Multiphase Equilibrium Calculations from Soave Equation of State with Chang-Twu/UNIFAC Mixing Rules for Mixtures Containing Water, Alcohols, and Esters

Gui-Bing Hong,[†] Cheng-Ting Hsieh,[‡] Ho-mu Lin,[§] and Ming-Jer Lee*,[§]

[†]Department of Cosmetic Application and Management, St. Mary's Medicine, Nursing and Management College, Yilan County, Taiwan

[‡]Physical Division, Institute of Nuclear Energy Research, Atomic Energy Council, 1000 Wenhua Road, Longtan Township, Taoyuan County, Taiwan

[§]Department of Chemical Engineering, National Taiwan University of Science and Technology, 43 Keelung Road, Section 4, Taipei 106-07, Taiwan

Ⓢ Supporting Information

ABSTRACT: Various versions of the Soave−Redlich−Kwong (SRK) equation of state incorporating different mixing rules were applied to calculate vapor−liquid equilibrium (VLE), liquid−liquid equilibrium (LLE), and vapor−liquid−liquid equilibrium (VLLE) properties for the systems containing water, alcohols, and esters. The calculated results showed that the SRK equation with the T-type α function and the Chung−Twu (CT) mixing rules embedded in the UNIFAC−Lyngby model (SRK-T/CT−UNIFAC− Lyngby) not only predicts accurately the VLE properties of the constituent binaries but also represents the ternary LLE and VLLE phase behavior reasonably well. Using this model, the vapor pressure data of the pure constituent components are the only required property for the phase equilibrium calculations.

1. INTRODUCTION

An equation of state (EoS) is a model to represent the relationship among temperature, pressure, and volume of fluids and their mixtures. A good EoS can be used not only for a reliable calculation of phase equilibrium properties, but also for calculations of other thermodynamic properties such as density, enthalpy, entropy, etc. The cubic equations of state such as the Soave modified Redlich−Kwong[1] (SRK) EoS and the Peng−Robinson[2] (PR) EoS are widely used for calculations of thermodynamic properties in industrial practice. In this study, the SRK equation was chosen for the calculation of vapor−liquid equilibrium (VLE), vapor−liquid−liquid equilibrium (VLLE), and liquid−liquid equilibrium (LLE), due to its simplicity, acceptable accuracy, and easy mathematical manipulation. Twu et al.[3,4] have compared a variety of cubic equations of state and found that the α function and the mixing rules of the attractive term were the key factors for improving the accuracy of thermodynamic property calculations. This study explored the applicability of this cubic equation of state for calculating the VLLE phase properties of a selected ternary system, and further tested the validity of using the cubic equation of state with the Chung−Twu−UNIFAC mixing rules for predicting the LLE and VLLE phase behaviors of ternary systems.

2. α FUNCTIONS

Wilson[5,6] first generalized the energy parameter a of the Redlich−Kwong[7] equation of state as a function of temperature,

$$a(T) = a_c \alpha(T) \tag{1}$$

where a_c is the parameter a at critical temperature. The $\alpha(T)$ was expressed as a function of reduced temperature and acentric factor:

$$\alpha(T) = T_r + (1.57 + 1.62\omega)(1 - T_r) \tag{2}$$

Unfortunately, this α function is poor for the calculation of vapor pressure of pure substances. In 1972, Soave developed a well-known α function:

$$\alpha(T) = [1 + m(1 - T_r^{0.5})]^2$$

$$\text{with } m = 0.480 + 1.574\omega - 0.176\omega^2 \tag{3}$$

This α function (denoted as S-type α) substantially improves the performance of the Redlich−Kwong type cubic EoS. Similar α functions have also been proposed such as by Mathias:[8]

$$\alpha(T) = [1 + c_1(1 - T_r^{0.5}) + c_2(1 - T_r)(0.7 - T_r^{0.5})]^2 \tag{4}$$

and by Mathias and Copeman:[9]

$$\alpha(T) = [1 + c_1(1 - T_r^{0.5}) + c_2(1 - T_r^{0.5})^2 + c_3(1 - T_r^{0.5})^3]^2 \tag{5}$$

Kontogeorgis et al.[10] developed an α function:

$$a(T) = a_0 \alpha(T) = a_0 [1 + c_1(1 - T_r^{0.5})]^2 \quad (6)$$

This α function (denoted as the K-type α) differs from the above-mentioned S-type α. There are two adjusted parameter a_0 and c_1 in the expression of the K-type α. Additionally, the parameter b in the repulsive term is the third adjustable parameter. The values of a_0, c_1, and b for a specific fluid can be determined by correlating the vapor pressures of pure substance.

Twu et al.[3] derived an α function from a probability distribution function (denoted as T-type α):

$$\alpha(T) = T_r^{N(M-1)} e^{L(1-T_r^{NM})} \quad (7)$$

The variables L, M, and N are adjustable parameters, whose values were also determined from the vapor pressure data. In this study, the SRK equation of state with the S, the K, or the T type α function was tested for the calculation of phase equilibrium properties.

3. MIXING RULES

As noted earlier, the mixing rule is also a key factor for improving the mixture property calculations by using the equations of state. The most popular mixing rules are the van der Waals (vdW) one-fluid mixing rules,

$$a_m = \sum_{i=1}^{n_c} \sum_{j=1}^{n_c} x_i x_j (1 - k_{ij}) \sqrt{a_i a_j} \quad (8)$$

$$b_m = \sum_{i=1}^{n_c} \sum_{j=1}^{n_c} x_i x_j (b_i + b_j)/2 \quad (9)$$

where n_c is the number of components and k_{ij} is a binary interaction parameter determined by fitting phase equilibrium data to the EoS. In general, the van der Waals mixing rules may represent well the phase behavior of nonpolar or slightly polar mixtures. However, it is not a case for the mixtures containing strong polar components or/and hydrogen-bonding compounds. As a consequence, there are various other mixing rules that have been proposed to improve the EoS for such complex systems. In recent years, several versions of EoS/A^E and EoS/G^E mixing rules were developed for highly nonideal systems. This type of mixing rules can be divided into three categories: (1) the infinite-reference-pressure mixing rules;[11−13] (2) the zero-reference-pressure mixing rules;[14−18] (3) the no-reference-pressure mixing rules.[19]

Chung and Twu[20] assumed $b = b_{vdw}$ to simplify the mixing rules of Twu et al.,[19] and successfully applied it to VLE and LLE calculations. These simplified mixing rules are given by

$$a^* = a_{vdw}^* + \frac{b_{vdw}^*}{C_v}\left[\frac{G^E}{RT} - \frac{G_{vdw}^E}{RT}\right] \quad (10)$$

$$b^* = b_{vdw}^* = \sum_{i=1}^{n_c} \sum_{j=1}^{n_c} x_i x_j b_{ij}^* \quad (11)$$

where

$$a^* = \frac{Pa}{R^2 T^2}, \quad b^* = \frac{Pb}{RT}, \quad b_{ij}^* = \frac{1}{2}(b_i^* + b_j^*) \quad (12)$$

$$C_v = \ln\left[\frac{v_{vdw}^*}{v_{vdw}^* + 1}\right], \quad v_{vdw}^* = \frac{v_{vdw}}{b_{vdw}} \quad (13)$$

$$\frac{G_{vdw}^E}{RT} = \frac{A_{vdw}^E}{RT} + \left(Z_{vdw} - \sum_{i=1}^{n_c} x_i Z_i\right) \quad (14)$$

and

$$\frac{A_{vdw}^E}{RT} = \sum_{i=1}^{n_c} x_i \left[\ln\left(\frac{b_i}{b_{vdw}}\right) + \ln\left(\frac{v_i^* - 1}{v_{vdw}^* - 1}\right)\right.$$
$$\left. + \frac{a_i}{RTb_i}\ln\left[\frac{v_i^* + 1}{v_i^*}\right] - \frac{a_{vdw}}{RTb_{vdw}}\ln\left(\frac{v_{vdw}^* + 1}{v_{vdw}^*}\right)\right] \quad (15)$$

In eq 13, C_v is a function of temperature. The v_{vdw}, a_{vdw}, b_{vdw}, and Z_{vdw} were calculated from the SRK equation with the van der Waals one-fluid mixing rules. In eq 10, the terms of $G^E/(RT)$ were calculated from an activity coefficient model such as the NRTL,[21] the UNIQUAC,[22] or the UNIFAC model.[23−25]

4. CORRELATION WITH THE SRK EQUATION OF STATE

In this section, the binary vapor−liquid and vapor−liquid−liquid equilibrium data of binary mixtures containing water, isopropyl alcohol, and isopropyl acetate were correlated with the SRK equation by using the S-, the K-, or the T-type α, and the vdW mixing rules or the Chung-Twu (CT) mixing rules to determine the optimal values of the binary interaction parameters.

4.1. Determination of Pure Component Parameter for α Function. The pure component parameters in the K- and the T-types α need to be determined prior to performing mixture property calculations. The SRK equation was defined as

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b)} \quad (16)$$

where $a = a_c \alpha$, and

$$a_c = 0.42747\frac{R^2 T_c^2}{P_c} \quad (17)$$

For both the S- and the T-types α, the value of b was calculated from the following equation:

$$b = 0.08664\frac{RT_c}{P_c} \quad (18)$$

The parameter b in the K-type α is an adjustable parameter which was determined by correlating vapor pressures of pure substance. The objective function of optimization for determination of pure component parameters is defined as

$$\pi = \sum_{k=1}^{n_p} \frac{|P_k^{calcd} - P_k^{expt}|}{P_k^{expt}} \quad (19)$$

where n_p is the number of data points. The physical properties of each pure compound are listed in Table 1. The optimized parameters and calculated results for each pure compound are reported in Table 2 and Table S1 (in the Supporting Information), respectively. Table S1 also lists the calculated results from the SRK equation by using the S-type α in

Table 1. Physical Properties and Parameters for the Constituent Compounds

compound	T_c (K)	P_c (MPa)	ω	UNIQUAC constants	
				r	q
methanol	512.64[a]	8.097[a]	0.565[a]	1.4311[b]	1.432[b]
ethanol	516.25[c]	6.3835[c]	0.6371[c]	2.1055[b]	1.972[b]
methyl acetate	506.80[a]	4.690[a]	0.3254[c]	2.8042[b]	2.576[b]
2-propanol	508.31[c]	4.7643[c]	0.6689[c]	2.7791[b]	2.508[b]
ethyl acetate	523.25[c]	3.8301[c]	0.3611[c]	3.4786[b]	3.116[b]
methyl propionate	530.60[a]	4.000[a]	0.349[a]	3.4786[b]	3.116[b]
1-butanol	563.05[a]	4.423[a]	0.590[a]	3.4543[b]	3.052[b]
PGME[d]	553.00[e]	4.340[e]	0.722[e]	3.6981[e]	3.288[e]
isopropyl acetate	532.00[e]	3.290[e]	0.368[e]	4.1522[b]	3.652[b]
1-pentanol	588.15[a]	3.909[a]	0.579[a]	4.1287[b]	3.592[b]
isopropyl propionate	554.97[f]	3.153[f]	0.431[g]	4.7976[h]	4.192[h]
PGMEA[i]	597.90[e]	3.009[e]	0.481[e]	5.0705[e]	4.432[e]
1-hexanol	611.40[a]	3.510[a]	0.573[a]	4.8031[b]	4.132[b]
butyl propionate	596.0[j]	2.56[j]	0.372[j]	5.5017[e]	4.736[e]
pentyl acetate	600.5[j]	2.68[j]	0.448[e]	5.5018[b]	4.736[b]
ethyl benzoate	668.70[k]	2.320[k]	0.480[k]	5.5992[b]	4.388[b]
water	647.29[c]	22.09[c]	0.3442[c]	0.9200[b]	1.400[b]

[a]Taken from Poling et al.[26] [b]Taken from Sorensen and Arlt.[27] [c]Taken from Daubert and Danner.[28] [d]Propylene glycol monomethyl ether. [e]Taken from Aspen Property Databank. [f]Estimated from the Joback method.[29] [g]Estimated from the definition of Pitzer et al.[30] [h]Estimated from Bondi method.[31] [i]Propylene glycol monomethyl ether acetate. [j]Taken from the TRC Tables.[32] [k]Taken from the Korea Thermophysical Properties Databank.[33]

comparison with the K-type and the T-type α. As shown in Table S1, the deviations of the SRK-S equation were obviously

Table 2. Optimized Values of the Parameters in α Function for Pure Compounds

compound	K-type α (SRK-K)			T-type α (SRK-T)		
	a_0	b	c_1	L	M	N
water	9.3810	42.1301	1.1927	0.412	0.876	2.20
methanol				0.562	0.886	2.34
ethanol				1.083	0.966	1.33
methyl acetate				0.381	0.829	2.01
isopropyl alcohol	14.2895	65.5226	1.3795	1.070	0.880	1.35
ethyl acetate				0.564	0.831	1.60
methyl propionate				0.327	0.818	2.24
1-butanol				1.202	0.779	1.09
PGME				0.826	0.989	2.10
isopropyl acetate	20.9288	89.5006	0.9488	0.527	0.814	1.67
1-pentanol				1.209	0.761	1.07
isopropyl propionate				0.685	0.998	1.83
PGMEA				0.416	0.808	2.28
1-hexanol				1.151	0.694	1.10
butyl propionate				1.004	0.543	0.94
pentyl acetate				0.752	0.802	1.38
ethyl benzoate				1.141	1.077	1.19

large, and the overall average absolute deviation (AAD) is as high as 8.0%. It is also shown that the calculated vapor pressures from the SRK-K equation are very sensitive to the values of parameter a_0, b, and c_1. The calculated deviations from the SRK-T equation are no greater than 1.7% with an overall AAD of 0.5%. Figure 1 shows the comparison of the experimental vapor pressures with the calculated values from the SRK-T equation, indicating that the calculated and experimental values agree satisfactorily well.

4.2. Phase Equilibrium Calculation with the vdW Mixing Rules. To evaluate the applicability of the above-mentioned models for VLE and VLLE calculations, we selected water + isopropyl alcohol + isopropyl acetate as a model system. In the first step, the binary interaction parameters of the constituent binaries, isopropyl alcohol + water, isopropyl alcohol + isopropyl acetate, and isopropyl acetate + water, were determined and then the determined binary parameters were used to estimate the VLLE properties for the ternary system.

At VLE, the equality of the fugacities of each species i in the vapor and the liquid phases should be obeyed:

$$\hat{f}_i^{\mathrm{V}} = \hat{f}_i^{\mathrm{L}} \Rightarrow \hat{\phi}_i^{\mathrm{V}} y_i P = \hat{\phi}_i^{\mathrm{L}} x_i P \tag{20}$$

where $\hat{\phi}_i^{\mathrm{V}}$ and $\hat{\phi}_i^{\mathrm{L}}$ are the fugacity coefficients of species i in vapor and liquid phases, respectively. The value of fugacity coefficient was calculated from the selected equation of state. The objective function of the optimal parameter determination is given by

$$\pi = \sum_{k=1}^{n_{\mathrm{p}}} \left(\frac{|P_k^{\mathrm{calcd}} - P_k^{\mathrm{expt}}|}{P_k^{\mathrm{expt}}} + |y_{1,k}^{\mathrm{calcd}} - y_{1,k}^{\mathrm{expt}}| \right) \tag{21}$$

At VLLE, the equality of fugacities of each species i in different phases should be followed:

$$\hat{f}_i^{\mathrm{V}} = \hat{f}_i^{\mathrm{I}} = \hat{f}_i^{\mathrm{II}} \Rightarrow \hat{\phi}_i^{\mathrm{V}} y_i P = \hat{\phi}_i^{\mathrm{I}} x_i^{\mathrm{I}} P = \hat{\phi}_i^{\mathrm{II}} x_i^{\mathrm{II}} P \tag{22}$$

where $\hat{\phi}_i^{\mathrm{V}}$, $\hat{\phi}_i^{\mathrm{I}}$ and $\hat{\phi}_i^{\mathrm{II}}$ were calculated from the fugacity coefficient expression of the SRK equation. The isothermal flash calculation procedure[35] was used in the VLLE calculation. In the flash calculations, the feed composition "z_i" was estimated from the average of the experimental liquid compositions of the coexistent organic phase and aqueous phase. Table S2 (in the Supporting Information) and Table 3 report the binary interaction parameters and the calculated results for isopropyl alcohol + water, isopropyl alcohol + isopropyl acetate, and isopropyl acetate + water, respectively. According to these calculated results, we found the following: (1) Effect of the binary interaction parameter k_{ij}. The calculated results were very sensitive to the value of the binary interaction parameter. (2) Effect of α function. As shown from Table S2 and Table 3, the calculated results from the SRK-S equation are the worst, especially for the water-containing systems, such as isopropyl alcohol + water and isopropyl acetate + water. (3) Using cubic equation of state with an appropriate α function and the quadratic mixing rules may reasonably represent the VLE and the VLLE behaviors of the binary systems.

The binary interaction parameters (k_{ij}) of constituent binaries as given in Table S2 and Table 3 were used to estimate the VLLE properties of the ternary system. The estimated results are presented in Table S3 (in the Supporting Information). Figure S1 (in the Supporting Information) shows the comparison of the estimated results with the experimental values. The phase equilibrium properties of the multi-
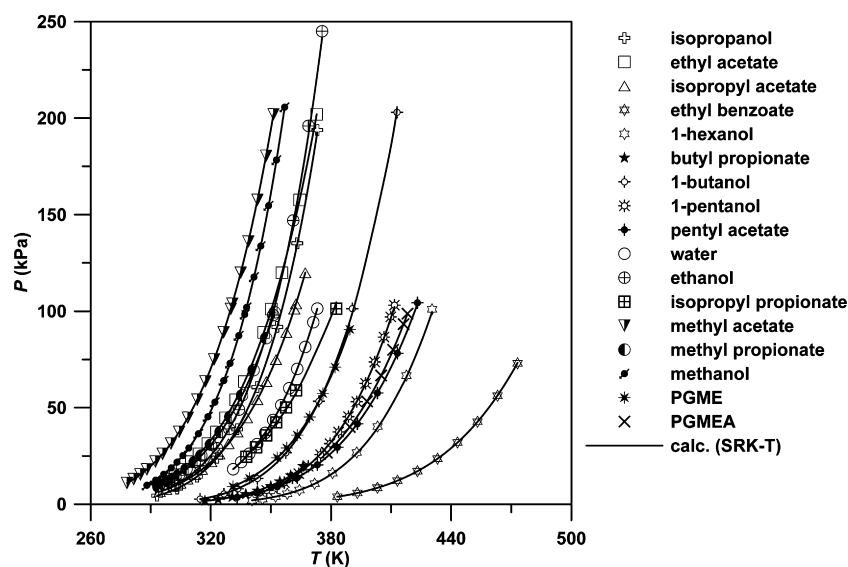
Figure 1. Comparison of the calculated vapor pressures with the experimental values of pure substances.

Table 3. Correlated VLLE Results for Isopropyl Acetate (1) + Water (2)[a]

α function	mixing rules	parameters	$10^2\,\Delta P/P$ AAD[b]	organic phase $10^2\Delta x^{\mathrm{I}}$ AAD[c]	aqueous phase $10^2\Delta x^{\mathrm{II}}$ AAD[c]	vapor phase $10^2\Delta y$ AAD[c]
S-type	vdW	$k_{ij} = 0.0$	1.1	7.9	0.35	4.7
		$k_{ij} = -0.126$	6.2	0.8	0.35	2.8
K-type	vdW	$k_{ij} = 0.0$	d	d	d	d
		$k_{ij} = 0.125$	1.4	1.2	0.36	1.2
T-type	vdW	$k_{ij} = 0.0$	4.1	7.2	0.35	0.9
		$k_{ij} = -0.109$	1.6	0.6	0.35	1.7
	CT-NRTL[e]	$\tau_{12},\ \tau_{21}$	1.2	0.4	0.01	1.4
	CT-UNIQUAC[e]	$\tau_{12},\ \tau_{21}$	1.3	0.4	0.01	1.3

[a]The binary VLLE data were taken from Hong et al.[36] [b]$\Delta P/P$ AAD $= (1/n_{\mathrm{p}})\sum_{k=1}^{n_{\mathrm{p}}}(|P_k^{\mathrm{calcd}} - P_k^{\mathrm{expt}}|/P_k^{\mathrm{expt}})$, where n_{p} is the number of data points. [c]ΔM AAD $= (1/n_{\mathrm{p}} \times n_{\mathrm{c}})\sum_{k=1}^{n_{\mathrm{p}}}(\sum_{j=1}^{n_{\mathrm{c}}}(|M_j^{\mathrm{calcd}} - M_j^{\mathrm{expt}}|)_k)$, where n_{c} is the number of components and M represents x^{I}, x^{II}, or y. [d]The calculation was unable to be converged. [e]Parameters were calculated from eqs 27 to 30.

component system may be estimated by using the parameters determined from the VLE or VLLE data of the constituent binaries. Unfortunately, the estimated results reveal that the phase boundary of the LLE can not be accurately predicted from the equation of state.

4.3. Phase Equilibrium Calculation with CT Mixing Rules. As mentioned above, the estimated results are unsatisfactory from the SRK equation with the vdW mixing rules and the binary interaction parameters determined from the phase equilibrium data of the constituent binaries. In this section, the SRK-T EoS with the CT mixing rules is tested for the same systems. The values of $\ln\gamma_i$ and G^{E}/RT in the CT mixing rules[20] were calculated from an activity coefficient model including the NRTL[21] and the UNIQUAC[22] models. The value of $\hat{\phi}_i^{\mathrm{L}}$ of the CT mixing rules[20] was calculated from the SRK equation with the vdW mixing rules. The adjustable binary interaction parameters of the CT mixing rules are the parameters of the embedded activity coefficient model. To extend the applicable temperature range, the parameters may be treated as linearly temperature-dependent. The calculated results are discussed as follows.

(1) VLE calculation. Because the temperature range of VLE data for isopropyl acetate + isopropyl alcohol is narrow, the parameters of this system are treated as temperature-independent, in which two adjustable parameters are to be determined. Although the temperature range of VLE data of isopropyl alcohol + water is only from 318.15 to 348.15 K, the

correlated results are unsatisfactory with the use of only two temperature-independent parameters. To improve the accuracy of correlation, the parameters τ_{21} of the NRTL model and τ_{12} of the UNIQUAC model were treated as linearly temperature-dependent. In other words, three adjustable parameters were determined from the VLE calculation for isopropyl alcohol + water. The optimal values of the parameters are as follows.

NRTL model:

$$\tau_{12} = -\frac{38.38}{T} \tag{23}$$

$$\tau_{21} = 3.1792 - \frac{243.2228}{T} \tag{24}$$

UNIQUAC model:

$$\tau_{12} = \exp\left(-0.8689 + \frac{183.3552}{T}\right) \tag{25}$$

$$\tau_{21} = \exp\left(\frac{73.90}{T}\right) \tag{26}$$

(2) VLLE calculation. The model parameters of isopropyl acetate + water are treated as linearly temperature-dependent at temperatures ranging from 308.15 to 358.15 K, which are given as follows.

Table 4. Results of VLLE Prediction from the SRK Equation for the Constituent Binaries

mixture[a]	n_p	SRK-S/CT-UNIFAC-Lyngby				SRK-T/CT-UNIFAC-Lyngby			
		$10^2\Delta P/P$ AAD[b]	organic phase $10^2\Delta x^{\mathrm{I}}$ AAD[b]	aqueous phase $10^2\Delta x^{\mathrm{II}}$ AAD[b]	vapor phase $10^2\Delta y$ AAD[b]	$10^2\Delta P/P$ AAD[b]	organic phase $10^2\Delta x^{\mathrm{I}}$ AAD[b]	aqueous phase $10^2\Delta x^{\mathrm{II}}$ AAD[b]	vapor phase $10^2\Delta y$ AAD[b]
M1	9	5.3	2.5	0.45	2.3	1.1	2.4	0.45	2.0
M2	11	5.2	1.9	0.19	3.3	1.4	1.9	0.19	1.5
M3	9	7.4	6.0	0.78	1.8	1.4	6.0	0.79	1.1
M4	9	7.1	3.7	0.16	1.0	1.2	3.7	0.16	1.4
M5	6	9.6	1.8	0.01	2.9	3.0	1.8	0.01	0.7
M6	2	6.0	1.1	0.02	6.2	0.9	1.1	0.02	0.4
M7	8	13.2	6.2	1.62	1.8	1.5	6.2	1.62	0.6
M8	7	4.6	2.1	0.07	3.1	1.8	2.1	0.07	5.0
M9	4	7.8	6.8	6.40	1.6	1.5	3.1	0.57	1.7
M10	11	10.9	6.7	0.05	2.2	6.4	6.7	0.05	3.4
overall AAD		7.8	4.1	0.71	2.4	2.2	3.9	0.41	1.9

[a]M1, ethyl acetate (1) + water (2);[37] M2, isopropyl acetate (1) + water (2);[36] M3, 1-butanol (1) + water (2);[39] M4, 1-pentanol (1) + water (2);[40] M5, pentyl acetate (1) + water (2);[40] M6, butyl propionate (1) + water (2);[39] M7, water (1) + PGMEA (2);[38] M8, water (1) + methyl propionate (2);[41] M9, water (1) + methyl acetate (2);[41] M10, water (1) + isopropyl propionate (2).[34] [b]As given in Table 3.

NRTL model:

$$\tau_{12} = -3.4323 + \frac{1299.22}{T} \tag{27}$$

$$\tau_{21} = 9.8673 - \frac{1553.01}{T} \tag{28}$$

UNIQUAC model:

$$\tau_{12} = \exp\left(2.9153 - \frac{1360.60}{T}\right) \tag{29}$$

$$\tau_{21} = \exp\left(-2.1142 + \frac{535.31}{T}\right) \tag{30}$$

The above-mentioned results of VLE and VLLE calculations are also listed in Supporting Information, Table S2 and Table 3, respectively. As can be seen from the tables, the phase behavior of the binary systems can be represented well by the SRK equation of state with the T-type α and the CT mixing rules. In order to further evaluate the performance of the model for predicting the ternary VLLE properties, the parameters of the constituent binaries were used in the VLLE properties estimation. The predicted results are given in Table S3 and Figure S1. Although the results of binary data correlation are satisfactory, this method can not reasonably estimate the liquid−liquid phase boundary of the ternary VLLE system. It is even worse that the SRK-T/CT-NRTL model predicts the system forming a homogeneous liquid phase at 338.15 and 358.15 K for water + isopropyl acetate + isopropyl alcohol. The SRK-T/CT-UNIQUAC model obviously overestimates the liquid−liquid immiscible region at all temperatures. It is shown that the EoS/A^{E} models are still needed to be further improved for multicomponent VLLE calculation.

5. APPLICATION OF SRK-T/CT-UNIFAC TYPE MODEL TO MULTIPHASE EQUILIBRIUM PREDICTION

The SRK equation with the S- or the T-type α function and the CT mixing rules embedded in the UNIFAC model (SRK-S/CT-UNIFAC or SRK-T/CT-UNIFAC) was used to improve the predictive capability of the equation of state for multi-component multiphase calculation. The SRK-T/CT-UNIFAC model does not contain any adjustable interaction parameters for mixture property calculations. The pure component parameters are the only adjustable parameters, which were often determined from vapor pressure data for each pure substance.

5.1. Prediction of VLE and VLLE Properties for Binary Systems. Table 4 and Table S4 (in the Supporting Information) present the results of VLLE and VLE calculations for the binary systems, respectively, from the SRK equation with the CT-UNIFAC-Lyngby mixing rules and the S- or the T-type α. Supporting Information Table S4 also lists the calculated results from the UNIFAC-Lyngby[25] model for comparison. Figures S2 to S4 (in the Supporting Information) show the comparison of the predicted results with the experimental data for three binary systems. On the basis of these calculated results we found that (1) the SRK-T/CT-UNIFAC-Lyngby model could satisfactorily predict the binary VLE and VLLE properties. As shown in Supporting Information Table S4, the overall AADs of equilibrium pressure and vapor-phase composition were 2.0% and 0.0093, respectively, from the UNIFAC-Lyngby model for the binary VLE system. When the SRK-T/CT-UNIFAC-Lyngby model was used to estimate the binary VLE properties, the grand AADs of equilibrium pressure and vapor-phase composition can be reduced to 1.8% and 0.0090, respectively. As shown in Table 4, the accuracy of the SRK-T/CT-UNIFAC-Lyngby model is even better than that of the SRK-S/CT-UNIFAC-Lyngby model for the estimation of the VLLE properties. (2) As seen from Supporting Information Table S4, the calculated results from the SRK equation with different α functions are substantially different for the aqueous systems (including M4, M5, M7, and M8). As shown in Supporting Information Figures S3 and S4, large deviations occur in the region of near pure water from the SRK-S/CT-UNIFAC-Lyngby model, resulting in underestimation of equilibrium pressures from this model.

Since the SRK-S model significantly underestimates the vapor pressures of pure water, this study further takes the variable m of the SRK-S/CT-UNIFAC-Lyngby model as an adjustable parameter, and redetermines its value by correlating the vapor pressure data of pure water. The values m of other pure substances are kept the same as those in the original S-type α. We denote this treatment as the MS-type α. The optimal value m of the MS-type α for pure water is 0.96. The calculated results from the SRK-MS equation are listed and
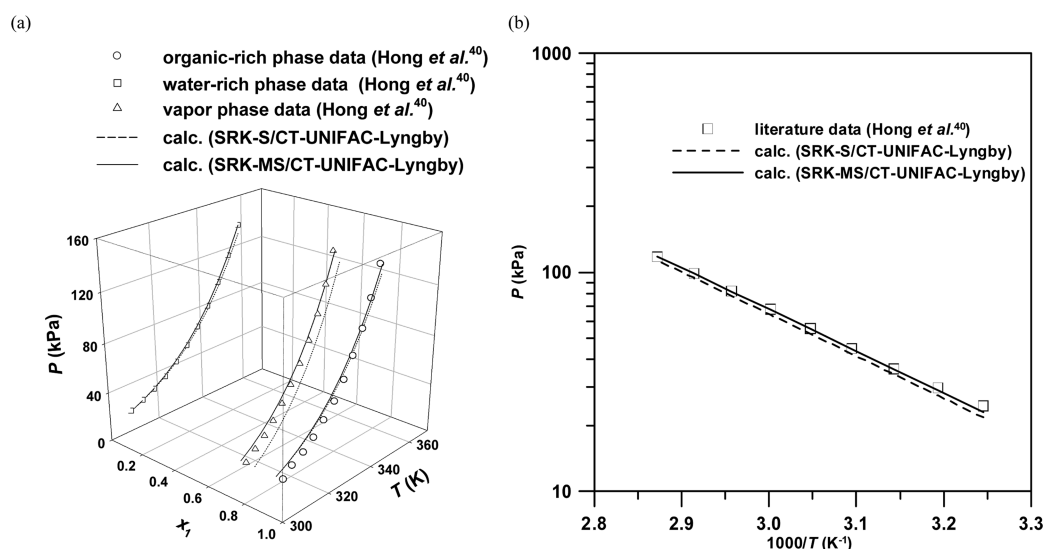
Figure 2. (a) Comparison of the VLLE prediction from the SRK equation with the experimental data for isopropyl acetate (1) + water (2). (b) $P-T$ diagram for isopropyl acetate (1) + water (2).

Table 5. Predicted Results from the SRK Equation for Ternary LLE Systems

		SRK-T/CT-UNIFAC-LL			SRK-T/CT-UNIFAC-Lyngby		
mixture[a]	T (K)	n_g[b]	organic phase $10^2 \Delta x^I$ AAD[c]	aqueous phase $10^2 \Delta x^{II}$ AAD[c]	n_g[b]	organic phase $10^2 \Delta x^I$ AAD[c]	aqueous phase $10^2 \Delta x^{II}$ AAD[c]
M1[d]	283.15−323.15	8	2.9	0.8	8	3.2	1.3
M2[d]	283.15−323.15	9	2.9	2.2	9	11.9	3.7
M3$_d$	283.15−323.15	10	1.6	0.9	10	3.5	1.0
M4[e]	283.15−323.15	7	2.8	0.9	10	3.6	1.5
overall AAD			2.5	1.2		5.8	1.9

[a]M1, water + ethanol +1-hexanol;[42] M2, water + ethanol + butyl propionate;[42] M3, water + isopropyl alcohol + ethyl acetate;[43] M4, water + isopropyl alcohol + isopropyl acetate.[43] [b]n_g is the number of calculated points. The calculated deviations only cover the data points which are in the predicted immiscible region; that is, n_g may not be equal to the number of experimental data points n_p. [c]ΔM AAD = $(1/n_g \times n_c) \sum_{k=1}^{n_g} (\sum_{j=1}^{n_c} (|M_j^{calcd} - M_j^{expt}|)_k)$, where n_c is the number of components and M represents x^I or x^{II}.

compared with those from the SRK-S equation in Table S5 (in the Supporting Information). Figures S3 and S4 also show the calculated results from the SRK-MS equation for ethanol + water and isopropyl alcohol + water, respectively. Figure 2 presents the predicted results for the VLLE properties of isopropyl acetate + water. The SRK-MS equation is obviously better than the SRK-S equation for aqueous systems, particularly, in estimation of equilibrium pressure and vapor-phase composition. For the binary systems M1, M2, M3, and M4 as reported in Supporting Information Table S5, the overall AADs from the SRK-S/CT-UNIFAC-Lyngby model are 6.6% and 0.031 for equilibrium pressure and vapor-phase composition, respectively. For the same systems, the overall AADs from the SRK-MS/CT-UNIFAC-Lyngby model are reduced to 3.0% and 0.015 for equilibrium pressure and vapor-phase composition, respectively. Although the SRK-MS/CT-UNIFAC-Lyngby model cannot make significant improvement on the estimation of the liquid-phase compositions, the accuracies of the calculated equilibrium pressure and the vapor-phase composition were substantially improved. Figure S5 (in the Supporting Information) shows the values of α varying with the reduced temperature for the S- and the MS-types for water. It is indicated that the accuracy of calculated vapor pressure of water is highly sensitive to the value of α used in the calculation.

5.2. Prediction for Ternary LLE and VLLE Properties. The SRK-MS model improved the vapor pressure calculation of

pure water and the VLE and the VLLE calculations for the binary aqueous systems, but its accuracy is still worse than that of SRK-T equation. As a consequence, the SRK-T equation was used here for estimating the LLE and VLLE properties of several selected aqueous ternary systems. Table 5 and Table S6 (in the Supporting Information) list the predicted results for the ternary LLE and VLLE systems, respectively. Figure 3 shows the estimated results for the ternary LLE systems by using the SRK-T/CT-UNIFAC type models, where the values of G^E in the CT mixing rules were calculated from either the UNIFAC-LL[24] or the UNIFAC-Lyngby[25] model. Figures 4 and 5 present the predictions for the ternary VLLE systems by using either the SRK-T/CT-UNIFAC-LL or the SRK-T/CT-UNIFAC-Lyngby model. According to these graphs, some findings are addressed as follow: (1) The estimated results from the SRK-T/CT-UNIFAC-LL model are better than those from the SRK-T/CT-UNIFAC-Lyngby model for the ternary LLE systems. (2) This study also attempts to test the applicability of the SRK-T/CT-UNIFAC-LL model for estimating the ternary VLLE properties. In general, the SRK-T/CT-UNIFAC-Lyngby model yields better prediction for the ternary VLLE prediction as shown in Supporting Information Table S6. It should also be noted that the SRK-T/CT-UNIFAC-LL model may be preferable for the VLLE property predictions for the type-II LLE systems, such as M9 and M10 in Table S6.
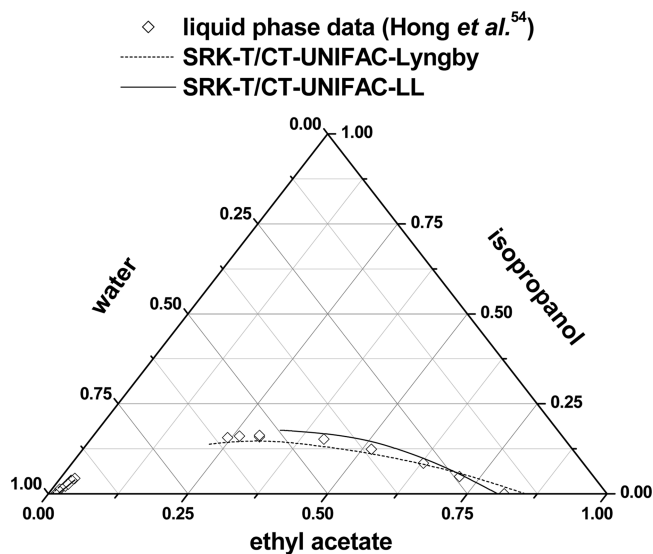
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◇ liquid phase data (Hong *et al.*[54])
········ SRK-T/CT-UNIFAC-Lyngby
——— SRK-T/CT-UNIFAC-LL

Figure 3. Comparison of the LLE prediction from the SRK equation with the experimental data for water + isopropyl alcohol + ethyl acetate at 323.15 K.
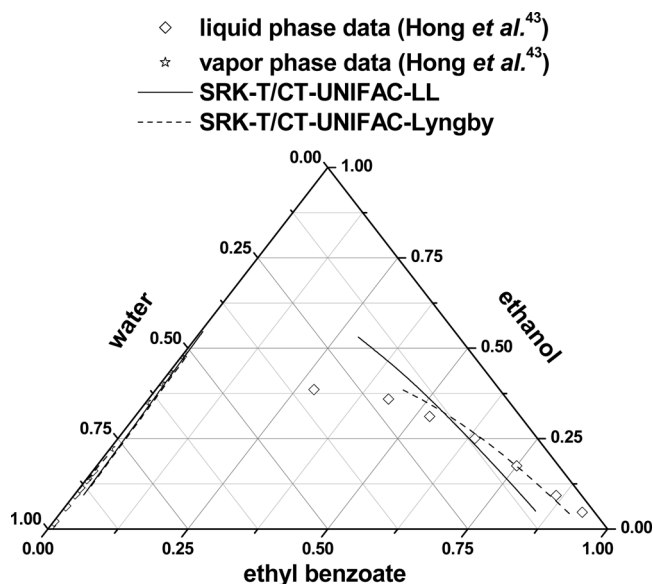
◇ liquid phase data (Hong *et al.*[43])
☆ vapor phase data (Hong *et al.*[43])
——— SRK-T/CT-UNIFAC-LL
------ SRK-T/CT-UNIFAC-Lyngby

Figure 4. Comparison of the VLLE prediction from the SRK equation with the experimental data for water + ethanol + ethyl benzoate at 353.15 K.

6. CONCLUSION

The SRK equation of state with several versions of α function and mixing rules have been tested with the VLE and VLLE data of binary and ternary mixtures containing water, alcohols, and esters. According to the results of the calculations, we found that the SRK-T/CT-UNIFAC-Lyngby model (T-type α function, CT mixing rule with UNIFAC-Lyngby) is applicable to the prediction of the VLE and the VLLE properties for the binary and the ternary aqueous systems. For the VLLE properties prediction of the type-II LLE systems, however, the SRK-T/CT-UNIFAC-LL model (T-type a function, CT mixing rule with UNIFAC-LL) may be preferable. The fluid-specific parameters, determined from vapor pressure data of each pure component, are the only required input-variables of these two methods for the phase equilibrium calculations.
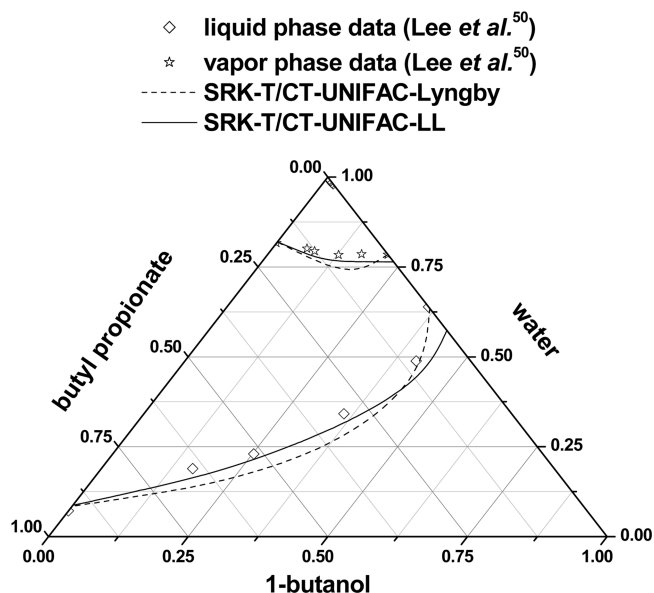
◇ liquid phase data (Lee *et al.*[50])
☆ vapor phase data (Lee *et al.*[50])
------ SRK-T/CT-UNIFAC-Lyngby
——— SRK-T/CT-UNIFAC-LL

Figure 5. Comparison of the VLLE prediction from the SRK equation with the experimental data for water +1-butanol + butyl propionate at 363.15 K.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
Supplementary tables and figures as described in the text have been prepared. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: mjlee@mail.ntust.edu.tw. Tel.: 886-2-2737-6626. Fax: 886-2-2737-6644.

Notes
The authors declare no competing financial interest.

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■ NOMENCLATURE

a, b = parameters of cubic equation of state
a_{ij} = parameters of the NRTL model, $(g_{ij} - g_{jj})/R$ (K)
b_{ij} = parameters of the UNIQUAC model, $(u_{ij} - u_{jj})/R$ (K)
G = Gibbs free energy
A = Helmholtz free energy
C_v = zero pressure function
f = fugacity
L, M, N = parameters in the T-type α function α
n_c = number of components
n_g = number of calculated points
n_p = number of data points
P = pressure (kPa)
q = surface area parameter of the UNIQUAC model
r = volume parameter of the UNIQUAC model
R = gas constant (J mol^{-1} K^{-1})
T = temperature (K)
V = molar volume (cm^3 mol^{-1})
v^* = reduced liquid molar volume

ν^*_{vdw} = reduced liquid molar volume of vdW fluid
x = mole fraction in liquid phase
y = mole fraction in vapor phase
Z = compressibility factor
α = temperature-dependent function
γ = activity coefficient
π = objective function
ϕ_i = fugacity coefficient of compound i
$\hat{\phi}_i$ = fugacity coefficient of component i in mixtures
ω = acentric factor

Subscripts

c = critical property
vdw = van der Waals
i, j = components i and j
ij = i–j pair interaction
m = mixture

Superscripts

E = excess property
* = reduced property
calcd = calculated
expt = experimental
lit = literature
L = liquid phase
S = saturation
I = organic phase
II = aqueous phase

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