# Excess Gibbs Energy of Binary Liquid Mixtures and the Wong–Sandler Postulates

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Wong and Sandler (1992) postulated that (1) the excess Helmholtz free energy of mixing is pressure independent and consequently that (2) the excess Gibbs free energy expression of an activity coefficient model can be equated with the excess Helmholtz free energy of an equation of state (EOS) evaluated at infinite pressure

$$A^E_{EOS}(T, P \rightarrow \infty, x_i) \approx A^E_{EOS}(T, P \rightarrow 0, x_i) \approx G^E(T, P \approx 0, x_i) = G^E_\gamma(T, x_i) \quad (1)$$

In this communication these conjectures are applied to the generalized van der Waals cubic EOS. It is shown that, for binary mixtures, they predict composition dependence for the excess free energy ($G^E_\gamma$) shared with several other empirical and local composition models.

Huron and Vidal (1979) proposed the following generalized form for the van der Waals cubic equation of state with $\lambda_1$ and $\lambda_2$ as numerical constants

$$P = \frac{RT}{(v - b)} - \frac{a}{(v + \lambda_1 b)(v + \lambda_2 b)} \quad (2)$$

For pure components the attraction parameter $a = a(T)$ and the covolume $b$ can be obtained from critical properties and vapor pressure data. For mixtures of nonpolar compounds the van der Waals mixing rules are used to describe the composition dependence of the parameters $a_{mix}$ and $b_{mix}$ (Hicks and Young, 1975; Vidal, 1977; Walas, 1985)

$$a_{mix} = \sum_i \sum_j a_{ij} x_i x_j \quad \text{and} \quad b_{mix} = \sum_i \sum_j b_{ij} x_i x_j \quad (3a,b)$$

where $a_{ii}$ and $b_{ii}$ are pure component EOS parameter values. The mixing rules also contain cross terms $a_{ij}$ and $b_{ij}$ that must be evaluated from experimental data or by postulating appropriate combining rules. Geometric combining rules $a_{12} = (1 - k_{12})\sqrt{a_{11}a_{22}}$ and $b_{12} = (1 - \xi_{12})\sqrt{b_{11}b_{22}}$ have been proposed (Good and Hope, 1970). However, it is more common to use the arithmetic mean for the covolume: $b_{12} = (1 - \ell_{12})(b_{11} + b_{22})/2$ (Walas, 1985). The binary interaction constants $k_{12}$, $\xi_{12}$, or $\ell_{12}$ are introduced to correct for slight deviations from these rules.

The "infinite pressure" state corresponds to a situation where there is no free volume. Thus as $P \rightarrow \infty$, $v \rightarrow b$ and $v_{ii} \rightarrow b_{ii}$ (that is, the molar volume of the mixture and the molar volumes of the pure components, respectively equal the covolume parameters $b$ and $b_{ii}$ (Vidal, 1977; Wong and Sandler, 1992)). Under these conditions the excess Helmholtz energy at infinite pressure reduces to (Huron and Vidal, 1979; Vidal, 1977)

$$A^E_{EOS,\infty} = \Lambda\left(\sum_i \frac{a_{ii}}{b_{ii}} x_i - \frac{a_{mix}}{b_{mix}}\right) \approx G^E_\gamma \quad (4)$$

where $\Lambda$ is a characteristic constant of the cubic equation of state that is used (Huron and Vidal, 1979). For $\lambda_1 = \lambda_2$, $\Lambda = 1/(1 + \lambda_1)$, whereas $\Lambda = \ln[(1 + \lambda_1)/(1 + \lambda_2)]/(\lambda_1 - \lambda_2)$ when $\lambda_1 \neq \lambda_2$.

It is convenient to define dimensionless cohesive energy parameters by scaling with respect to the molar thermal energy $RT$ and the covolume parameters as follows

$$w_{ij} \equiv \frac{\Lambda a_{ij}}{RT\sqrt{b_{ii}b_{jj}}} \quad (5)$$

Substituting the van der Waals mixing rules defined by Eq. 3 into Eq. 4 and using Eq. 5, after tedious but straightforward algebra, yields

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**Table 1. Empirical Activity Coefficient Models as Special Forms of the van der Waals Infinite Pressure Form**

| Covolume Combining Rule | Energy Parameter Combining Rule | Model | $G^E_\gamma/(x_1x_2RT)$ | Consequence |
|---|---|---|---|---|
| $b_{12} = b_{11} = b_{22}$<br>$\Rightarrow b = b_{ij} = b_{ii}$ | — | Porter | $A$ | $A = w_{11} + w_{22} - 2w_{12}$ |
|  | — | Van Laar (a) | $\dfrac{A_{12}A_{21}}{A_{21}x_1 + A_{12}x_2}$ | $A_{ij} = w_{ii}\dfrac{b_{jj}}{b_{ii}} + w_{jj} - 2w_{ij}\sqrt{\dfrac{b_{jj}}{b_{ii}}}$ |
| $b_{12} = \dfrac{b_{11} + b_{22}}{2}$<br>$\Rightarrow b = b_{11}x_1 + b_{22}x_2$ | $w_{12} = \dfrac{w_{11} + w_{22}}{2}$ | Van Laar (b) | $\dfrac{A_{12}A_{21}}{A_{21}x_1 + A_{12}x_2}$ | $A_{ij} = w_{ii}\left(\dfrac{b_{jj}}{b_{ii}} - \sqrt{\dfrac{b_{jj}}{b_{ii}}}\right) + w_{jj}\left(1 - \sqrt{\dfrac{b_{jj}}{b_{ii}}}\right)$ |
|  | $w_{12} = \sqrt{w_{11}w_{22}}$ | Scatchard–Hildebrandt | $\dfrac{b_{11}b_{22}A}{b_{11}x_1 + b_{22}x_2}$ | $A = \left(\sqrt{\dfrac{w_{11}}{b_{11}}} - \sqrt{\dfrac{w_{22}}{b_{22}}}\right)^2$ |
|  | — | Scatchard–Hamer*<br>$q_1 = \sqrt{b_{11}}$ &<br>$q_2 = \sqrt{b_{22}}$ | $\dfrac{q_1^2A_{12}x_1 + q_2^2A_{21}x_2}{(q_1x_1 + q_2x_2)^2}$ | $A_{ij} = w_{ii}\left(2\sqrt{\dfrac{b_{jj}}{b_{ii}}} - 1\right) + w_{jj} - 2w_{ij}\sqrt{\dfrac{b_{jj}}{b_{ii}}}$ |
| $b_{12} = \sqrt{b_{11}b_{22}}$<br>$\Rightarrow b = (\sqrt{b_{11}}\,x_1 + \sqrt{b_{22}}\,x_2)^2$ | $w_{11} = w_{22}$ | SSF (two-parameter)<br>$p = \left(\dfrac{b_{22}}{b_{11}}\right)^{1/4}$ | $\dfrac{A}{\left(\dfrac{x_1}{p} + px_2\right)^2}$ | $A = w_{11} + w_{22} - 2w_{12} = 2(w_{11} - w_{12}) = 2(w_{22} - w_{12})$ |
|  | $w_{12} = \dfrac{w_{11} + w_{22}}{2}$ | Van Laar (c) | $\dfrac{A_{12}A_{21}}{A_{21}x_1 + A_{12}x_2}$ | $A_{ij} = (w_{ii} - w_{jj})\left(\sqrt{\dfrac{b_{jj}}{b_{ii}}} - 1\right)$ |

*Note that Scatchard and Hamer actually assumed that $q_i = b_{ii}$ (Scatchard and Hamer, 1935).

$$\frac{G^E_\gamma}{x_1x_2RT} = \frac{x_1b_{11}A_{12} + x_2b_{22}A_{21}}{b_{11}x_1^2 + 2b_{12}x_1x_2 + b_{22}x_2^2} \tag{6}$$

with

$$A_{ij} = w_{ii}\left(2\frac{b_{ij}}{b_{ii}} - 1\right) + w_{jj} - 2w_{ij}\sqrt{\frac{b_{jj}}{b_{ii}}} = \ln\gamma_j^\infty \tag{7}$$

Equation 6 gives the general van der Waals composition dependence for the excess Gibbs free energy of a binary mixture. Note that it embodies a new activity coefficient model if the parameters $b_{12}$, $A_{12}$, and $A_{21}$ are regarded as adjustable empirical parameters. Several "classic" and local composition models show exactly the same composition dependence. In fact the empirical and "random mixture" models of Porter (1921), Van Laar, Scatchard–Hildebrand (Scatchard, 1931), two-parameter SSF (Rogalski and Malanowski, 1977), and Scatchard and Hamer (1935) can all be obtained from Eqs. 6 and 7 by applying appropriate combining rules for the energy and covolume cross parameters. See Table 1 for details.

The "random mixture" models may have utility for nonpolar mixtures but are deemed inadequate for mixtures that contain polar and associating components (Raal and Mühlbauer, 1998; Walas, 1985). For such systems local composition activity coefficient models give more satisfactory performance [such as the nonrandom two-liquid (NRTL) model (Renon and Prausnitz, 1968)]

$$\frac{G^E}{x_1x_2RT} = \frac{x_1(\tau_{21}G_{12}G_{21} + \tau_{12}G_{12}) + x_2(\tau_{12}G_{12}G_{21} + \tau_{21}G_{21})}{G_{12}x_1^2 + (G_{12}G_{21} + 1)x_1x_2 + G_{21}x_2^2} \tag{8}$$

Note that the binary NRTL and Eq. 6 share a common functional form for the composition dependence. This suggests that NRTL might be obtained by appropriate transformation of the EOS parameters, such as the covolume parameters. Suppose a good fit of the excess Gibbs free energy of the liquid mixture is obtained by using revised covolume parameters $b^*_{ij}$ in the activity model, that is,

$$\frac{G^E_\gamma}{x_1x_2RT} = \frac{x_1b^*_{11}A_{12} + x_2b^*_{22}A_{21}}{b^*_{11}x_1^2 + 2b^*_{12}x_1x_2 + b^*_{22}x_2^2} \tag{9}$$

with

$$A_{ij} = w_{jj} + w_{ii}\left(2\frac{b^*_{ij}}{b^*_{ii}} - 1\right) - 2w_{ij}\sqrt{\frac{b^*_{jj}}{b^*_{ii}}} \tag{10}$$

Suppose further that the following hold:

(1) The liquid mixture covolume parameters are obtained by "translating" the EOS parameters according to

$$b^*_{11} = b_{11}e^{-\alpha\tau_{12}} \qquad \text{and} \qquad b^*_{22} = b_{22}e^{-\alpha\tau_{21}} \tag{11}$$

(2) The covolume cross-parameter is given by a geometric combining rule, as follows

$$b^*_{12} = \sqrt{b^*_{11}b^*_{22}}\cosh\left[\frac{\alpha}{2}(\tau_{12} + \tau_{21})\right] \tag{12}$$

(3) The local composition factors $G_{ij}$ are redefined as

**Table 2. Linking the Modified Local Composition Activity Coefficient Models with the van der Waals Infinite Pressure Form**

| Model | $G^E_\gamma/(x_1x_2RT)$ or $A^E_\infty/(x_1x_2RT)$ | Implicit Relationship for $\tau_{ij}$ |
|---|---|---|
| NRTL | $\dfrac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \dfrac{\tau_{12}G_{12}}{x_1G_{12} + x_2}$ | $\tau_{ij} = \left[\dfrac{G_{ij} - 1}{G_{ij}(G_{ij}G_{ji} - 1)}\right](w_{ii} + G_{ij}G_{ji}w_{jj} - 2\sqrt{G_{ij}G_{ji}}\, w_{ij})$ |
| Morisue | $\dfrac{\tau_{21}}{x_1 + x_2G_{21}} + \dfrac{\tau_{12}}{x_1G_{12} + x_2}$ | $\tau_{ij} = \left(\dfrac{G_{ij} - 1}{G_{ij}G_{ji} - 1}\right)(w_{ii} + G_{ij}G_{ji}w_{jj} - 2\sqrt{G_{ij}G_{ji}}\, w_{ij})$ |
| Bruin* | $\dfrac{\tau_{12} + \tau_{21}}{(x_1G_{12} + x_2)(x_1 + x_2G_{21})}$ | $\tau_{12} + \tau_{21} = w_{11}(1 + G_{12}G_{21}) - 2\sqrt{G_{12}G_{21}}\, w_{12}$ |

*Note: Bruin model assumes $w_{11} = w_{22}$.

$$G_{ij} = \sqrt{\frac{b_{ii}}{b_{jj}}}\, e^{-\alpha\tau_{ij}} \tag{13}$$

Substituting Eqs. 11 and 12 into Eqs. 9 and 10 yields the NRTL form, Eq. 8, with

$$\tau_{ij} = \left[\frac{G_{ij} - 1}{G_{ij}(G_{ij}G_{ji} - 1)}\right](w_{ii} + G_{ij}G_{ji}w_{jj} - 2\sqrt{G_{ij}G_{ji}}\, w_{ij}) \tag{14}$$

A similar approach can be used for the local composition models proposed by Morisue (Morisue et al., 1972) and Bruin (1970). See Table 2 for details.

Thus the NRTL, Morisue, and Bruin local composition models may be interpreted in terms of a transformation of the EOS parameters to new values that are more suitable for describing the liquid phase excess free energy. However, matching the corresponding excess Gibbs free energy models with the van der Waals form, Eq. 6, suggests

- Modified definitions for the local composition factors $G_{ij}$, and
- Geometric mean combining rule for the covolume parameter $b_{12}$.

Huron and Vidal (1979) proposed an alternative modification of the classical NRTL model. They redefined local compositions as corrected volume fractions. In the present notation this is expressed by

$$G_{ij} = \frac{b_{ii}}{b_{jj}}\, e^{-\alpha\tau_{ij}} \tag{15}$$

Orbey and Sandler (1995) showed that, with this definition, NRTL reduces to the Scatchard–Hildebrandt when $\alpha = 0$.

These various NRTL versions all share the common form for the composition dependence defined by Eq. 6. The differences in the definition of the coefficients should affect the competence of these activity coefficient models to represent real data. Therefore their ability to correlate low-pressure isothermal vapor–liquid equilibrium data was tested. The selected data sets all complied with the DECHEMA thermodynamic consistency tests (Gmehling et al., 1977–1996) and constituted 12 binary systems, 56 isothermal VLE data sets, and a total of 771 *P*–*x*–*y* data points. Badenhorst et al. (2003) provide details of the data reduction procedures. The adjustable constants were determined for each isothermal data set by minimizing the average absolute error in either the vapor phase composition or the system pressure.

Figures 1 and 2 summarize the data correlation results. They suggests comparable model performance, although, on the whole, Huron and Vidal's NRTL version fared slightly worse. NRTL and van der Waals gave the best overall performance with respect to the vapor composition and total pressure, respectively.

The normalized excess Gibbs energy, $g = G^E/(x_1x_2RT)$, for the acetone–chloroform system is plotted in Figure 3. The van der Waals model fits reasonably well, following the same trend as the experimental data. However, the NRTL model predicts curvature opposite to that of the experimental data. This curious flaw in the behavior of NRTL for systems with negative deviations from Raoult's law, such as acetone–chloroform, can be explained as follows.

For nearly every binary liquid mixture the $G^E/(x_1x_2RT)$ curve is concave up as illustrated by the behavior of the acetone-chloroform system in Figure 2. Concave up means that the first derivative of the function $g$ increases with the variable $x_1$. This implies that the second derivative with respect to $x_1$ must be positive. For NRTL models, it is given by

$$\frac{d^2}{dx_1^2}\left(\frac{G^E}{x_1x_2RT}\right) = \frac{2\tau_{21}G_{21}(G_{21} - 1)^2}{(x_1 + x_2G_{21})^3} + \frac{2\tau_{12}G_{12}(G_{12} - 1)^2}{(x_1G_{12} + x_2)^3} \tag{16}$$

The $G_{ij}$ values are always positive definite because they are exponentials. Inspection of Eq. 16 reveals that

- If $\tau_{12}$, $\tau_{21} > 0$, then $d^2g/dx_1^2 > 0$ and $g$ is concave up.
- When $\tau_{12}$, $\tau_{21} < 0$, however, then $d^2g/dx_1^2 < 0$ and $g$ is concave down.

With the NRTL models the infinite dilution activity coefficients are defined by

$$\ln \gamma_1^\infty = \tau_{12}G_{12} + \tau_{21} \quad \text{and} \quad \ln \gamma_2^\infty = \tau_{21}G_{21} + \tau_{12} \tag{17}$$

The infinite dilution activity coefficients assume values that are less than unity when the system shows negative deviations from Raoult's law. This implies that $\ln \gamma_i^\infty < 0$. From Eq. 17 it then follows that both $\tau_{12}$ and $\tau_{21}$ may be negative. As indicated above, NRTL will in that case predict a concave-down curve for the normalized Gibbs energy. Fitting NRTL models to such data may nevertheless provide reasonable correlation of

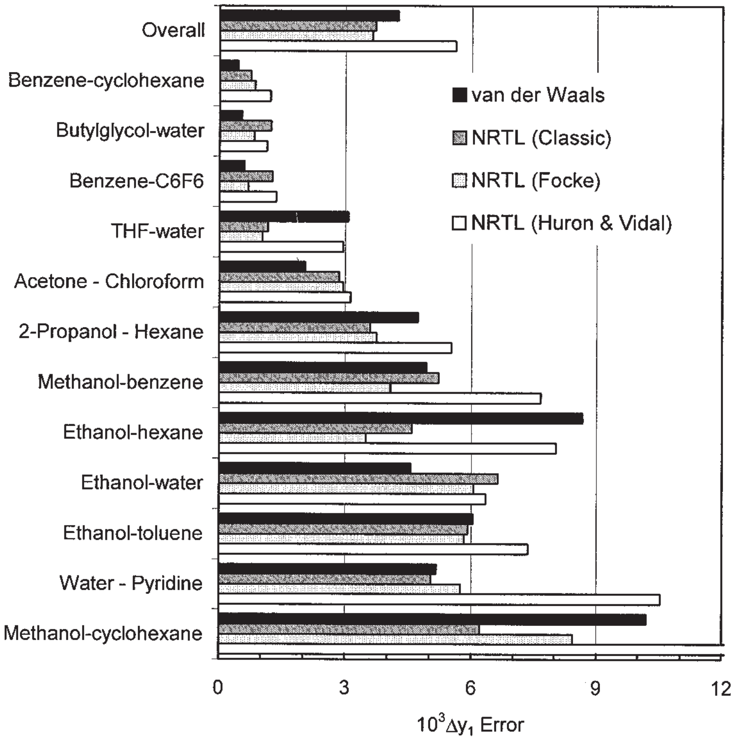

**Figure 1. Mean vapor composition errors averaged over all isothermal data sets per system.**

The adjustable model constants were determined for each isothermal data set by minimizing the average absolute error in the vapor phase composition.

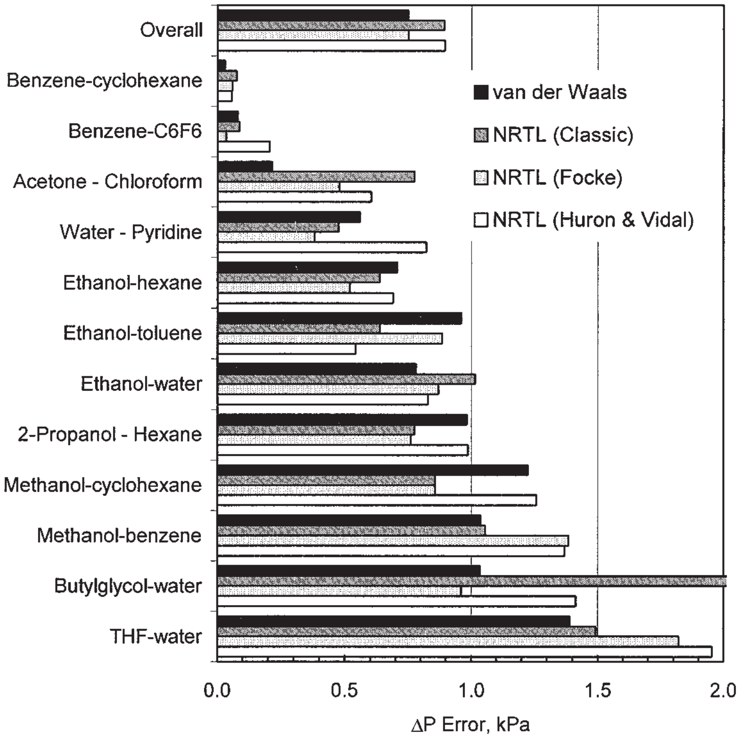

**Figure 2. Mean system pressure errors averaged over all isothermal data sets per system.**

The adjustable model constants were determined for each isothermal data set by minimizing the average absolute error in the vapor phase composition.

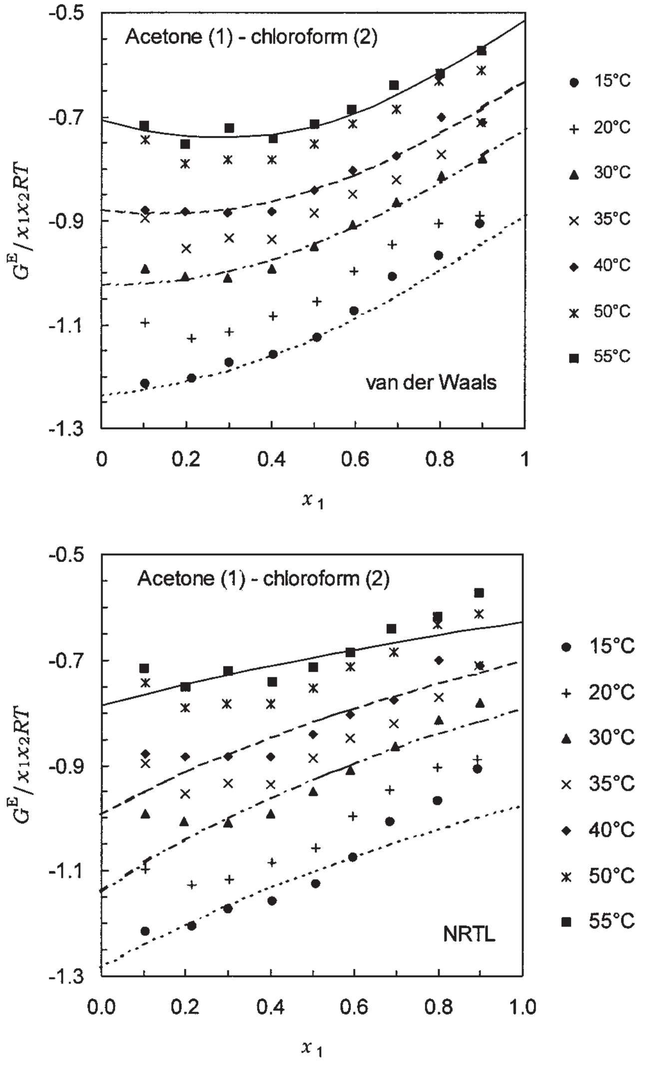

**Figure 3. Normalized excess Gibbs energy function for the acetone–chloroform system.**

Points show experimental data values. The lines for 15, 30, 40, and 55°C show predicted values obtained when the error in the system pressure was minimized.

data for midrange compositions. However, the predicted infinite dilution activity coefficients will certainly be incorrect. Care should therefore be taken with NRTL models when properties in the dilute regions are important.

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## Notation

$a$ = cubic EOS attraction parameter, J m$^3$ m$^{-2}$ mol$^{-2}$
$A_{ij}$ = constant, Eqs. 6 and 7, —
$A$ = constants in activity coefficient models, —
$A^E$ = excess Helmholtz free energy, J/mol
$b$ = cubic EOS covolume parameter, m$^3$/mol
$g$ = normalized excess Gibbs energy [$G^E/(x_1x_2RT)$], —
$G^E$ = excess Gibbs free energy, J/mol
$G_{ij}$ = local composition factor, Eq. 8, —
$k_{12}$ = binary interaction parameter for $a_{12}$, —
$\ell_{12}$ = binary interaction parameter for $b_{12}$ (arithmetic mean combining rule), —
$p$ = constant in SSF model, —
$P$ = pressure, Pa
$q$ = constant in Scatchard–Hamer model
$R$ = gas constant ($R$ = 8.3143214), J mol$^{-1}$ K$^{-1}$
$T$ = absolute temperature, K
$v$ = molar volume, m$^3$/mol
$w$ = dimensionless energy parameter, Eq. 5, —
$x$ = liquid mole fraction

### Greek letters

$\alpha$ = adjustable parameter in local composition factor, —
$\xi_{12}$ = binary interaction parameter for $b_{12}$ (geometric mean combining rule), —
$\gamma$ = activity coefficient, —
$\lambda$ = numerical constants, Eq. 2, —
$\Lambda$ = constant, Eq. 4, —
$\tau$ = dimensionless local composition interaction energy parameter, —

### Subscripts

$i, j$ = component indices
$EOS$ = pertaining to the cubic equation of state
$mix$ = mixture
$\gamma$ = pertaining to an activity coefficient model
1, 2 = components
$\infty$ = infinite pressure

### Superscripts

$E$ = excess
$\infty$ = infinite dilution
$*$ = revised for liquid phase

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