that the MHV1 mixing rule is a special case of the TCB( $r$ ) mixing rule. Also, a connection between zero-pressure mixing rules and infinite-pressure mixing rules was established.

Very recently, Twu *et al.*<sup>107</sup> introduced a new CEOS/ $A^E$  mixing rule with no reference pressure.

The starting equation is

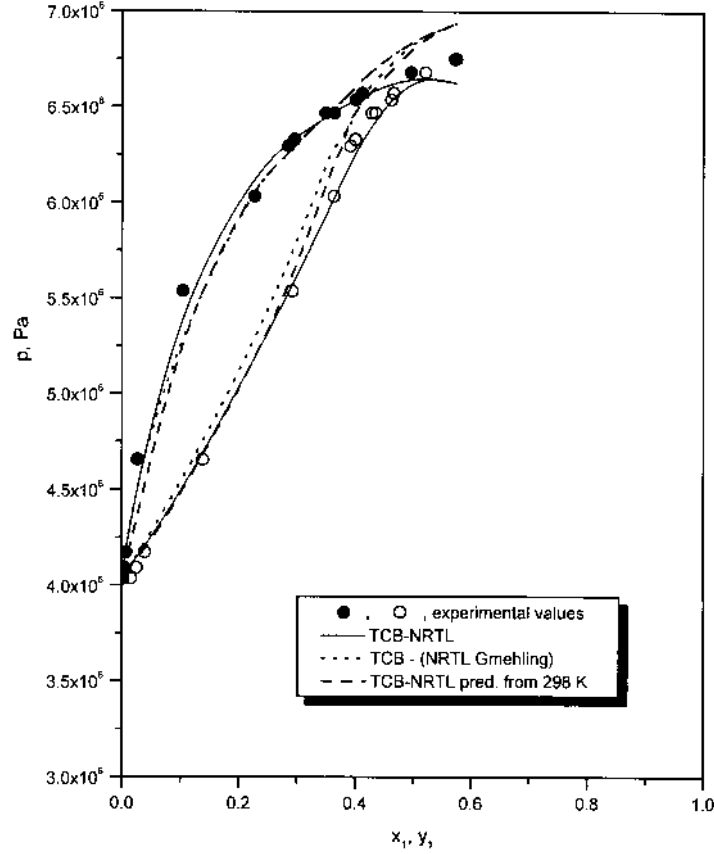


Fig. 6. VLE Correlation and prediction of the system acetone(1)+water(2) at 523 K, with the TCB-NRTL model and the PRSV EOS. The solid line denotes the results using the TCB-NRTL model parameters:  $\tau_{12} = 0.686435 \quad \tau_{21} = 0.546765 \quad 10^4/RT$ ,  $\tau_{12} = 0.262017$ . The dashed line denotes the prediction using the parameters from 298 K given in the legend of Fig. 5. The dotted line represents the prediction using the Gmehling *et al.*<sup>115</sup> NRTL parameters from 298 K. The points are experimental data.<sup>115</sup>

$$\frac{A^E}{RT} - \frac{A_{vdW}^E}{Rt} \ln \frac{v_{vdW}^*}{v^*} \frac{1}{1} - \frac{b_{vdW}}{b} \frac{1}{w} \frac{1}{u} \frac{a^*}{b^*} \ln \frac{v^*}{v^*} \frac{w}{u} - \frac{a_{vdW}^*}{b_{vdW}} \ln \frac{v_{vdW}^*}{v_{vdW}^*} \frac{w}{v_{vdW}^*} \quad (44)$$

By assuming  $v^*$  to be the same as  $v_{vdW}^*$ , they obtained a simplified form where  $a$  is based on no reference pressure

$$a^* = b^* \frac{a_{vdW}^*}{b_{vdW}^*} \frac{1}{C_{v0}} \frac{A^E}{RT} - \frac{A_{vdW}^E}{RT} \ln \frac{b_{vdW}}{b} \quad (45)$$



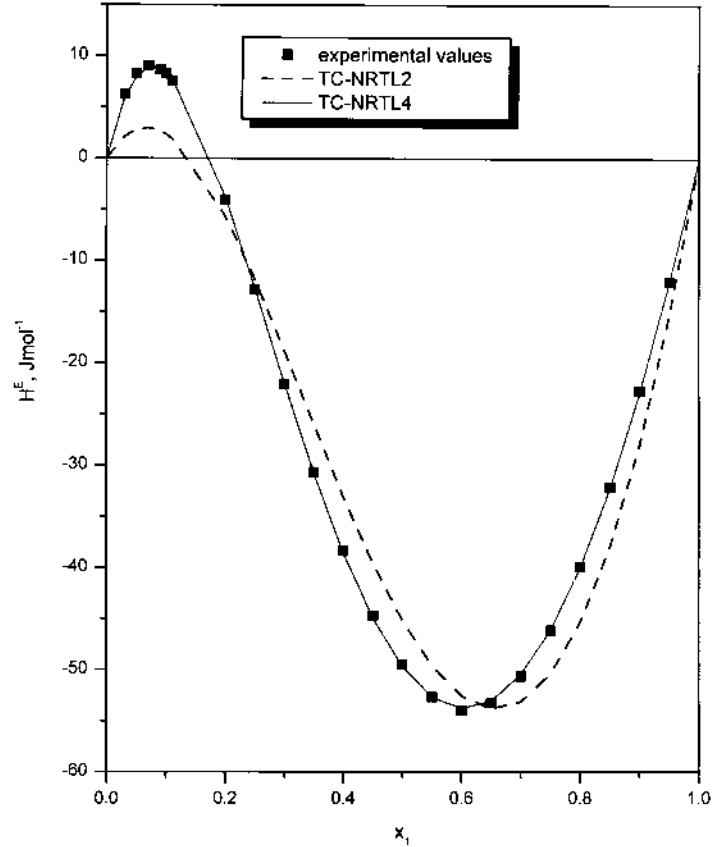


Fig. 7.  $H^E$  Correlation of the system 2-butanone(1)+benzene(2) at 298 K, with the TC-NRTL models and the PRSV EOS. The dashed line represents the results of the TC-NRTL2 model with the parameters:  $_{12} = (-0.137026 \cdot 10^4)/RT$ ,  $_{21} = (0.225378 \cdot 10^4)/RT$ ,  $_{12} = 0.3$ . The solid line reflects the results of the TC-NRTL4 model with the parameters:  $_{12} = (0.546444 \cdot 10^4 - 0.328042 \cdot 10^2 T)/RT$ ,  $_{21} = (-0.113204 \cdot 10^5 + 0.49719 \cdot 10^2 T)/RT$ ,  $_{12} = 0.3$ . The points are experimental data of Brown and Smith.<sup>116</sup>

where  $C_{v0}$  is given by Eq. (43) with  $v_0^* = v^*$ . Using the connection between  $A^E$  and  $G^E$

$$\frac{A^E}{RT} = \frac{A_{vdW}^E}{RT} - \frac{G^E}{RT} - \frac{G_{vdW}^E}{RT} \quad (46)$$

Eq. (45) becomes

$$a^* - b^* \frac{a_{vdW}^*}{b_{vdW}^*} = \frac{1}{C_{v0}} - \frac{G^E}{RT} - \frac{G_{vdW}^E}{RT} - \ln \frac{b_{vdW}}{b} \quad (47)$$

The  $b$  parameter was used both with and without the second virial coefficient constraint.

Now it is clear that any  $G^E$  model, such as the NRTL or the UNIFAC model, can be used for VLE, LLE, *etc.* calculations.

Orbey and Sandler<sup>16</sup> presented VLE correlations and predictions of the acetone(1) + water(2) system at various temperatures using the HV, WS, HVOS, MHV1, MHV2 and LCVM mixing rules combined with different activity coefficient models (van Laar, NRTL) and with PRSV EOS. To demonstrate the correlative and predictive capabilities of the TCB-NRTL model, we correlated VLE data of the same system at 298 K and 523 K. The TCB-NRTL model with no temperature dependent parameters was tested. As can be seen from Fig. 5, the obtained result at 298 K shows that the correlation is excellent and for this reason more complicated models with temperature dependent parameters are not needed. This Figure, also, includes the results of the TCB model using the NRTL parameters obtained at the same temperature from the DECHEMA Chemistry Data Series. In this case the prediction is good but slightly less accurate than those obtained by the TCB-NRTL model. The aforementioned results calculated by the TCB-NRTL model are comparable to those suggested by Orbey and Sandler<sup>16</sup> which use the van Laar excess free energy model (the exception is the MHV1 model because the saturation pressure is underestimated).

For the 523 K isotherm of the same system, shown in Fig. 6, the results of TCB-NRTL model are comparable to those obtained by the following mixing rules<sup>16</sup>: WS, HVOS, MHV1, MHV2 and LCVM combined with the van Laar excess free-energy model and the PRSV EOS. The predictions of VLE behavior at 523 K with the parameters generated from 298 K in both the TCB-NRTL models (NRTL parameters fitted to experimental data and with the NRTL parameters reported in the DECHEMA tables for 298 K) are comparable to those obtained using the HVOS, WS and LCVM mixing rules and they are superior to those obtained with the MHV1 and MHV2 models.

The  $H^E$  data of the system 2-butanone (1)+benzene (2) at 298.15 K with negative asymmetric curve and a small positive part for the infinite dilution of component (1) (Fig. 7) are described by the TC-NRTL2 and TC-NRTL4 models. The correlation performed using the TC-NRTL4 model is quite accurate throughout the whole concentration range. On the contrary, the TC-NRTL2 model gave very poor results. The shape of curve for this model is dislocated with respect to the experimental points for most of the concentration range.\*

#### 9. VLE CALCULATION IN POLYMER SOLUTIONS USING EOS/ $G^E$ MODELS

The EOS/ $G^E$  models could be very convenient and useful for the calculation of the VLE of polymer solutions.

Recently the EOS/ $G^E$  models have been applied to the VLE of polymer solutions.<sup>57,66,108–110</sup> Orbey and Sandler<sup>108</sup> used the PRSV-WS model with the Flory-Huggins equation as the  $G^E$  model to correlate the VLE of various polymer+solvent systems. By setting  $A^E$  to zero, Zhong and Masuoka<sup>109</sup> proposed a simplified form of the WS mixing rule. As of recent, only one binary interaction parameter ( $k_{ij}$ ) is needed. The results obtained for 10 polymer solutions show that the simplified mixing

\* Good binary  $V^E$  correlations were obtained with all Twu *et al.* models.<sup>117</sup>

rule is suitable and comparable with others such as WS-FH and KHFT for the VLE correlation of these solutions. The same authors<sup>57</sup> predicted Henry's constant of liquids and gases in polymer systems using the SRK-MHV1 model coupled with a new modified UNIFAC equation. For most polymers, this model gave good predictions, which were better than both the original UNIFAC and the UNIFAC-FV models.

Tochigi *et al.*<sup>110</sup> extended the applicability of the PR ASOG-FV group contribution method to predicting the solvent activities in polymer solutions. The accuracy of the PR ASOG-FV model compared with the ASOG-FV and UNIFAC-FV models is very satisfactory.

Louli and Tassios<sup>66</sup> applied the PREOS to the modeling of VLE of polymer-solvent systems. Correlation of VLE data is performed by using these mixing rules including the ZM and MHV1-FH ones. Very satisfactory results are obtained with the ZM mixing rule, especially since no phase split is detected with it. Extrapolation with respect to temperature and polymer molecular weight is very good, especially when the ZM mixing rule is employed.

Finally, we would like to emphasize that only at infinite pressure is the CEOS/ $G^E$  approach algebraically rigorous and well defined at all temperatures, and that all the zero pressure mixing rules require *ad hoc* approximations at same conditions as indicated by Orbey and Sandler.<sup>52</sup>

## 10. SUMMARY

The thermodynamic representation of highly non-ideal mixtures containing non-polar and polar compounds that are similar or very dissimilar in size and shape, over large ranges of temperature and pressure, has traditionally been a difficult task.

The CEOS/ $G^E$  or CEOS/ $A^E$  models coupled with various EOS and  $G^E$  activity models enable reasonably good correlations and predictions of VLE for these types of systems.

Usually the parameters of these models are slightly temperature dependent, but satisfactory predictions can be obtained when they are assumed to be temperature independent. In these cases, the already published  $G^E$  model parameters can be taken, for example, from DECHEMA Data Series. If VLE data are available for a very broad temperature interval, fitting the data at all temperatures should provide a single set of parameters for use over the entire temperature range. But, if no experimental data are available, the CEOS/ $G^E$  models are still capable of providing high quality predictions based on group contribution methods (for example the PSRK). In addition, it has been shown by many authors that VLE can be adequately described with a limited number of interaction parameters.

CEOS/ $G^E$  models with temperature independent parameters are useful for correlations and predictions of LLE of non-associating and self-associating mixtures. But, for cross-associating mixtures that exhibit a closed solubility loop, temperature-dependent parameters are needed to reproduce accurately the complex LLE behaviour of such systems.

Excess properties of liquid mixtures, such as excess enthalpy and excess heat capacity, can be correlated very successfully using the temperature dependent CEOS/ $G^E$  models. The functional form of the temperature dependence of the parameters and a number of adjustable coefficients in the multi-parameter CEOS/ $G^E$  models are very important for the simultaneous fitting of two or more thermodynamic properties (VLE+ $H^E$ , VLE+ $c_p^E$ ,  $H^E + c_p^E$ , VLE+ $H^E+c_p^E$ , *etc.*).

The successful use of the CEOS/ $G^E$  models presented above for a number of complex systems highly recommends them for further development and application. Orbey and Sandler<sup>16</sup> suggest the following systematic investigation of the CEOS/ $G^E$  models: (i) thermodynamic modeling of mixture behavior at high dilution, (ii) simultaneous correlation and prediction of VLE and other mixture properties such as enthalpy, entropy, heat capacity, *etc.*, (iii) polymer-solvent and polymer-supercritical fluid VLE and LLE, (iv) simultaneous representation of chemical reaction and phase equilibrium and the evaluation of phase envelopes of reactive mixtures, (v) correlation of phase equilibrium for mixtures that form microstructures micellar solutions, (vi) LLE and VLLE for non-electrolyte mixtures.

#### LIST OF SYMBOLS

$A^E$  – molar excess Helmholtz free energy

$a, b$  – equation of state parameters

$B$  – second virial coefficient

$c_p^E$  – excess heat capacity

$G^E$  – molar excess Gibbs energy

$H^E$  – molar excess enthalpy

$p$  – pressure

$R$  – gas constant

$T$  – absolute temperature

$v$  – molar volume

$V^E$  – molar excess volume

$x$  – molar fraction

$z$  – compressibility factor

*Greek letters*

– fugacity coefficient

*Subscripts*

$j, i, ij$  – components

0 – condition for the reference pressure  $p = 0$

– condition for the reference pressure  $p =$

– activity coefficient model

vdW – van der Waals fluid

## ИЗВОД

## ПРАВИЛА МЕШАЊА ЗА МОДЕЛЕ ДОПУНСКЕ СЛОБОДНЕ ЕНЕРГИЈЕ

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Термодинамичко приказивање јако неидеалних смеша са неполарним и поларним компонентама које су сличне или различите по величини и облику у широком опсегу температуре и притиска је традиционално тежак задатак. CEOS/ $G^E$  или CEOS/ $A^E$  модели са различитим једначинама стања (EOS) и моделима за коефицијенте активности ( $G^E$  модели) омогућавају задовољавајуће корелисање и предсказивање равнотеже пара-течност (VLE) за овакве типове система. Код оваквих модела параметри су обично незнатно зависни од температуре, међутим задовољавајућа предсказивања претпостављају да су параметри температурно независни. У таквим случајевима могуће је користити већ публиковане параметре  $G^E$  модела у базама података као што је DECHEMA Data Series. Уколико су VLE подаци на располагању за широк интервал температуре, фитовањем података за све температуре обезбеђује се јединствен сет параметара који се користе у ширем опсегу температуре. Међутим, ако не постоје експериментални подаци CEOS/ $G^E$  модели још увек обезбеђују квалитетно предсказивање на бази примене метода доприноса група (нпр. PSRK). Такође је показано од многих аутора да VLE може бити адекватно описано са ограниченим бројем интеракционих параметара. CEOS/ $G^E$  модели са температурно независним параметрима су корисни за корелисање и предсказивање равнотеже течност-течност неасосованих и само-асосованих смеша. Међутим, код смеша са унакрсном асоцијацијом које показују затворену немешљивост температурно зависни параметри су потребни да би се тако репродуковало комплексно LLE понашање таквих система. Допунске особине течних смеша као што су допунске енталпије и допунски топлотни капацитети се успешно могу корелисати са температурно зависним CEOS/ $G^E$  моделима. Функционални облик температурне зависности параметара и број оптимизованих коефицијената код вишепараметарских CEOS/ $G^E$  модела је врло важан за симултано фитовање две или више термодинамичких особина (VLE+ $H^E$ , VLE+ $c_p^E$ ,  $H^E+c_p^E$ , VLE+ $H^E+c_p^E$ , итд.). Успешно коришћење CEOS/ $G^E$  модела приказано у раду за бројне сложене системе високо их препоручује за даљи развој и примену. Orbey и Sandler<sup>16</sup> предлажу следеће систематско истрживање CEOS/ $G^E$  модела: (1) термодинамичко моделовање понашања смеша разблажених раствора, (2) симултано корелисање и предсказивање VLE и других особина смеша као што су енталпије, ентропије, топлотни капацитети и др., (3) VLE и LLE за полимер-растварач и полимер-надкритични флуид (4) симултано презентовање хемијске реакције и равнотеже фаза и одређивање фазне енвелопе реактивних смеша, (5) корелисање фазне равнотеже за смеше које формирају микроструктурне разноврсне растворе, (6) LLE и VLLE за не-електролитне смеше.

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