

## CORRELATIONS

# Correlation of Vapor–Liquid Equilibrium Data for Methyl Acetate–Methanol–Water–Acetic Acid Mixtures

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A new correlation for the prediction of the vapor–liquid equilibrium of methyl acetate–methanol–water–acetate acid mixtures has been developed. It is based on the NRTL model for predicting liquid activity coefficients and Marek's method (Marek and Standart, 1954; Marek, 1955) for predicting the vapor–liquid equilibrium of the system containing association components. When compared with the experimental data by Sawistowski and Pilavakis (1982), the new correlation has fewer parameters, is easier to be incorporated into computer simulation programs and shows a better agreement than the third-order Margules equation suggested by these authors.

## Introduction

Catalytic distillation for acetic acid esterification catalyzed by Amberlyst 15 is an attractive process for manufacturing of methyl acetate or removing dilute acetic acid from water. Accurate prediction of the vapor–liquid equilibrium of the system is vital to the simulation and design of the process.

To correlate the vapor–liquid equilibrium in mixtures containing an associating substance like acetic acid, Marek's method (Marek and Standart, 1954; Marek, 1955) in combination with liquid activity coefficient models is usually used.

At present, there are more than six different types of correlations for the prediction of activity coefficients in chemical systems. Since the superiority of one method over the others is not always obvious, practice must rely on experience and analogy. The most comprehensive comparison of five of the methods (van Laar, Margules, Wilson, NRTL, and UNIQUAC) was made in the DECHEMA Vapor Liquid Equilibrium Data Collection (Gmehling et al., 1977a,b, 1982, 1988). From this statistical analysis, the Wilson equation was found to be the best, and the van Laar and UNIQUAC methods tied for last. However, there are also marked differences for a given class of substances. For example, the NRTL was found to be the best model for aqueous systems (Walas, 1985).

Sawistowski and Pilavakis (1982) experimentally studied the vapor–liquid equilibrium behavior of the quaternary system, methyl acetate–methanol–water–acetic acid.

To correlate their experimental data, they tried third-order Margules (Marek, 1954), Wilson, and NRTL models for liquid activity coefficients and concluded that the Wilson and NRTL models could not correlate the quaternary system as well as the third-order Margules equation. Therefore, they finally chose the third-order Margules equation.

Suzuki et al. (1970) tried to formulate relations between the liquid and vapor compositions of the same quaternary system. They failed to obtain good correlation results with the Margules equation modified by Marek (1954). Sawistowski and Pilavakis (1982) explained that the failure may be due to the fact that they used only quaternary experimental data to fit their constants. Suzuki et al. (1970) then rearranged the Margules equation, which contains 64 constants for the quaternary system. They claimed that the calculated values were in good agreement with experimental data in practical use. However, Sawistowski and Pilavakis (1982) later tested their equation with binary, ternary, and quaternary vapor and liquid equilibrium data, and the results were found to be unsatisfactory.

Compared with the Margules equation, the Wilson and NRTL models have two major advantages: (1) only binary parameters are required for the multicomponent system; (2) they can predict the effect of temperature, which is especially useful for distillation. Therefore, the Wilson and NRTL models are preferred for most chemical systems.

In fact, Sawistowski and Pilavakis' work was conducted before 1974 (Pilavakis, 1974). With more reliable vapor–liquid equilibrium data available now, we were able to review their conclusion by correlating the quaternary experimental data using new Wilson and NRTL model parameters (Gmehling et al., 1977a,b, 1982, 1988).

In this study, both the Wilson and NRTL models were used in combination with Marek's method (Marek and Standart, 1954; Marek, 1955) for predicting the vapor–liquid equilibrium of the quaternary system containing the associating component acetic acid. The calculated results are then compared with the third-order Margules equation suggested by Sawistowski and Pilavakis' (1982).

## Vapor–Liquid Equilibria in Mixtures Containing Acetic Acid

For a mixture that contains an associating component (e.g., acetic acid), a model was developed by Marek and

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**Table 1. Binary Model Parameters ( $P = 760$  mmHg)**

system (1-2)	$\Delta\lambda_{12}$	$\Delta\lambda_{21}$	$\Delta g_{12}$	$\Delta g_{21}$	$\alpha_{12}$	refs
methyl acetate-methanol	-125.69	891.14	566.15	456.94	1.0293	Gmehling and Onken (1977a,b)
methyl acetate-water	887.37	1966.71	879.14	1709.49	0.3830	Gmehling and Onken (1977a,b)
methyl acetate-acetic acid	-696.50	1123.14	1218.87	-635.89	0.3600	Gmehling et al. (1982)
methanol-water	216.85	468.60	-245.90	921.33	0.2989	Gmehling and Onken (1977a,b)
methanol-acetic acid	1.7144	2.1503	-39.582	0.5767	0.3055	Gmehling et al. (1988)
water-acetic acid	870.21	-65.80	981.10	-187.72	0.2960	Gmehling and Onken (1977a,b)

Standart (1954) and Marek (1955) to correlate the vapor-liquid equilibrium data. For the associating component A,

$$P y_A Z_A = p_{AC} x_A \gamma_A \quad (1)$$

where

$$Z_A = \frac{[1 + 4KPy_A(2 - y_A)]^{1/2} - 1}{2KPy_A(2 - y_A)} \quad (2)$$

$$p_{AC} = \frac{\sqrt{1 + 4k_A p_A^s} - 1}{2k_A} \quad (3)$$

For the nonassociating component B,

$$P y_B Z_B = p_B^s x_B \gamma_B \quad (4)$$

where

$$Z_B = \frac{2(1 - y_A + \sqrt{1 + 4KPy_A(2 - y_A)})}{(2 - y_A)(1 + \sqrt{1 + 4KPy_A(2 - y_A)})} \quad (5)$$

The factors  $Z_A$  and  $Z_B$ , which express the influence of the vapor-phase association of A, may be evaluated from a knowledge of its association constant  $K$ . The association constant of acetic acid at 760 mmHg was obtained by Marek (1955). The dependence of  $K$  on temperature was expressed as

$$-\log K = 9.7535 + 0.00425t - \frac{3166}{t + 273.2} \quad (6)$$

where  $t$  is the temperature in °C.

The equation for the factor  $Z_B$  is a correlation for the nonideality in the vapor phase and may be evaluated from various generalized relationships. At atmospheric pressure,  $Z_B \rightarrow 1.0$ . For the associating substance A, the nonideality of the vapor phase is usually included in the correlation of the association constant.

The corrected vapor pressure of the association component,  $p_{AC}$ , may be determined from the association constant of pure acetic acid,  $k_A$ , at its vapor pressure,  $p_A^s$ . The correlations between  $k_A$  and  $p_A^s$  as well as  $p_A^s$  and temperature have been given by Marek (1955). With these correlations and eq 3,  $p_{AC}$  can finally be expressed as a function of temperature (Marek, 1955):

$$\log p_{AC} = 15.6699 - \frac{10821.1}{t + 698.09} \quad (7)$$

The vapor pressure of the nonassociation component  $p_B^s$  may be determined using the Antoine equation.

The liquid-phase nonideality is influenced by a number of factors. It is impossible to rigorously evaluate the liquid-phase association constant from the equilibrium data alone. It is a common practice to include the

liquid-phase association constants in the empirical constants for the correlation of the activity coefficients.

### Activity Coefficients

For multicomponent systems, the dependence of the activity coefficients on the liquid-phase composition for the Wilson and NRTL models was expressed respectively by eqs 8 and 10.

Wilson:

$$\ln \gamma_i = -\ln \left( \sum_{j=1}^m x_j \Lambda_{ij} \right) + 1 - \sum_{k=1}^m \frac{x_k \Lambda_{ki}}{\sum_{j=1}^m x_j \Lambda_{kj}} \quad (8)$$

where

$$\Lambda_{ij} = \frac{V_j^L}{V_i^L} \exp \left( -\frac{\lambda_{ij} - \lambda_{ii}}{RT} \right) \quad (9)$$

$$\Lambda_{ii} = \Lambda_{jj} = 1$$

NRTL:

$$\ln \gamma_i = \frac{\sum_{j=1}^m \tau_{ji} G_{ji} x_j}{\sum_{l=1}^m G_{li} x_l} + \sum_{j=1}^m \frac{x_j G_{ij}}{\sum_{l=1}^m G_{lj} x_l} \left( \tau_{ij} - \frac{\sum_{n=1}^m x_n \tau_{nj} G_{nj}}{\sum_{l=1}^m G_{lj} x_l} \right) \quad (10)$$

where

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT}$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad (11)$$

$$\tau_{ii} = \tau_{jj} = 0$$

$$G_{ii} = G_{jj} = 1$$

The binary model parameters in the above equations were obtained from the DECHEMA Vapor Liquid Equilibrium Data Collection (Gmehling et al., 1977a,b, 1982, 1988) and are listed in Table 1. The original experimental data can be found from the references listed in Table 1.

### Results and Discussion

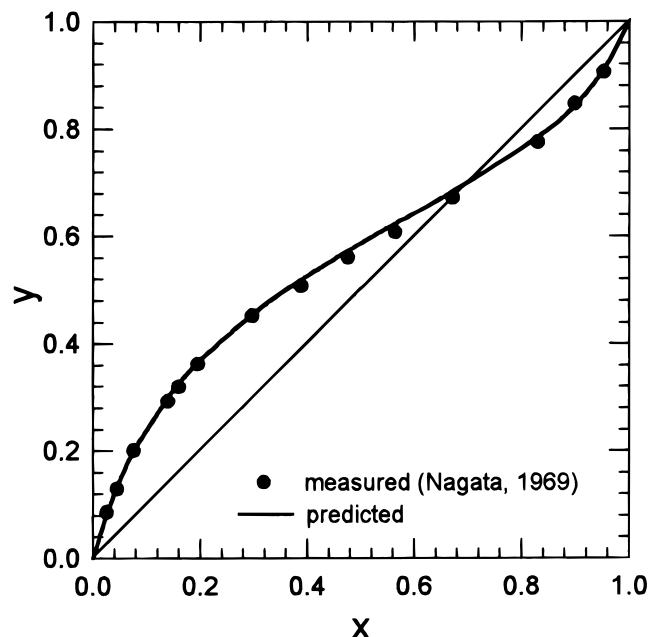
The saturation pressure of pure components was calculated by the Antoine equation:

$$\log p_i^s = A_i - \frac{B_i}{C_i + t} \quad (12)$$

The Antoine constants recommended by DECHEMA (Gmehling et al., 1977a,b, 1982, 1988) were used, and

**Table 2. Constants in Equations 12 and 13**

components	$A_i$	$B_i$	$C_i$	$D_i$	$E_i$	$F_i$
methyl acetate	7.065 24	1157.630	219.726	135.998	-0.46705	$9.221 \times 10^{-4}$
methanol	8.080 97	1582.271	239.726	64.5109	-0.19716	$3.874 \times 10^{-4}$
water	8.071 31	1730.630	233.426	23.0130	-0.03710	$6.960 \times 10^{-5}$
acetic acid	7.559 6	1644.048	233.524	34.0350	0.08220	$-9.375 \times 10^{-6}$

**Figure 1.** Measured and predicted vapor compositions for the methyl acetate-methanol system.**Table 3. Statistical Errors for the Margules, Wilson, and NRTL Models**

model param	Margules Sawistowski, and Pilavakis, 1982	Wilson Table 1	NRTL Table 1	NRTL Table 1 with $\alpha_{12} = 0.37$
rmsd	0.0229	0.0252	0.0232	0.0217
md	0.0171	0.0182	0.0164	0.0145
mrd	0.126	0.121	0.109	0.099

their values are listed in Table 2. The molar volume of the pure liquid was obtained from Holmes and van Winkle (1970). The molar volume dependence on temperature was correlated by

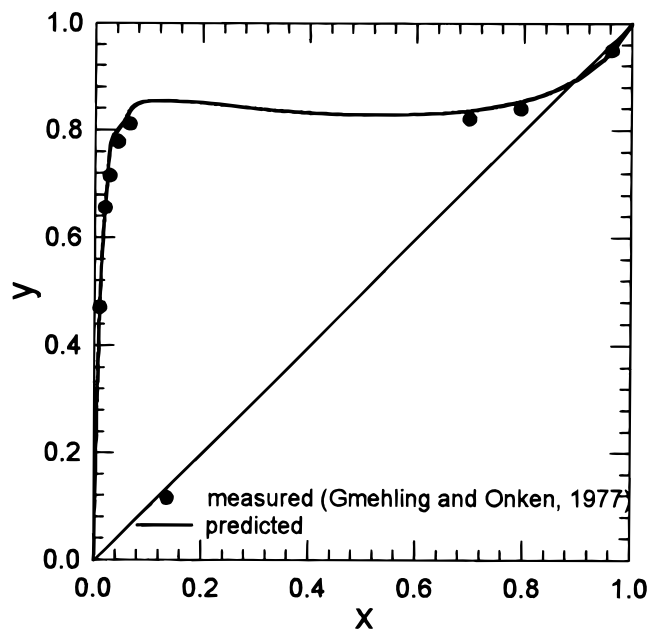
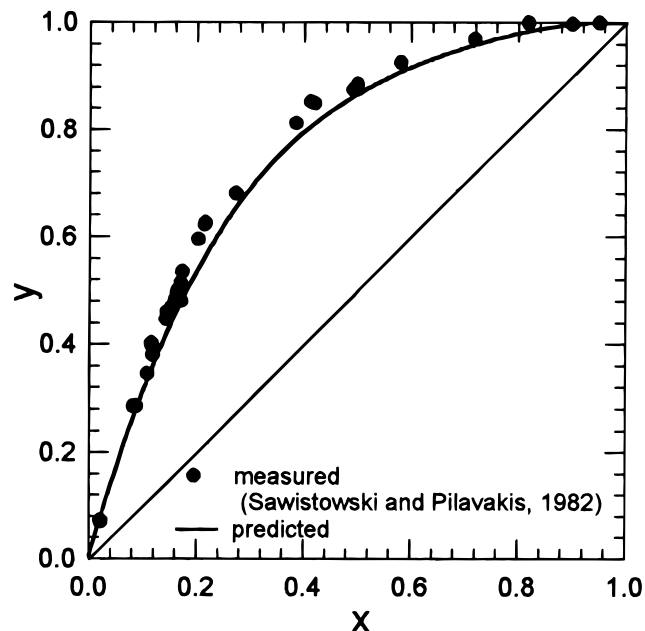
$$V_i^L = D_i + E_i T + F_i T^2 \quad (13)$$

The values of the constants in eq 13 are also listed in Table 2.

With eqs 1–13 and the data listed in Tables 1 and 2, we are able to predict the vapor composition by both the Wilson and NRTL models in combination with Marek's method. A total of 113 sets of experimental data was obtained for the quaternary system by Sawistowski and Pilavakis (1982). The deviation between these measured data and the correlated values was expressed by the root mean square deviation (rmsd) as used by Sawistowski and Pilavakis (1982):

$$\text{rmsd} = \sqrt{\frac{\sum_{i=1}^m \sum_{j=1}^n (\Delta y_{ij})^2}{mn}} \quad (14)$$

The value of rmsd was found to be 0.023 by using the

**Figure 2.** Measured and predicted vapor compositions for the methyl acetate-water system.**Figure 3.** Measured and predicted vapor compositions for the methyl acetate-acetic acid system.

third-order Margules equation (Sawistowski and Pilavakis, 1982). The computational results from this study show that rmsd is 0.025 for the Wilson model and 0.023 for the NRTL model. It can be seen that the NRTL model is comparable with the third-order Margules equation while the Wilson model is slightly poorer than the other two.

The number of model parameters required by the third-order Margules, Wilson, and NRTL equations is 16, 12, and 18, respectively. It can be seen that the Wilson model needs fewer model parameters than the

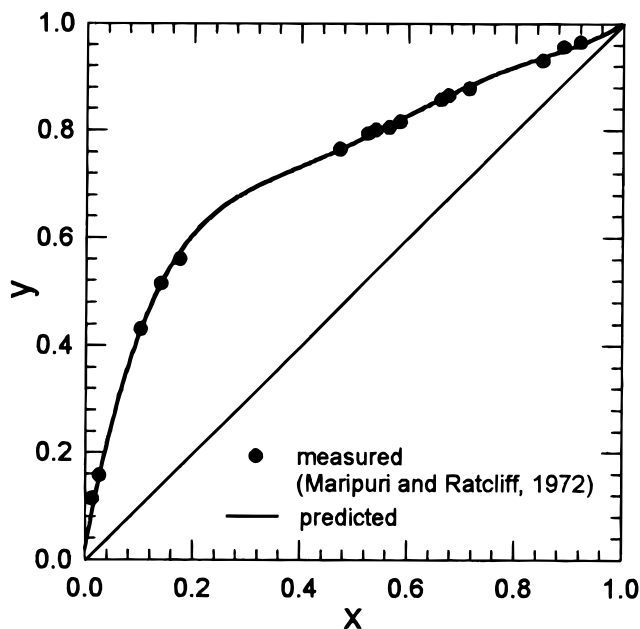


Figure 4. Measured and predicted vapor compositions for the methanol-water system.

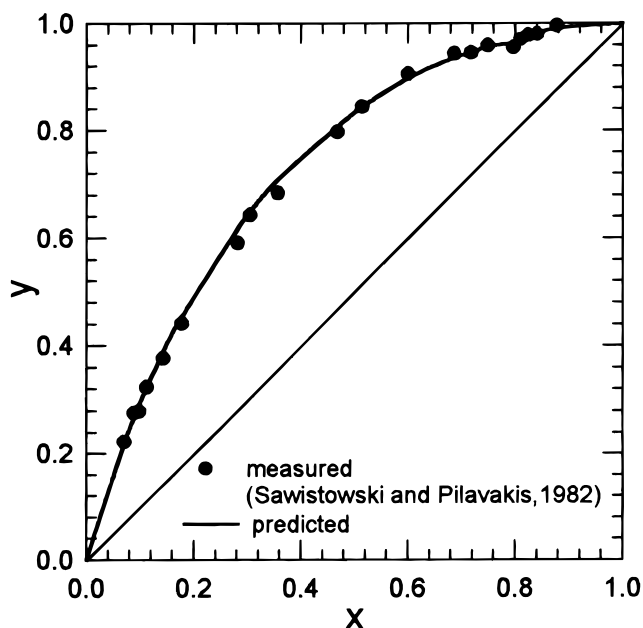


Figure 5. Measured and predicted vapor compositions for the methanol-acetic acid system.

others. For the NRTL model, Walas (1985) pointed out that the activity coefficients were relatively insensitive to the third model parameter,  $\alpha_{12}$ , in the range 0.1–0.5. From Table 1, it can be seen that most of the values of  $\alpha_{12}$  are in this range. Walas (1985) also concluded that if an estimation of  $\alpha_{12}$  has to be made, it should be about 0.3 for nonaqueous mixtures and about 0.4 for aqueous organic mixtures. This information indicates that we may use one value of  $\alpha_{12}$  for the six binary mixtures instead of six separate values. In this way, the number of NRTL model parameters for the quaternary system can be reduced from 18 to 13. By first trial of  $\alpha_{12} = 0.35$ , we obtained the same value of rmsd (0.023) as that for the 18 parameters. In fact, the value of rmsd was found to be insensitive to the value

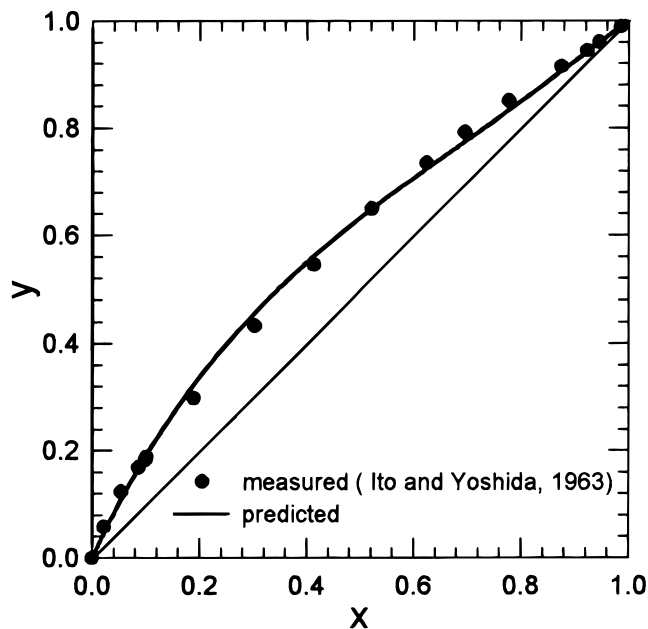


Figure 6. Measured and predicted vapor compositions for the water-acetic acid system.

Table 4. Mean Deviations between Measured and Predicted Vapor Compositions

system	Gmehling et al. (1977a,b, 1982, 1988)	this work
methyl acetate-methanol	0.0071	0.0072
methyl acetate-water	0.0157	0.0182
methyl acetate-acetic acid	0.0124 <sup>a</sup>	0.0259
methanol-water	0.0057	0.0056
methanol-acetic acid	0.0243	0.0076
water-acetic acid	0.0123	0.0100

<sup>a</sup> Two liquid compositions are different from the original data (Sawistowski and Pilavakis, 1982).

of  $\alpha_{12}$  in the range 0.3–0.4. The optimum value of  $\alpha_{12}$  is 0.37, and the corresponding value of rmsd is 0.022.

In addition to the rmsd, the accuracy of prediction can be more directly described by the mean deviation (md) and mean relative deviation (mrd), which are defined by

$$\text{md} = \frac{1}{mn} \sum_i \sum_j |\Delta y_{ij}| \quad (15)$$

$$\text{mrd} = \frac{1}{mn} \sum_i \sum_j \frac{|\Delta y_{ij}|}{y_{ij}} \quad (16)$$

Table 3 lists the statistical values of rmsd, md, and mrd between the experimental data (Sawistowski and Pilavakis, 1982) and the values predicted by using the Margules equation (Sawistowski and Pilavakis, 1982) and the Wilson and NRTL models. From the table it can be seen that the NRTL model gives the best results for the correlation of the quaternary system.

The above models for the quaternary system can be used for predicting the vapor-liquid equilibrium of the six binary systems (methyl acetate-methanol, methyl acetate-water, methyl acetate-acetic acid, methanol-water, methanol-acetic acid, and water-acetic acid) by assigning the concentrations of the two components not present in the system to zero.

Figures 1–6 show the comparison of the predicted vapor compositions with the experimental values. The NRTL model is used for all the predictions. From these figures, it can be seen that the model can well predict vapor–liquid equilibrium of the six binary systems, including the azeotropic behavior in methyl acetate–methanol and methyl acetate–water systems.

Table 4 shows the mean deviations between the measured and the predicted vapor compositions. The mean deviations obtained by Gmehling et al. (1977a,b, 1982, 1988) are also shown in the table for comparison. It can be seen that these two sets of deviation values are comparable.

## Conclusions

The vapor–liquid equilibrium data of the methyl acetate–methanol–water–acetic acid system can be correlated by using the Wilson and NRTL models instead of the third-order Margules equation, as suggested by Sawistowski and Pilavakis (1982). Compared with the third-order Margules equation, the NRTL model has fewer model parameters, includes the effect of temperature, is easier to be incorporated into computer simulation programs, and can better predict the vapor–liquid equilibria of the methyl acetate–methanol–water–acetic acid system. The best correlation was the NRTL model with the third model parameter  $\alpha_{12} = 0.37$  for all six binary mixtures.

The models can also be used for the prediction of vapor–liquid equilibrium of the binary systems. **The predictions of vapor compositions by the NRTL model for the six binary systems agree well with the measured values.**

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## Nomenclature

$A_i, B_i, C_i$  = Antoine constants in eq 12

$D_i, E_i, F_i$  = constants in eq 13

$\Delta g_{ji}$  = NRTL model parameters ( $=g_{ji} - g_{ij}$ )

$K$  = association constant in the vapor phase, 1/mmHg

$k_A$  = equilibrium constant in the pure gaseous associating substance, 1/mmHg

$m$  = number of components

$n$  = number of data sets

$P$  = total pressure, mmHg

$p_i^s$  = saturated vapor pressure, mmHg

$p_{AC}$  = corrected vapor pressure of acetic acid, mmHg

$t, T$  = temperature in °C, K, respectively

$V_i^L$  = liquid molar volume of component  $i$

$x_i$  = mole fraction of component in the liquid phase

$y_i$  = mole fraction of component in the vapor phase

$Z_A$  = factor for the influence of the vapor phase association of A

$Z_B$  = factor for the influence of the vapor phase association of B

$z_B$  = factor for the correction of nonideality in the vapor phase

$\alpha_{12}$  = NRTL third parameter

$\gamma_i$  = activity coefficient of component  $i$

$\Delta\lambda_{ij}$  = Wilson model parameter, ( $=\lambda_{ij} - \lambda_{ji}$ )

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