Study of EOS-G^{ex} Mixing Rules for Liquid–Liquid Equilibria

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The performance of two Gibbs free-energy-based equation-of-state (EOS) mixing rules is tested for the correlation and prediction of liquid–liquid equilibria (LLE). The LLE of ten binary mixtures were examined using the Peng–Robinson EOS combined with the Wong–Sandler and MHV1 mixing rules with two excess free-energy models (NRTL and UNIQUAC). Good agreement with low-pressure experimental data was obtained for nonassociating and self-associating mixtures using temperature-independent parameters. However, in the case of aqueous mixtures that exhibit both a lower and an upper critical solution temperature, it was necessary to use temperature-dependent parameters, as is also true when activity coefficient models are used directly to describe such systems. The Wong–Sandler mixing rule was capable of predicting the high-pressure phase behavior of the systems studied using parameters from correlation of only low-pressure LLE data, while the MHV1 model required the introduction of a binary interaction parameter. Consequently, the MHV1 model was useful for the correlation, but not for the prediction of high-pressure LLE from low-pressure data.

Introduction

Liquid–liquid equilibria (LLE) has been traditionally described using activity coefficient (or excess free energy, G^{ex}) models. However, this method is unable to represent the pressure effects on the LLE. Moreover, G^{ex} models cannot fit the temperature effects on the LLE unless a temperature dependence is assigned to the model parameters, so that their predictive capability is limited. Equations of state (EOS) have been a very valuable tool for the study of complex mixture phase behavior. Since an EOS accounts for the compressibility of fluids, it can describe the effects of pressure on phase behavior. However, few systematic studies of LLE using cubic EOS have appeared in the literature.

Kolasinka et al. (1983) used a van-der-Waals-type EOS that included an association model to describe the LLE of mixtures of associating and nonassociating substances that exhibit an upper critical point using temperature-dependent parameters in the mixing rules. This model was able to give a good representation of the LLE (including the critical region) of mixtures, including an associating and a nonassociating species, provided that a parameter representing a specific association scheme (i.e., dimers, trimers) was included in the mixing rule. Mathias and Copeman (1983) used the Peng–Robinson (1976) EOS in combination with density-dependent local composition mixing rules to study the LLE of mixtures of water + hydrocarbons. They demonstrated the poor performance of the classic van der Waals mixing rules in describing the LLE of these systems. They then suggested that a density-dependent mixing rule should be used together with a temperature-dependent binary interaction parameter to give an accurate description of these systems. However, these authors did not study the behavior of their model in the critical region.

Suen et al. (1989) were able to obtain a qualitative description of LLE and vapor–liquid–liquid equilibrium (VLLE) of mixtures containing alcohols using the Patel–Teja (1982) EOS with a Huron–Vidal-type (1979) mixing rule. Ludecke and Prausnitz (1985) used a modified van der Waals EOS with the Mansoori et al. (1971) expression for the repulsive term and density-dependent mixing rules to correlate LLE data of binary mixtures containing water + hydrocarbons. This approach was successful for correlating LLE remote from the critical region using temperature-independent parameters;

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however, the performance of the model near the critical point was rather poor. Huang (1991) calculated LLE and VLLE in ternary systems using the Patel-Teja equation of state with the Huron–Vidal-type mixing rules of Kurihara et al. (1987). Wong and Sandler (1992) have also applied their mixing rule to describe the LLE of some aqueous binary mixtures. Chou and Wong (1994) correlated LLE of ternary mixtures using the Peng–Robinson EOS with good results in the region far from the plait point. Filho and Costa (1996) correlated LLE data of various binary mixtures using several mixing rules that include a G^{ex} model with the Soave EOS with the purpose of determining the influence of the mixing rule on the LLE calculation. However, these authors considered the parameters in the free-energy model to be temperature dependent, and they did not examine the predictive capabilities of the mixing rules. Also, none of these previous studies considered the influence of the pressure on the LLE, or the predictive capabilities of the EOS models. Furthermore, these studies have been limited to the study of nonassociating and self-associating mixtures that only exhibit an upper critical point.

Recently, mixing rules incorporating a Gibbs free-energy model have been used in simple cubic EOS. Among these, the Wong–Sandler (WS) (Wong and Sandler, 1992) and the MHV1 (Michelsen, 1990) mixing rules have been widely used for correlations and predictions of vapor–liquid equilibria (VLE). The WS mixing rule equates the excess Helmholtz free energy from an EOS at the infinite-pressure limit with that obtained from an activity coefficient model. On the other hand, the MHV1 mixing rule equates the excess Gibbs free energy from an EOS at the zero-pressure limit. Orbey and Sandler (1997) compared different mixing rules based on the zero-pressure limit and found that none of these mixing rules was clearly superior to the others, though the MHV2 (Dahl and Michelsen, 1990) model was the least accurate. Therefore, in this article we use the MHV1 model to test the zero-pressure approach.

Despite the fact that several authors (Wang et al., 1996; Voustas et al., 1996) have compared such mixing rules in their capabilities of correlating and predicting VLE, little work has been done on LLE. Here we compare the capabilities of the WS and MHV1 mixing rules for LLE. More specifically, the models are compared with respect to their performance in correlating low-pressure LLE data, and their ability to yield good predictions of the high-pressure LLE of binary mixtures using these low-pressure correlation parameters. The mixtures studied include polar, nonpolar, nonassociating, self-associating, and cross-associating components, and provides a rigorous test of the models.

Thermodynamic Model

In our study, we used the original Peng–Robinson (PR) EOS

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

where P is pressure, R is the universal gas constant, T is temperature, v is molar volume, and a, which is a function of temperature, and b are pure component parameters obtained from

$$a(T) = 0.45724\frac{RT_c^2}{P_c}\left\{1+\kappa\left[1-\left(\frac{T}{T_c}\right)^{1/2}\right]\right\}^2 \tag{2}$$

$$b = 0.07780\frac{RT_c}{P_c}, \tag{3}$$

where T_c is the critical temperature and P_c is the critical pressure. In Eq. 2 κ is a constant given by

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2, \tag{4}$$

where ω is the acentric factor. Using the WS mixing rule, the mixture parameters a and b of this EOS are given by

$$a = RT\frac{QD}{1-D} \tag{5}$$

$$b = \frac{Q}{1-D}, \tag{6}$$

where Q and D are given by

$$Q = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij} \tag{7}$$

$$D = \sum_i x_i \frac{a_{ii}}{b_{ii}RT} + \frac{A^{ex}}{CRT}, \tag{8}$$

where x_i is the mole fraction. In these equations, C is a constant that depends on the EOS, and for the PR EOS it is equal to

$$C = -\frac{1}{\sqrt{2}}\ln(1+\sqrt{2}).$$

In Eq. 8 A^{ex} is the Helmholtz free energy at infinite pressure calculated from an activity coefficient model, and a_{ii} and b_{ii} are the pure component EOS parameters. In all cases, we used the combination rule

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{\left(b_{ii} - \frac{a_{ii}}{RT}\right) + \left(b_{jj} - \frac{a_{jj}}{RT}\right)}{2}(1-k_{ij}), \tag{9}$$

where k_{ij} is a binary interaction parameter.

In the MHV1 model the mixture parameters are given by

$$\frac{a}{bRT} = \sum_i x_i\left(\frac{a_{ii}}{b_{ii}RT}\right) + \frac{1}{q_1}\left[\frac{G^{ex}}{RT} + \sum_i x_i \ln\left(\frac{b}{b_{ii}}\right)\right], \tag{10}$$

where G^{ex} is the Gibbs free energy at zero pressure calculated using an activity coefficient model. In Eq. 19, we used the value of $q_1 = -0.53$ suggested by Michelsen (1990) for the PR EOS. In the MHV1 model one of the following mixing rules rules is used for the b parameter

$$b = \sum_i x_i b_{ii} \tag{11}$$

$$b = \sum_i \sum_j x_i x_j b_{ij}. \tag{12}$$

In Eq. 12, we used the following combination rule

$$b_{ij} = \frac{b_{ii} + b_{jj}}{2}(1 - k_{ij}). \tag{13}$$

One excess free-energy model used in Eqs. 8 and 10 is the NRTL model (Renon and Prausnitz, 1965)

$$\frac{G^{ex}}{RT} = \sum_i x_i \frac{\sum_j \tau_{ji} g_{ji} x_j}{\sum_k g_{ki} x_k}, \tag{14}$$

where

$$\tau_{ij} = \frac{\Delta G_{ij}}{RT} \tag{15}$$

$$\ln g_{ij} = -\alpha_{ij}\tau_{ij}. \tag{16}$$

Here ΔG_{ij} is a characteristic energy and α_{ij} is a nonrandomness parameter. The other free-energy model we used is the UNIQUAC model (Abrams and Prausnitz, 1975).

$$\frac{G^{ex}}{RT} = \sum_i x_i \ln \frac{\Phi_i}{x_i} + \frac{z}{2} \sum_i q_i x_i \ln \frac{\theta_i}{\Phi_i} - \sum_i q_i x_i \ln \sum_j \theta_j \tau_{ji} \tag{17}$$

$$\Phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad \text{and} \quad \theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \tag{18}$$

$$\ln \tau_{ij} = -\frac{u_{ij}}{RT}, \tag{19}$$

where u_{ij} is an energy parameter characterizing the interaction of molecule i with molecule j; r and q are, respectively, the pure component volume and area parameters; and the coordination number, z, has been set equal to 10 (Reid et al., 1988).

Methodology

In this study we computed the number of liquid phases and their equilibrium compositions using an approach based on the minimization of the Gibbs free energy of the system that follows closely the procedure proposed by Michelsen (1982a, b). A rigorous stability test was done for each of the calculated phases. The stability criterion is given by

$$\sum_i y_i(\ln \phi_i + \ln y_i - h_i) \geq 0, \tag{20}$$

where ϕ_i is the fugacity coefficient of component i and y_i are the mole fractions of component i in a trial phase. In Eq. 20

$$h_i = \ln z_i - \ln \phi_i(z). \tag{21}$$

here z_i is the composition of component i and z the composition vector of the investigated phase. The adjustable parameters in the models were fitted to the experimental data using the Levenberg–Marquardt (IMSL, 1979) method. In this case, we correlated the experimental data using the following objective function:

$$F = \sum_i^{N_c - 1} \sum_j^{N_p} \left(\frac{x_{ij}^{ex} - x_{ij}^{calc}}{x_{ij}^{ex}} \right)^2, \tag{22}$$

Table 1. WS–NRTL Optimized Parameters

System	α_{12}	k_{12}	$a_{12,1} \times 10^{-3}$ (cal/mol)	$a_{12,2} \times 10^{0}$ (cal/mol·K)	$a_{12,3} \times 10^{-6}$ (cal·K/mol)	$a_{21,1} \times 10^{-3}$ (cal/mol)	$a_{21,2} \times 10^{0}$ (cal/mol·K)	$a_{21,3} \times 10^{-6}$ (cal·K/mol)
Nitromethane (1) Cyclohexane (2)	0.15	−0.690	2.506	0	0	2.400	0	0
Methanol (1) Hexane (2)	0.2	0.349	0.294	0	0	1.469	0	0
Furfural (1) Cyclohexane (2)	0.22	−0.481	1.331	0	0	2.555	0	0
Methanol (1) Carbon disulfide (2)	0.125	−3.250	2.832	0	0	5.736	0	0
Styrene (1) Water (2)	0.2	0.940	2.783	0	0	3.503	0	0
1-Butanol (1) Water (2)	0.4	0.692	8.827	−18.02	−1.168	4.551	4.81	−1.247
2-Butanol (1) Water (2)	0.2	0.325	11.199	−21.14	−1.680	8.510	0.53	−1.706
Cyclohexanone (1) Water (2)	0.2	0.170	−0.876	6.21	0.017	8.563	3.32	−1.785
2-Butoxyethanol (1) Water (2)	0.35	0.600	44.132	−64.44	−7.960	−25.684	46.15	4.594

Table 2. WS–UNIQUAC Optimized Parameters

System	k_{12}	$a_{12,1}$ $\times 10^{-3}$ (cal/mol)	$a_{12,2}$ $\times 10^{0}$ (cal/mol·K)	$a_{12,3}$ $\times 10^{-6}$ (cal·K/mol)	$a_{21,1}$ $\times 10^{-3}$ (cal/mol)	$a_{21,2}$ $\times 10^{0}$ (cal/mol·K)	$a_{21,3}$ $\times 10^{-6}$ (cal·K/mol)
Nitromethane (1) Cyclohexane (2)	−0.988	0.300	0	0	1.44	0	0
Methanol (1) Hexane (2)	0.310	−0.066	0	0	1.74	0	0
Furfural (1) Cyclohexane (2)	−0.414	0.125	0	0	1.22	0	0
Methanol (1) Carbon disulfide (2)	0.05586	0.388	0	0	1.78	0	0
1-Butanol (1) Water (2)	0.175	7.956	−13.16	−1.114	3.76	−2.14	−0.745
2-Butanol (1) Water (2)	0.215	2.566	−4.59	−0.328	4.93	−4.38	−0.936
Cyclohexanone (1) Water (2)	0.42	4.130	−7.28	−0.214	1.18	0.074	−0.351
2-Butoxyethanol (1) Water (2)	0.527	17.518	−25.43	−3.169	−22.04	33.31	3.965

where N_c is the number of components and N_p the number of phases present in the system.

The adjustable parameters in the thermodynamic models used in this work are the binary parameter k_{ij} in Eq. 9 or 13, and the parameters of the excess models ΔG_{ij}, α_{ij}, and u_{ij} in Eqs. 15, 16 and 19, respectively. However, as when using an activity coefficient model directly (that is, not in an EOS), we found that it was necessary to use temperature-dependent interaction parameters to correlate LLE in mixtures that exhibit both an upper and a lower consolute temperature. In this case, we used

$$A_{ij} = a_{ij,1} + a_{ij,2}T + \frac{a_{ij,3}}{T}, \tag{23}$$

where A_{ij} corresponds to the ΔG_{ij} or u_{ij} in the NRTL and UNIQUAC parameters in Eqs. 15 and 19, respectively.

No LLE critical data were directly used for parameter fitting. However, for some systems, several different parameter sets provided almost equally good correlations of the low-pressure experimental data; in these cases, critical-region data were used as a basis for selecting the best parameter set. All of the optimized parameters and the absolute average deviations are summarized in Tables 1 to 6.

Results and Discussion

The binary mixtures studied were classified into three groups according to their likelihood of forming hydrogen bonds:

1. Polar + nonpolar (nonassociating)
2. Nonassociating + self-associating
3. Cross-associating

All the systems considered are strongly nonideal. Further complications arise from the fact that most of the compounds studied are hydrogen-bonding species. Therefore, this set of binary mixtures represents a very stringent test for the models studied. The critical constants of the pure substances were obtained from Reid et al. (1988) with the exception of 2-butoxyethanol. For this substance we used the critical pres-

Table 3. MHV1–NRTL Optimized Parameters

System	α_{12}	k_{12}	$a_{12,1}$ $\times 10^{-3}$ (cal/mol)	$a_{12,2}$ $\times 10^{0}$ (cal/mol·K)	$a_{12,3}$ $\times 10^{-6}$ (cal·K/mol)	$a_{21,1}$ $\times 10^{-3}$ (cal/mol)	$a_{21,2}$ $\times 10^{0}$ (cal/mol·K)	$a_{21,3}$ $\times 10^{-6}$ (cal·K/mol)
Nitromethane (1) Cyclohexane (2)	0.15	−5.01	0.984	0	0	1.081	0	0
Methanol (1) Hexane (2)	0.2	0.15	0.633	0	0	0.812	0	0
Furfural (1) Cyclohexane (2)	0.2	−5.96	0.092	0	0	1.614	0	0
Methanol (1) Carbon disulfide (2)	0.15	−7.83	−0.158	0	0	1.938	0	0
Cyclohexanone (1) Water (2)	0.15	0.3	9.112	−19.00	−1.159	−1.170	17.63	−0.432
1-Butanol (1) Water (2)	0.2	0.25	10.664	−21.50	−1.475	6.208	4.08	−1.345
2-Butanol (1) Water (2)	0.2	0.25	7.340	−15.32	−1.095	8.323	−0.56	−1.586.
2-Butoxyethanol (1) Water (2)	0.25	0.4	46.397	−68.02	−8.421	−27.317	49.59	4.958

Table 4. MHV1–UNIQUAC Optimized Parameters

System	k_{12}	$a_{12,1}$ $\times 10^{-3}$ (cal/mol)	$a_{12,2}$ $\times 10^{0}$ (cal/mol·K)	$a_{12,3}$ $\times 10^{-6}$ (cal·K/mol)	$a_{21,1}$ $\times 10^{-3}$ (cal/mol)	$a_{21,2}$ $\times 10^{0}$ (cal/mol·K)	$a_{21,3}$ $\times 10^{-6}$ (cal·K/mol)
Nitromethane (1) Cyclohexane (2)	−3.631	0.073	0	0	0.994	0	0
Methanol (1) Hexane (2)	−0.667	−0.055	0	0	1.204	0	0
Furfural (1) Cyclohexane (2)	−5.485	−0.127	0	0	0.848	0	0
Methanol (1) Carbon disulfide (2)	−4.273	0.160	0	0	1.162	0	0
Cyclohexanone (1) Water (2)	0.500	4.500	−9.06	−0.296	−2.213	5.22	0.149
1-Butanol (1) Water (2)	−0.150	−0.683	−0.79	0.259	3.185	−1.09	−0.709
2-Butanol (1) Water (2)	0.170	−0.105	−1.04	0.091	5.154	−4.90	−0.973
2-Butoxyethanol (1) Water (2)	0.340	15.207	−21.87	−2.777	−17.057	25.60	3.113

sure and temperature reported by Schneider and Wilhelm (1959), while the acentric factor was estimated by fitting vapor pressure data (Boublík et al., 1973).

Nonassociating mixtures

The correlation of the experimental data for the system nitromethane + cyclohexane (Sørensen and Arlt, 1979) is shown in Figure 1. This is a mixture of two nonassociating compounds with a large difference in polarities: 3.1 debye for nitromethane and 0.3 debye for cyclohexane (Reid, 1988). The NRTL free-energy model was used in the WS mixing rule. It is worth noting that in this case all the parameters are independent of the temperature, and the good agreement with the experimental data, including in the critical LLE region, was obtained with the WS model. Good agreement was also obtained with the MHV1 mixing rules combined with the NRTL model and Eq. 12 for the b parameter, and this is also shown in the figure. Similar results were obtained using the UNIQUAC model in both mixing rules. In Figure 1 we show the poor preformance when the NRTL model with temperature-independent parameters is used driectly (i.e., not in an EOS mixing rule) to fit the data. It is interesting that the direct use of the NRTL model with temperature-independent parameters leads to poor results, while because of the inherent temperature dependence of an EOS, using the same model with constant parameters in an EOS yields very good results.

Mixtures of nonassociating + self-associating compounds

The second type of mixture we considered contained a self-associating component, that is, mixtures in which one component is capable of forming hydrogen bonds while the second component cannot. In Figures 2 to 6 we show the binodal curves obtained for the sytems: furfural + cyclohexane (Sørensen and Arlt, 1979), methanol + hexane (Hölscher et al., 1986), methanol + carbon disulfide (Sørensen and Arlt, 1979), styrene + water (Sørensen and Arlt, 1979), and benzene + water (Sørenen and Arlt, 1979). In each of these cases we used the combination rule of Eq. 12 in the MHV1 mixing rule. In general, we observe that both the WS and MHV1

Table 5. Average Absolute Deviation using the NRTL Model in the Mixing Rules

System	Phase Rich in Comp. 1		Phase Rich in Comp. 2	
	W–S	MHV1	W–S	MHV1
(1) Nitromethane–(2)cyclohexane	6.1×10^{-3}	1.7×10^{-2}	4.1×10^{-3}	5.1×10^{-3}
(1) Furfural–(2) cyclohexane	1.8×10^{-2}	2.2×10^{-2}	3.0×10^{-3}	4.7×10^{-3}
(1) Methanol–(2) hexane	1.7×10^{-2}	1.8×10^{-2}	2.0×10^{-2}	3.5×10^{-2}
(1) Methanol–(2) carbon disulfide	6.7×10^{-3}	5.5×10^{-3}	6.1×10^{-3}	4.6×10^{-3}
(1) Styrene–(2) water	6.0×10^{-4}	*	9.3×10^{-6}	*
(1) Benzene–(2) water	4.6×10^{-4}	**	9.3×10^{-5}	**
(1) Cyclohexanone–(2) water	3.9×10^{-3}	7.9×10^{-3}	1.5×10^{-4}	2.1×10^{-3}
(1) 1-Butanol–(2) water	8.3×10^{-3}	1.7×10^{-2}	4.6×10^{-3}	4.9×10^{-3}
(1) 2-Butanol–(2) water ($P = 1$ atm)	6.2×10^{-3}	6.3×10^{-3}	2.2×10^{-3}	2.3×10^{-3}
(1) 2-Butanol–(2) water ($P = 800$ atm)	6.0×10^{-3}	3.1×10^{-3}	1.4×10^{-3}	1.9×10^{-3}
(1) 2-Butoxyethanol–(2) water (1 bar)	3.4×10^{-3}	7.4×10^{-3}	1.7×10^{-3}	2.6×10^{-3}
(1) 2-Butoxyethanol–(2) water (201 bar)	9.1×10^{-3}	7.9×10^{-3}	5.4×10^{-3}	5.6×10^{-3}
(1) 2-Butoxyethanol–(2) water (401 bar)	1.4×10^{-2}	1.2×10^{-2}	5.0×10^{-3}	6.2×10^{-3}
(1) 2-Butoxyethanol–(2) water (601 bar)	3.4×10^{-3}	3.9×10^{-3}	1.2×10^{-3}	1.3×10^{-3}
(1) 2-Butoxyethanol–(2) water (781 bar)	2.1×10^{-3}	6.2×10^{-3}	1.2×10^{-3}	3.6×10^{-3}

*No optimized parameters were found.
**LLE was predicted only with the WS mixing rule.

Table 6. Average Absolute Deviation using the UNIQUAC Model in the Mixing Rules

System	Phase Rich in Comp. 1		Phase Rich in Comp. 2	
	W-S	MHV1	W-S	MHV1
(1) Nitromethane-(2) cyclohexane	1.0×10^{-3}	6.8×10^{-3}	1.7×10^{-3}	3.1×10^{-3}
(1) Furfural-(2) cyclohexane	2.0×10^{-2}	1.7×10^{-2}	4.1×10^{-3}	3.6×10^{-3}
(1) Methanol-(2) hexane	6.0×10^{-2}	3.2×10^{-2}	4.2×10^{-2}	1.4×10^{-2}
(1) Methanol-(2) carbon disulfide	1.1×10^{-2}	3.1×10^{-2}	9.7×10^{-3}	1.9×10^{-3}
(1) Cyclohexanone-(2) water	6.1×10^{-3}	1.9×10^{-2}	1.6×10^{-4}	4.1×10^{-3}
(1) 1-Butanol-(2) water	1.6×10^{-2}	2.1×10^{-2}	3.6×10^{-3}	5.7×10^{-3}
(1) 2-Butanol-(2) water ($P=1$ atm)	9.2×10^{-3}	1.5×10^{-2}	3.5×10^{-3}	6.2×10^{-3}
(1) 2-Butanol-(2) water ($P=800$ atm)	7.9×10^{-3}	7.8×10^{-3}	2.0×10^{-2}	1.5×10^{-2}
(1) 2-Butoxyethanol-(2) water (1 bar)	2.4×10^{-3}	3.7×10^{-3}	1.4×10^{-3}	1.9×10^{-3}
(1) 2-Butoxyethanol-(2) water (201 bar)	9.6×10^{-3}	1.0×10^{-2}	5.6×10^{-3}	5.9×10^{-3}
(1) 2-Butoxyethanol-(2) water (401 bar)	1.3×10^{-2}	1.3×10^{-2}	4.7×10^{-3}	4.9×10^{-3}
(1) 2-Butoxyethanol-(2) water (601 bar)	1.0×10^{-2}	8.5×10^{-3}	4.3×10^{-3}	4.0×10^{-3}
(1) 2-Butoxyethanol-(2) water (781 bar)	8.9×10^{-3}	6.9×10^{-3}	9.6×10^{-3}	8.3×10^{-3}

mixing rules with the NRTL model give good correlations of the LLE data with temperature-independent parameters. In contrast, we again see the poor performance of the direct use of the NRTL and UNIQUAC models with temperature-independent parameters. This again shows the advantage of the built-in temperature dependence of cubic EOS over the activity-coefficient approach, in that with the EOS we are able to eliminate the temperature dependence of the activity-coefficient parameters and yet represent accurately the effect of temperature on the LLE for these systems.

In the case of the styrene + water system (Figure 5), there is remarkably good agreement between the experimental data and the calculated values when using the WS mixing rule, even though the difference in the compositions of the two liquid phases is approximately four orders of magnitude. In contrast, it was not possible to obtain a good correlation of the data for this system using the MHV1 model, and these results are not shown since they do not fit on the scale of these graphs. Finally, the parameters used for the system benzene + water (Figure 6) are those reported by Wong and Sandler (1992) at 25°C. Despite the fact that these parameters were not optimized over the whole temperature range, there is a reasonable agreement between the predicted values and the experimental compositions using the WS mixing rule with the NRTL model. We do see that both the WS and MHV1 models tend to predict higher critical temperatures for these systems than actually occurs. This happens to a greater extent with the MHV1 model; for example, in the case of the methanol–hexane system (Figure 3) the MHV1 model predicts an LLE critical point about 12 deg higher than the reported experimental value, but the prediction is only 4 degrees higher with the WS model.

Mixtures of cross-associating components

The last type of binary system we considered was cross-associating mixtures; in these systems the components can form

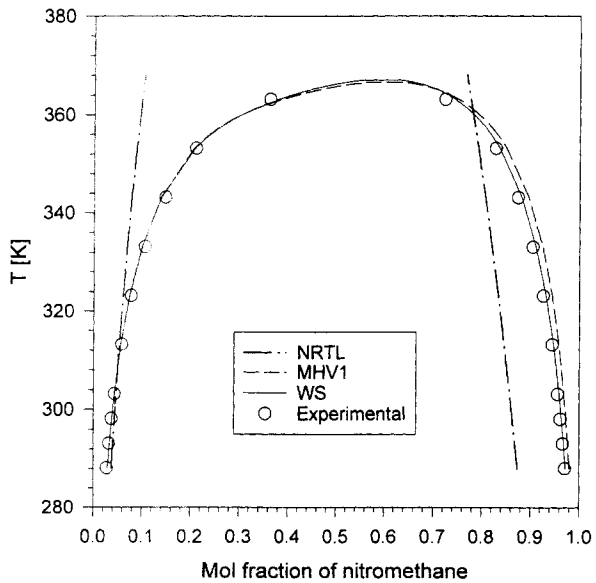

Figure 1. Correlation of the LLE of the nitromethane + cyclohexane system using the WS and MHV1 mixing rules, the PR EOS, and the NRTL model with temperature-independent parameters.

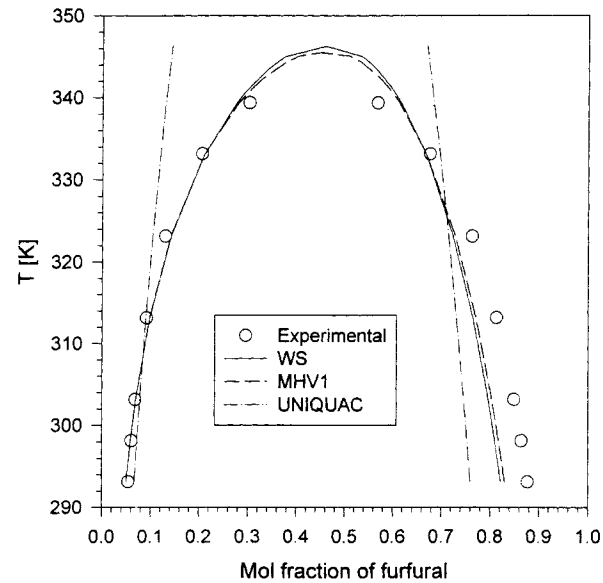

Figure 2. Correlation of the LLE of the furfural + cyclohexane system using the WS and MHV1 mixing rules, the PR EOS, and the UNIQUAC model with temperature-independent parameters.

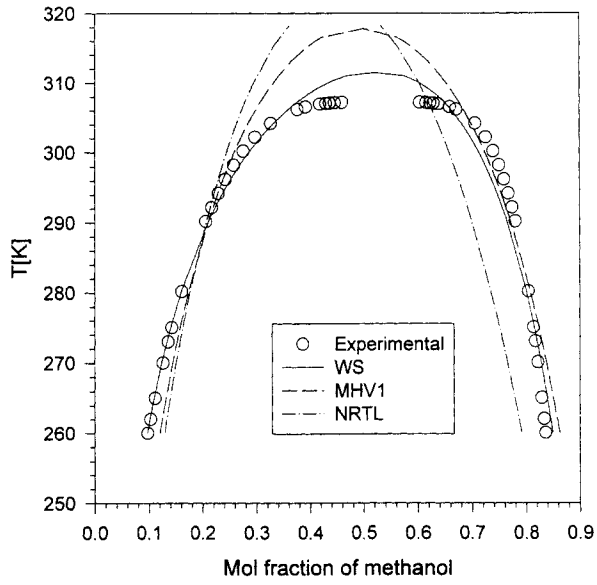

Figure 3. Correlation of the LLE of the methanol + hexane system using the WS and MHV1 mixing rules, the PR EOS, and the NRTL model with temperature-independent parameters.

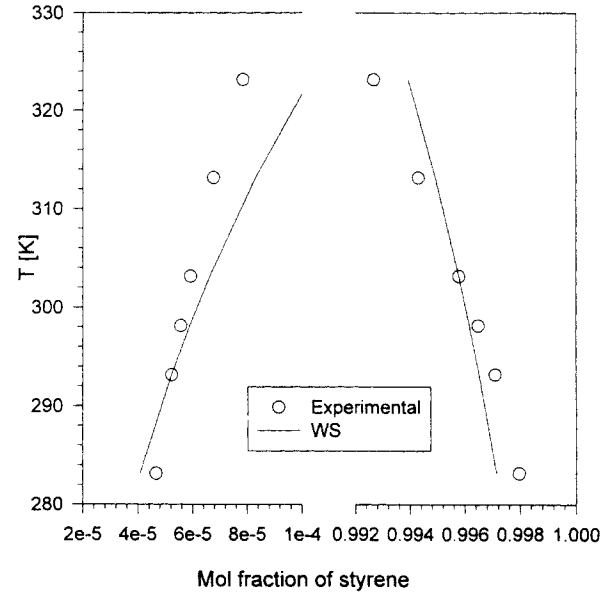

Figure 5. Correlation of the LLE of the styrene+water system using the WS mixing rule, the PR EOS, and the NRTL model with temperature-independent parameters.

a mixed hydrogen bond, and may also self-associate. Furthermore, the systems we considered exhibit a closed-loop or almost closed-loop liquid-phase split (i.e., an upper and a lower critical point) characteristic of type VI phase behavior. This behavior cannot be calculated using cubic EOS with the classic van der Waals mixing rules (van Konynenburg and Scott, 1980). The first mixture we considered is cyclohexanone + water (Sørensen and Arlt, 1979). In this case, cyclohexanone forms hydrogen bonds only with water, and the lower critical point of this mixture is masked by the mixture freezing point.

We found that the models we were studying could not represent the LLE of these sytems with temperature-independent parameters. Indeed, we know of no model with temperature-independent parameters that can describe such systems. Therefore, we introduced temperature-dependent parameters into the activity-coefficient models we were using

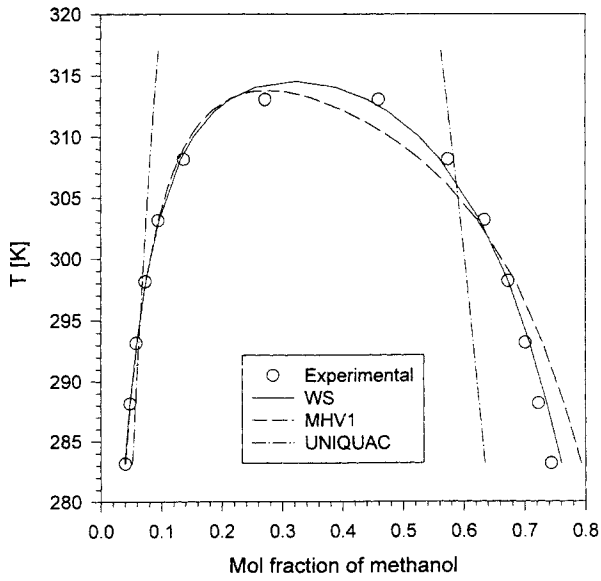

Figure 4. Correlation of the LLE of the methanol + carbon disulfide system using the WS and MHV1 mixing rules, the PR EOS, and the UNIQUAC model with temperature-independent parameters.

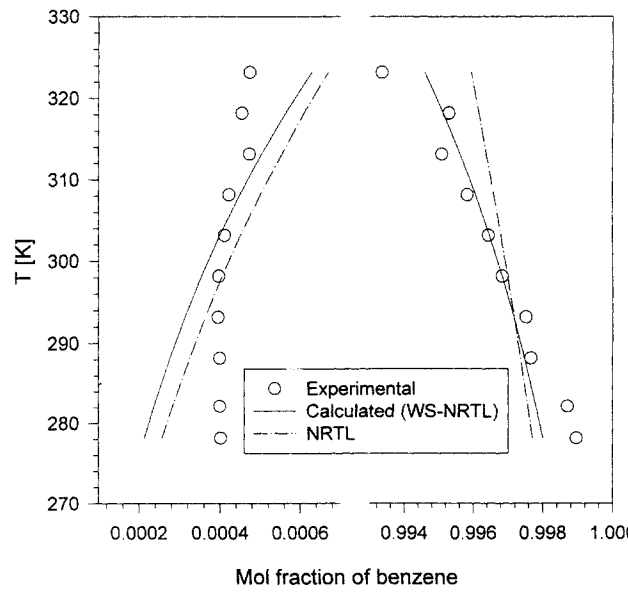

Figure 6. Prediction of the LLE of the benzene+water system using the WS mixing rule, the PR EOS, and the NRTL model with the parameters reported by Wong and Sandler (1992) at 25°C.

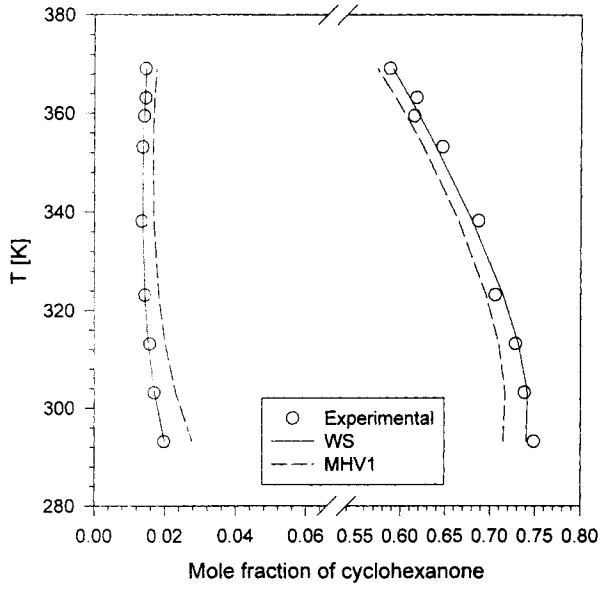

Figure 7. Correlation of the LLE of the cyclohexane+water system using the WS and MHV1 mixing rules, the PR EOS, and the UNIQUAC model with temperature-dependent parameters.

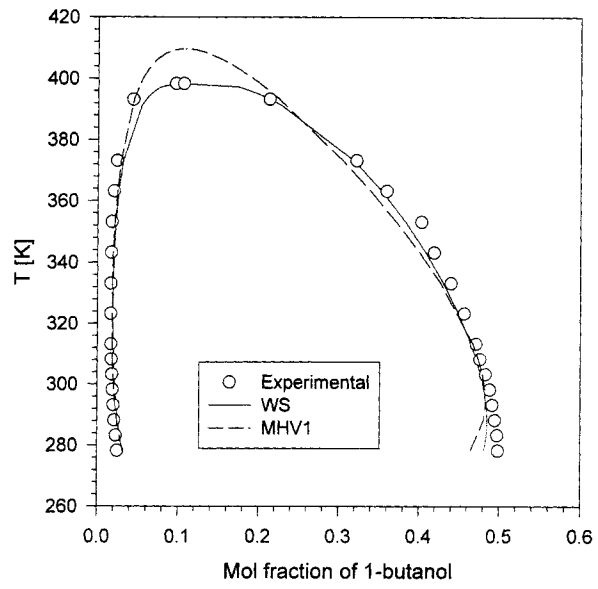

Figure 8. Correlation of the LLE of the 1-butanol+water system using the WS and MHV1 mixing rules, the PR EOS, and the NRTL model with temperature-dependent parameters.

through Eq. 23. It should be stressed that temperature-dependent parameters are also needed when an activity-coefficient model is used directly (i.e., not in an EOS mixing rule as here) to correlate LLE of systems that exhibit both upper and lower critical-solution temperatures. We used the UNIQUAC model with the two EOS mixing rules for the cyclohexanone+water system. Excellent agreement between the experimental data and our correlation was obtained using the WS mixing rule (Figure 7). The MHV1 mixing rule was less successful, although the results are still acceptable. Similar results were obtained for the 1-butanol+water system; in this case, we used the NTRL model in both mixing rules (Figure 8). In both cases, the MHV1 model underpredicted the compositions in the organic-rich phase and overpredicted the critical temperature. Similar results were observed when the UNIQUAC model was used in the mixing rules.

Figure 9 shows the excellent agreement between the experimental and predicted values for the mixture 2-butanol+water (Moriyoshi et al., 1975) using the WS mixing rule combined with the UNIQUAC model. In this case, the parameters were optimized using the experimental data at $P = 1$ atm, and temperature-dependent UNIQUAC model parameters were used as is necessary for mixtures of this type. Again, the capabilities of this model are confirmed by the good prediction of the high-pressure phase behavior using parameters fitted only to low-pressure data. While the MHV1 model was as successful as the WS model for the correlation of the low-pressure data, using Eq. 11 for the b parameter, the MHV1 model did not accurately predict the high-pressure LLE behavior of this system (Figure 10). Similar failure was reported for the MHV2 model by Knudsen et al. (1994) in their study of this mixture. Therefore, we introduced a binary interaction parameter using Eq. 13, and in this way obtained a good prediction of the high-pressure behavior for this binary mixture. However, when the UNIQUAC model was used in the MHV1 mixing rule it was not possible to predict the occurrence of an upper critical point at $P = 1$ atm, because the model incorrectly predicted the existence of a VLLE region. A similar problem was not found with the WS mixing rule. An important observation is that the EOS-G^{ex} models considered here are capable of representing the pressure dependence of liquid–liquid equilibria, something that is not possible with the direct use of activity coefficient models.

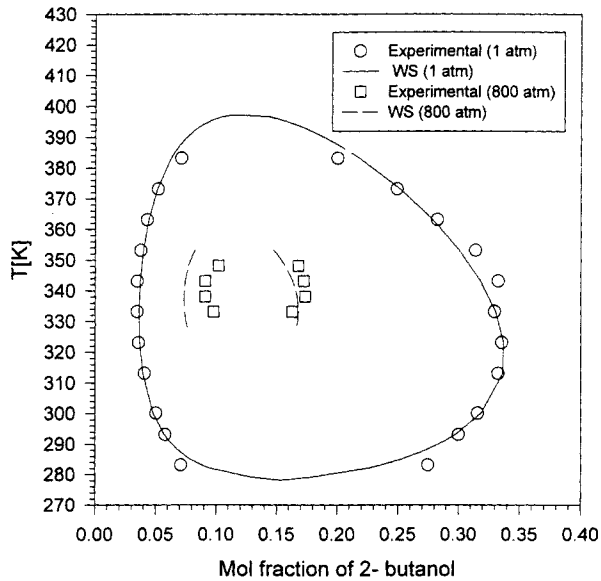

Figure 9. Correlation of the low-pressure LLE and prediction of the high-pressure LLE of the 2-butanol+water system using the WS mixing rule, the PR EOS, and the UNIQUAC model with temperature-dependent parameters.

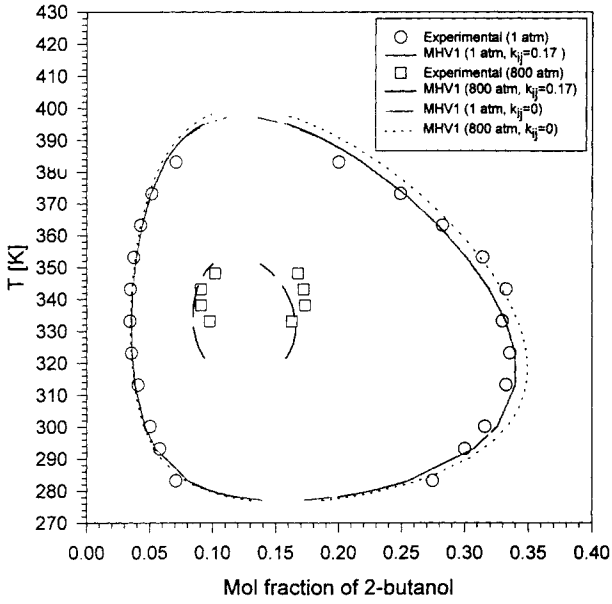

Figure 10. Correlation of the low-pressure LLE and prediction of the high-pressure LLE of the 2-butanol + water system using the MHV1 mixing rule, the PR EOS, and the NRTL model with temperature-dependent parameters.

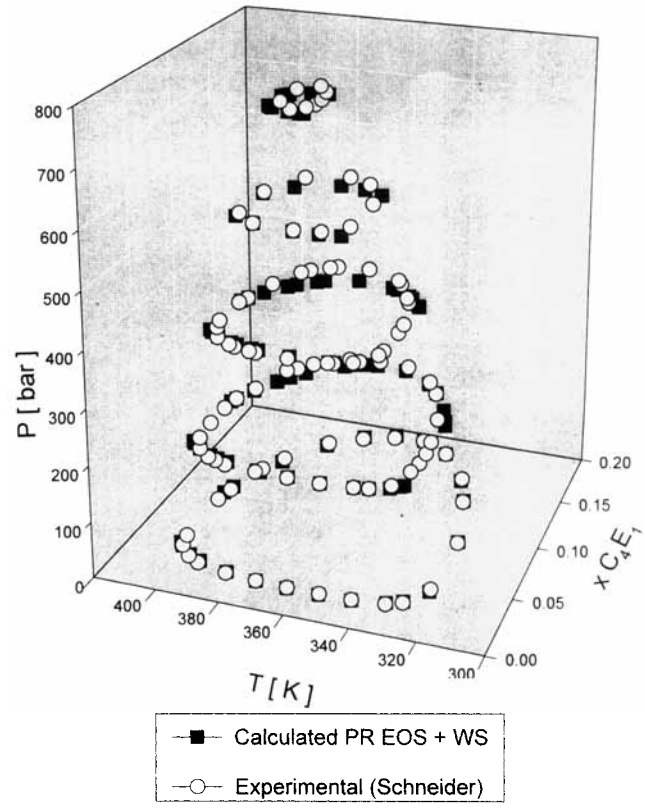

Figure 11. Correlation of the low-pressure LLE and prediction of the high-pressure LLE of the 2-butoxyethanol (C_4E_1) + water system using the WS mixing rule with the NRTL model with temperature-dependent parameters in the PR EOS.

Figure 11 shows in a three-dimensional $P-T-x$ projection the LLE of the more complicated 2-butoxyethanol + water (Schneider, 1963) system predicted by the WS mixing rule with the NRTL model (we also studied this mixture using UNIQUAC, obtaining similar results). As before, we correlated the parameters of the NRTL model using only low-pressure data. The predictions of the WS mixing rule and the correlation in the MHV1 mixing rule led to good descriptions of the phase behavior at 201, 401 and 601 bar, and a fair description of the LLE at 781 bar. In particular, the UCST and LCST of this system were described reasonably well. A comparison of the results in Figures 9–11 with the results presented by Knudsen et al. (1994), who studied these systems using the SRK EOS as modified by Mathias and Copeman and the MHV2 mixing rule, shows the better performance of the WS mixing rule.

Conclusions

We have performed a detailed study of the capabilities and limitations of the PR EOS with the WS and MHV1 mixing rules for the correlation and prediction of LLE by considering a number of representative systems. We observe that these EOS models with temperature-independent parameters are useful for the description of nonassociating and self-associating mixtures, though the direct use of the NRTL and UNIQUAC models with temperature-independent parameters cannot describe the LLE of these mixtures satisfactorily. Our results show that the performance of the two mixing rules are both satisfactory, though the WS mixing rule proved to be more accurate for the correlation of LLE data for the nonassociating and self-associating binary mixtures studied. Our results also suggest that the free-energy model used in the mixing rule has little influence on the performance of the WS and MHV1 models.

However, these models with temperature-independent parameters were not satisfactory for the description of cross-associating mixtures that exhibit a closed solubility loop. This failure is not attributable to the EOS approach, but rather to the capabilities of the excess Gibbs free-energy model used in these mixing rules. With the available G^{ex} models, such mixtures can only be described using empirical temperature-dependent parameters that have little physical meaning. Nevertheless, with temperature-dependent parameters, the WS mixing rule is able to reproduce accurately the LLE of these systems as a function of pressure, including at conditions very different from those at which the parameter optimization was carried out. This is an important result that shows one of the advantages of the EOS over the activity-coefficient approach. We have also shown that when using the MHV1 model, in addition to the correlation parameters obtained from low-pressure data, it is also necessary to introduce a binary interaction parameter in Eq. 10 in order to obtain a satisfactory representation of the high-pressure LLE behavior.

Our results do show, however, that cubic equations of state can predict closed-loop liquid–liquid miscibility gaps characteristic of type VI phase behavior when they are used in combination with mixing rules that include an excess Gibbs free-energy model with temperature-independent parameters. In-

deed, the most significant conclusion of this work may be that simple EOS can be used to describe complex liquid–liquid phase behavior provided free-energy-based mixing rules are used.

Acknowledgments

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