Mixing Rules for van der Waals-Type Equations of State Based on Activity-Coefficient Models

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A new approach for incorporation of the excess free energy from an activity coefficient model (ACM) into an equation of state (EOS) has been proposed. The approach is based on a concept that any ACM is valid at a low but finite value of compressibility factor. This condition allows us to analyze the "infinite pressure" approximation in a general way. It is shown that the "infinite pressure" approach neglects the contribution of the repulsive term of the EOS to the excess free energy of a mixture. This, in turn, introduces inconsistency which results in the difference in the calculated excess free energy of the EOS and the base ACM. The new approach defines parameter a of the EOS as an implicit function of compositions and temperature, thus requiring an iterative procedure using the "infinite pressure limit" as a starting point. The new approach can be modified to provide the correct composition dependence of a mixture second virial coefficient. Applicability of the new method has been tested for binary systems under vapor–liquid and liquid–liquid equilibrium conditions.

KEY WORDS: activity coefficient models; equation of state; excess functions; mixing rules.

1. INTRODUCTION

The various approaches to connect pressure-independent activity-coefficient models (ACMs) with an equation of state have been reviewed recently by Heidemann [1] and Orbey and Sandler [2]. Such connection has the following goals:

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1. to make EOS mixing rules more flexible than the traditional one-fluid mixing rules;

2. to make qualitatively correct extrapolation into the range of elevated temperatures beyond the critical temperature of a volatile component where ACM is not valid;

3. to avoid "Michelsen–Kistenmacher syndrome," from which many "flexible" empirical mixing rules suffer (see, for example, Ref. 3);

4. to use extensive data banks of ACM parameters.

Any approach for incorporating ACM into EOS should imply equivalence of excess free energy (Gibbs or Helmholtz) defined by both models. To provide this equivalence, one has to eliminate density as an independent variable to reduce free energy from a function of density, temperature, and compositions to a function of temperature and compositions only. Therefore, it is necessary to define density (or pressure) by some suitable condition to eliminate one degree of freedom. This condition should be valid at a low value of pressure to be consistent with the range of validity of ACM [4]. The variety of ways in which this condition is defined produces the variety of approaches for incorporating ACM into EOS and presents a key to the success or failure of any approach. The two commonly used approaches will be briefly discussed below.

2. "INFINITE PRESSURE" APPROACH

The extensive series of investigations in this field was initiated by the pioneering work of Huron and Vidal [5]. These authors defined Gibbs free energy departure as the difference in Gibbs energy of the real system and that of the ideal gas at the same *pressure*, temperature, and compositions. This definition differs from the standard definition in that the ideal gas state is at the system pressure. This definition helps avoid singularity at the limit of high density, but produces some restrictions and inconsistencies. In the strictest sense, the only possibility to realize this condition for a pure component implies that the real system is a saturated liquid and the ideal gas is a saturated vapor. In other words, the consideration should be restricted by the range of low pressures where a saturated vapor obeys the ideal gas law. Moreover, the condition of the same pressure, temperature, and compositions for a liquid system and the ideal gas is not applicable for any mixture because of the difference in bubble and dew curves; this condition is valid for a mixture at an azeotropic point only.

Wong and Sandler [6] later showed that it is more advantageous to use Helmholtz free energy instead of Gibbs free energy. The Helmholtz free

energy departure for any van der Waals-type EOS using the definition mentioned above could be written as

$$\Delta A = -(a/b)\, f(b/V) - RT \ln[\, p(V, T)(V-b)/(RT)\,] \qquad (1)$$

The expression for $f(b/V)$ depends on a given form of the EOS (van der Waals (vdW), Redlich Kwong (RK), Peng-Robinson (PR), etc.). Equation (1) is assumed to be valid for a mixture and any of its constituent components. The next step of incorporating ACM into EOS is to eliminate volume as an independent variable in Eq. (1). Huron and Vidal chose the simplest way for this by introducing the "infinite pressure limit"; that is, at infinite pressure,

$$V = b \qquad (2)$$

This condition necessarily implies that the free energy departure at infinitely high pressure is not substantially different from the value defined by Eq. (1) at low pressure. Note also that the "infinite pressure limit" is inconsistent with the definition of free energy departure used to derive Eq. (1) because it is not realistic to assume an ideal-gas state at infinite pressure. Although being extremely crude, this assumption does not affect drastically the final result. The reason will be explained below.

Substituting Eq. (2) into Eq. (1) results in the simple expression,

$$\Delta A/c = -a/b \qquad (3)$$

where c is a constant depending on a given EOS. Applying Eq. (3) for both the mixture and its constituent components yields for the excess Helmholtz free energy:

$$A_{ex}/c = \sum_i x_i (a/b)_i - (a/b)_m \qquad (4)$$

Equation (4) is the final result of the "infinite pressure" approach. It connects excess free energy with the ratio $(a/b)_m$ for the mixture EOS through compositions and known parameters $(a/b)_i$ of the pure components. Huron and Vidal assumed linear dependence of b_m on compositions; substituting A_{ex} from an ACM into Eq. (4), they obtained a new mixing rule for parameter a_m expressed in terms of ACM. They also pointed out that the EOS based on the new mixing rule did not reproduce the base ACM result if the original ACM parameters were used. They attributed this to the approximation (Eq. (2)). Therefore, they reregressed the ACM parameters used in the new mixing rule (Eq. (4)) and obtained a satisfactory fit of experimental data.

Wong and Sandler [6] revitalized this approach in 1992. They used two constraints for the EOS parameters to arrive at correct composition dependence of the mixture second virial coefficient which commonly is not satisfied by Eq. (4). They introduced an adjustable parameter formally related to the second virial coefficient but, in fact, assigned to correct the approximation (Eq. (2)). Adjusting this parameter replaced the necessity to redetermine parameters of the ACM.

3. "ZERO PRESSURE" APPROACH

Another fundamental approach to incorporate ACM into EOS was developed by Mollerup [4], Heidemann and Kokal [7], Michelsen [8], and Dahl and Michelsen [9]. The approach uses the "zero pressure" condition to eliminate density as an independent variable:

$$Z = 0 \tag{5}$$

This condition is consistent with the validity range of any ACM. The most popular variant of the "zero pressure" approach—MHV2 [9] successfully reproduces base ACM results. However, some problems exist with calculations at elevated temperatures. Although Eq. (5) can be solved over a wide range of the reduced inverse temperature $\alpha = a/(bRT)$ (almost up to the critical point where $\alpha \approx 5$), the authors pointed out that the usage of direct solutions in the range of $\alpha = 6$ to 9 does not provide good results. The probable reason is the significant difference in the value of the real liquid density at high temperature (and pressure) and the value defined by Eq. (5). They proposed a quadratic function of α in the range of $\alpha = 9$ to 14, then extrapolate the function into the range of low α values. The proposed extrapolation to high temperatures creates the obvious problem for applicability of the MHV2 model to any three-parameter cubic EOS.

4. "FINITE PRESSURE" APPROACH

We proposed a new approach for incorporating ACM into EOS. Analysis of this approach explains the reason of partial success and common failure of the "infinite pressure" approach. It is based on a condition for density which is almost identical to Eq. (5) at low temperatures (and pressures) but provides substantially nonzero pressure at high temperatures including the near critical range thus avoiding the problem related to the "zero pressure" approach.

The main idea of the present approach is to reduce the degrees of freedom of EOS by defining a condition in which the compressibility factor

is equal to a small but finite value. We chose the dimensionless "free volume" as the suitable value, thus

$$Z(v_f, T) = v_f \qquad (6)$$

where $v_f = 1 - b/V$ and $b < V$.

This condition implies validity of an ACM in the range of compressiblity factor equal to Z as calculated by Eq. (6). This choice brings algebraic convenience and looks reliable in a physical aspect; it provides increasing pressure with increasing temperature along the cross section of the thermodynamic surface defined by Eq. (6). Therefore, it could be considered as the better basis for extrapolation to high temperatures. Note that pressures of pure components and a mixture along this cross section are different and appear to violate the definition of an excess function, which should be obtained at the same pressure and temperature for a mixture and its constituent components. However, the problem does not really exist due to independence of thermodynamic functions on pressure for liquids at low pressures. The possible deviation has the same order of magnitude as the error due to the re-assignment of an ACM to the excess Helmholtz free energy instead of the excess Gibbs free energy. We can state that validity of the approach based on Eq. (6) has no additional restrictions than any ACM.

We will consider the excess Helmholtz free energy of a liquid mixture calculated by an EOS of the van der Waals type under the condition of Eq. (6). The Helmholtz free energy departure for pure components and a mixture could be defined as a difference in values of the Helmholtz free energy of a real system and the ideal gas as the system of zero density at the same temperature and compositions. Therefore,

$$\Delta A = RT \int_0^\rho (Z - 1) \, d\rho/\rho \qquad (7)$$

and, for any EOS of van der Waals type,

$$\Delta A = - RT \ln(v_f) - (a/b) \, f(v_f) \qquad (8)$$

We will use the Redlich–Kwong–Soave (RKS) EOS as an illustrative example:

$$\Delta A = - RT \ln(v_f) - (a/b) \ln(2 - v_f) \qquad (9)$$

Using the condition of Eq. (6) to express RT in terms of v_f

$$RT = (a/b) \, v_f/[(1 + v_f)(2 - v_f)]$$

one can obtain:

$$\Delta A/c = -(a/b)[1 - \varphi(v_f)/c] \tag{10}$$

where $c = \ln 2$, and

$$\varphi(v_f) = -v_f \ln(v_f)/[2(1 + v_f)(1 - v_f/2)] - \ln(1 - v_f/2) \tag{11}$$

The first term in Eq. (11) corresponds to the repulsive contribution of the EOS. The second term is the small part of the attractive contribution (the main part of the attractive contribution is represented by unity in the square brackets of Eq. (10)). The first term is substantially larger than the second term when $v_f \ll 1$ which is common in a liquid state. Therefore, the function $\varphi(v_f)$ is contributed mostly by the repulsive intermolecular forces.

By setting v_f to zero, $\varphi(v_f)$ becomes zero, and Eq. (10) reduces to the original Huron–Vidal result (Eq. (3)). However, such conversion is inconsistent because Eq. (10) has been derived using Eq. (6) which is not applicable at $v_f = 0$ because the compressibility factor Z of any EOS goes to infinity at $v_f = 0$. In other words, Eq. (6) has no solution at $v_f = 0$.

However, we can show that Eq. (4) of Huron-Vidal can be obtained using another assumption. Based on Eq. (10), the expression for A_{ex} is

$$A_{ex}/c = \left(\Delta A_m - \sum_i x_i \Delta A_i\right)\Big/c$$

$$= \sum_i x_i(a/b)_i [1 - \varphi(v_{fi})/c] - (a/b)_m [1 - \varphi(v_{fm})/c] \tag{12}$$

Equation (12) can be converted to the Huron–Vidal result (Eq. (4)) by setting

$$\Delta A_{ex} = (a/b)_m \varphi(v_{fm}) - \sum_i x_i(a/b)_i \varphi(v_{fi}) = 0 \tag{13}$$

Although both Eqs. (2) and (13) allow Eq. (4) to be obtained from Eqs. (10) and (12), the underlying assumptions and physical meaning are different. According to analysis of Eqs. (10) and (11), the function $\varphi(v_f)$ represents the contribution of the repulsive term of EOS to the free energy departure (the first term in the right hand side of Eq. (11)). This contribution to $\varphi(v_f)$ is larger by an order of magnitude than the attractive contribution which is represented by the second term in the right hand side of Eq. (11). Setting $V = b$ removes the contribution of the repulsive forces from the free energy departure—an unreasonable assumption. While Eq. (13), assumes that the *excess* free energy resulting from the repulsive

forces is negligible—a plausible assumption which explains the reasonable results of the "infinite pressure" approach. Nevertheless, using Eq. (13) to arrive at Eq. (4), still introduces inconsistency in the calculation of excess free energy. In phase equilibrium calculations, Eq. (8) is used without the assumption of Eq. (13), while the mixing rules used in Eq. (8) are derived using Eq. (13).

The ratio $\Delta A_{ex}/A_{ex}$ can be considered as a measure of this inconsistency. To avoid the inconsistency, one has to use implicit mixing rules presented by Eq. (6) and the following expression for $(a/b)_m$:

$$(a/b)_m = \left[\sum_i x_i(a/b)_i \left[1 - \varphi(v_{fi})/c \right] - A_{ex}^{ACM}/c \right] \Bigg/ \left[1 - \varphi(v_{fm})/c \right] \quad (14)$$

where A_{ex}^{ACM} is the excess Helmholtz free energy calculated by ACM. The system of Eqs. (6) and (14) should be solved for the unknown variables $(a/b)_m$ and v_{fm}. Equation (4) can be used as a good zeroth approximation for $(a/b)_m$. For RKS EOS, Eq. (6) results in

$$v = V/b = \left[1 + \alpha + (\alpha^2 - 2\alpha + 9)^{0.5} \right]/(2\alpha - 4) \quad (15)$$

where $\alpha = a/(bRT)$. Note that $\alpha = 2$ is the singular point for v, and Eq. (15) becomes meaningless for $\alpha \leqslant 2$. However, this singularity and negative values of v have no practical impact on analytical behavior of φ as a function of α. The function φ is plotted in Fig. 1 as the solid line. The function
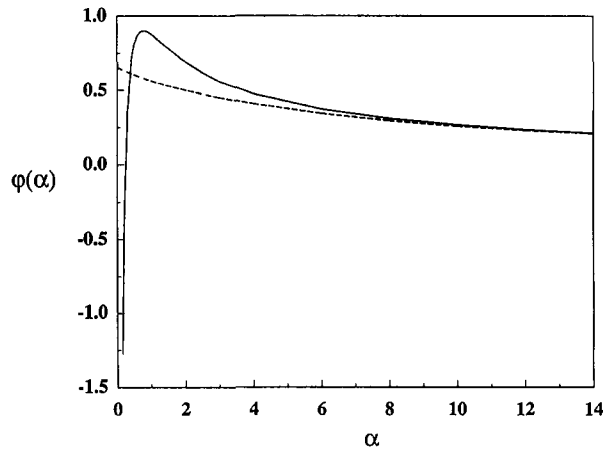

Fig. 1. Original (solid line) and modified (dash line) function $\varphi(\alpha)$ for RK EOS.

is smooth up to $\alpha = 1$ which provides validity of Eq. (14) up to a temperature of $5T_c$.

It is possible to extend the applicability of Eqs. (11) and (14) up to infinitely high temperatures by expanding the second term of Eq. (11) in powers of $v_f/2$ and then keeping only the linear term. By also neglecting v_f^2 in the denominator of the first term of Eq. (11), we obtain

$$\varphi(v_f) = -v_f \ln(v_f)/(2 + v_f) + v_f/2 \tag{16}$$

This simplified function is shown as dash line in Fig. 1. The difference in Eqs. (11) and (16) is negligible at $v_f \ll 1$ (large value of α), but Eq. (16) provides the smooth extrapolation to infinitely high reduced temperature ($\alpha \to 0$), which is important for calculation of $\varphi(v_{fi})$ for highly volatile components (such as hydrogen).

Starting from an approximate $(a/b)_m$ which is the Huron–Vidal result, we calculate α from its definition. From Eq. (15), we calculate v which allows us to obtain v_f; v_f is used in Eq. (16) to obtain $\varphi(v_f)$. Calculating $\varphi(v_{fi})$ and $\varphi(v_{fm})$ leads to the next approximation for $(a/b)_m$; the iterative procedure is continued until convergence. A simple algorithm providing fast convergence is described in the Appendix. An explicit solution of $(a/b)_m$ as a function of α_i and A_{ex}^{ACM} can also be obtained and will be presented in a future study.

To complete the procedure of incorporating ACM into EOS, we must define the mixing rules for parameter b_m. We have chosen the theoretically based expression for b_m:

$$b_m = \sum_i x_i \sum_j x_j [(b_i^{1/3} + b_j^{1/3})(1 - l_{ij})/2]^3 \tag{17}$$

where l_{ij} is an adjustable parameter defining nonadditivity of the size parameter. It can be nonzero for components of substantially different molecular shape and size.

5. RESULTS

Table I contains the numerical values of the ACM parameters used for the calculations described below. We used the following temperature dependent form of parameters for all ACM:

$$\tau_{ij} = \tau_{ij}^{(0)} + \tau_{ij}^{(1)}/T + \tau_{ij}^{(2)} \ln T \tag{18}$$

Figures 2a and 2b show the results of calculating $\Delta A_{ex}/A_{ex}$ and $r = (a/b)_m/(a/b)_m^{(0)}$ for two binary mixtures, where $(a/b)_m^{(0)}$ is the Huron–

Table I.   ACM Parameters for Systems Studied

Binary system (1)/(2)	ACM	$\tau_{12}^{(0)}$	$\tau_{12}^{(1)}$	$\tau_{12}^{(2)}$	$\tau_{21}^{(0)}$	$\tau_{21}^{(1)}$	$\tau_{21}^{(2)}$	C_R
n-butane/methanol	WILSON	−0.481	−433.3	0	3.618	−1968	0	—
acetone/water	UNIQUAC	3.051	−1380	0	−2.607	924.2	0	—
ammonia/water	NRTL	1.389	−887.7	0	2.792	−1017	0	0.3
2-butanol/water	NRTL	266.0	−11102	−39.85	133.4	−6462	−19.09	0.4985

Vidal approximation. We can see that inconsistency of this approximation increases rapidly with temperature which emphasizes the well known importance of repulsive contribution at high temperature (and pressure). The plots explain the need to redetermine ACM parameters in the Huron–Vidal approach (or additional parameter by Wong–Sandler). Any approach based on the simple equation such as Eq. (4) must be corrected to compensate for the fact that the important contribution by Eq. (13) was neglected.

To illustrate the present approach we used some strongly nonideal systems which were not used by other authors in previous studies. These are ammonia-water, n-butane-methanol, and 2-butanol-water binary mixtures. It is impossible to reproduce exactly by an EOS the results for equilibrium properties calculated by the base ACM. Equation (14) provides equality of the excess free energy along the cross-section of thermodynamic surface defined by Eq. (6), but its derivatives with respect to compositions at constant volume and temperature can be different for an EOS and ACM. This difference can be negligible in the range where liquid properties are almost independent of pressure, but can be substantial where dependence on pressure becomes significant.

VLE in ammonia-water system.   This well investigated binary mixture is an ideal subject to test the extrapolation capability of any approach for incorporating an ACM into EOS.

The NRTL model was used as a base model. The parameters were obtained by fitting the 0.1013 and 1.013 MPa data of Chu et al. [10]. Figure 3a shows that the present approach with RKS EOS and the NRTL model can reproduce the results of the base model and the original experimental data. Parameter l_{ij} is zero for this system because of a small difference in the values of b_i: $b_1/b_2 = 1.23$. The results of the PSRK [11], MHV2 [9], and WS [6] methods are shown in Fig. 3b. The parameter k_{12} for the WS model was determined by fitting the datum point of equimolar composition at 1.013 MPa. The k_{12} value was abnormally high ($k_{12} = -1.2$). The attempt to determine this value by using data at atmospheric pressure led to an inappropriate value of $k_{12} < -3$ which distorted the shape of the
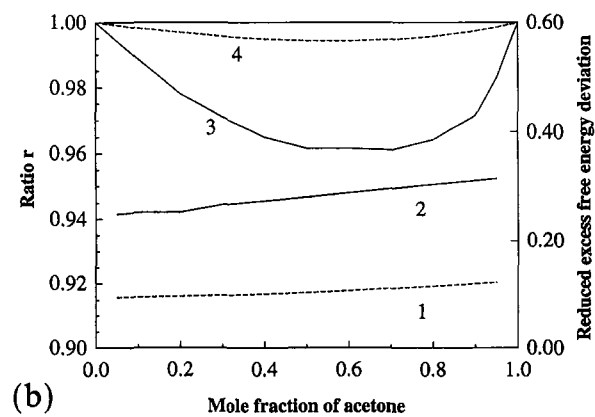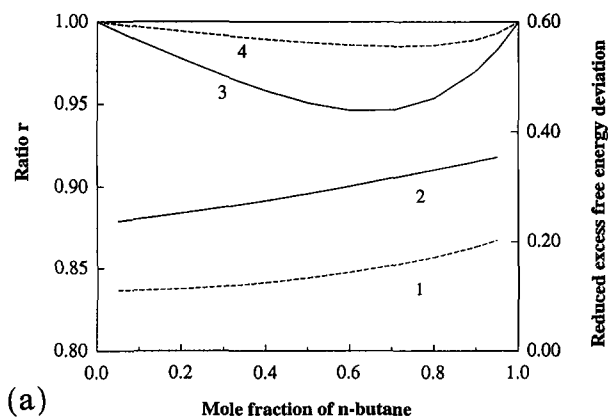
Fig. 2. (a) Illustration of inconsistency of "infinite pressure" approach for n-butane-methanol system. The curves 1, 2 are assigned to the right axis, and the curves 3, 4—to the left one. The dash lines are for $T = 273$ K, and the solid lines are for $T = 373$ K. The calculations of A_{ex}^{ACM} were done using Wilson model with parameters from ASPEN PLUS data bank. (b) Illustration of inconsistency of "infinite pressure" approach for acetone-water binary system. The assignment to axes is the same as described for (a). The dash lines are for $T = 298$ K, and the solid lines are for $T = 473$ K. The calculations of A_{ex}^{ACM} were done using UNIQUAC model with parameters from ASPEN PLUS data bank.
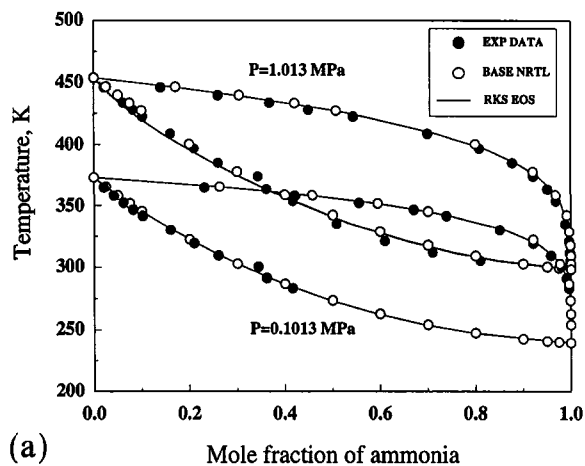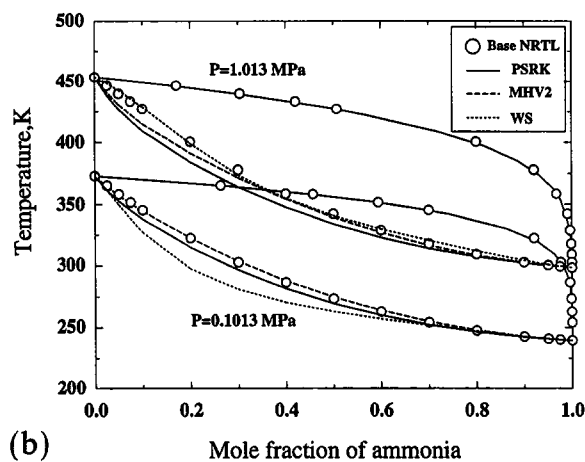
Fig. 3. (a) Reproducing the base ACM and the original experimental VLE data for ammonia-water system by the present approach. (b) Reproducing the base ACM results for ammonia-water system by the commonly used models.

1.013 MPa isobar. This failure of the WS model is an example of the difficulty in compensating for internal inconsistency of the model by using an adjustable parameter.

Figures 4a and 4b show the extrapolation capability of the various methods. The experimental points are taken from Ref. [12]. Note that the RKS EOS based on the present method and the MHV2 model predict
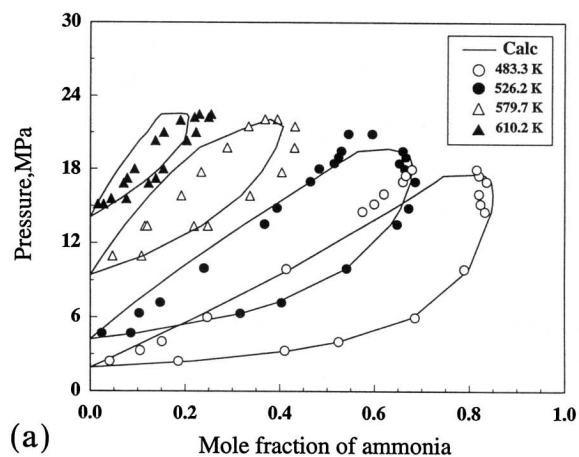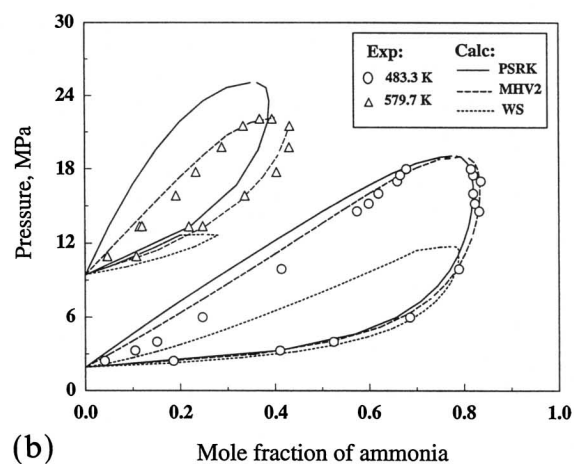
Fig. 4. (a) Comparison of experimental VLE data for ammonia-water system at high temperatures with extrapolation using the present approach. (b) Comparison of experimental VLE data for ammonia-water system at high temperatures with extrapolation using the common models.

maxima in the critical loci close to the critical point of water. This agrees with experimental data of Refs. [12] and [13], but contradicts recent measurements [14].

VLE in n-butane-methanol system. The Wilson ACM was used as a base model for this system. The data at 323 K from Ref. [15] were used to

determine the l_{12} parameter for the present approach and the k_{12} parameter for the WS model. We found the value of $l_{12} = 0.029$ by adjusting pressure to match the ACM value at $x_1 = 0.025$, and $k_{12} = 0.157$ for the WS model by regressing the data over the entire range of compositions. The data at 373 K were used for comparison only. Results are shown in Figs. 5a and 5b.

LLE in 2-butanol-water system. The LLE data used for this system exhibit a closed loop behavior. Temperature-dependent parameters of the NRTL model were obtained by regressing data [16, 17] at atmospheric pressure. Data [16] are available in the wide range of pressure (up to 81 MPa) and provide the unique opportunity to investigate the capability of the present approach to represent LLE at high pressure using pressure-independent ACM approximation.

We tested prediction of LLE by different EOS using the present approach: Redlich–Kwong–Soave and Peng–Robinson. Parameter l_{12} was determined by matching the datum point at 283 K [16]. The value $l_{12} = 0.098$ defines substantial nonlinearity of b_m and can be explained by the large size differences of the components ($b_1/b_2 = 4.37$). The same value was used for the PR EOS. The two equations reproduce sufficiently the base ACM result (see Fig. 6a). According to experimental data [16], phase splitting degrades with increasing pressure and disappears at a pressure higher than 81 MPa. However, calculated phase splitting degrades more rapidly and disappears at a pressure higher than 30 MPa.
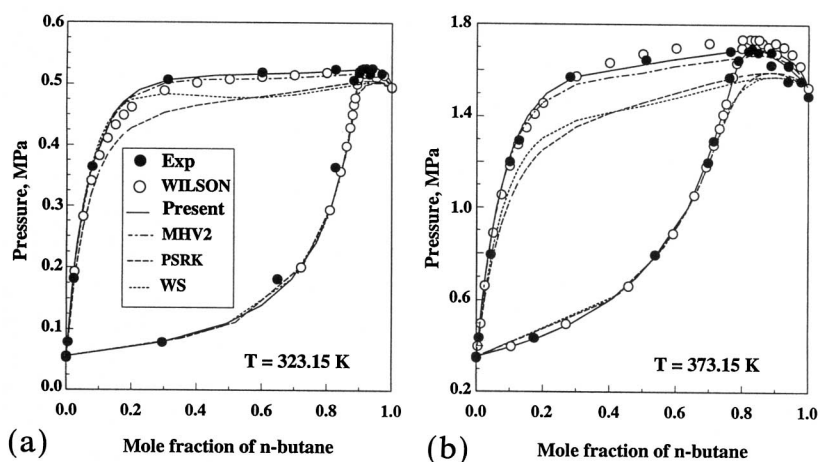

Fig. 5. (a) Reproducing the base ACM and the original experimental VLE data for n-butane-methanol system at $T = 323$ K by the present approach and the commonly used models. (b) The same as for (a) at $T = 373$ K.
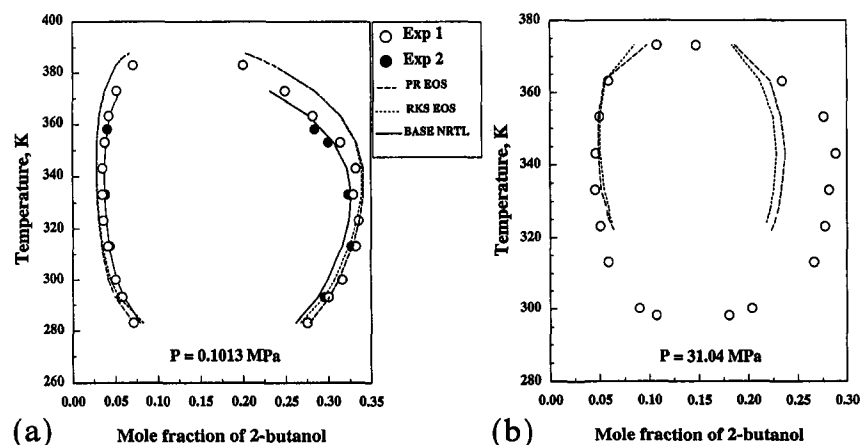
Fig. 6. (a) Reproducing the base NRTL model and experimental data on LLE in 2-butanol-water system at 0.1013 MPa by different EOS using the present approach. "Exp 1" and "Exp 2" are data from Refs. [16] and [17], respectively. (b) The same as for (a) at 30 MPa.

The results of similar calculations using common methods are shown in Figs. 7a and 7b. The MHV2 and PSRK do not reproduce properly the base model and do not show any degradation of phase splitting if pressure increases. High pressure results remain almost the same as those for 0.1013 MPa for the whole experimental range. The possible reason may be
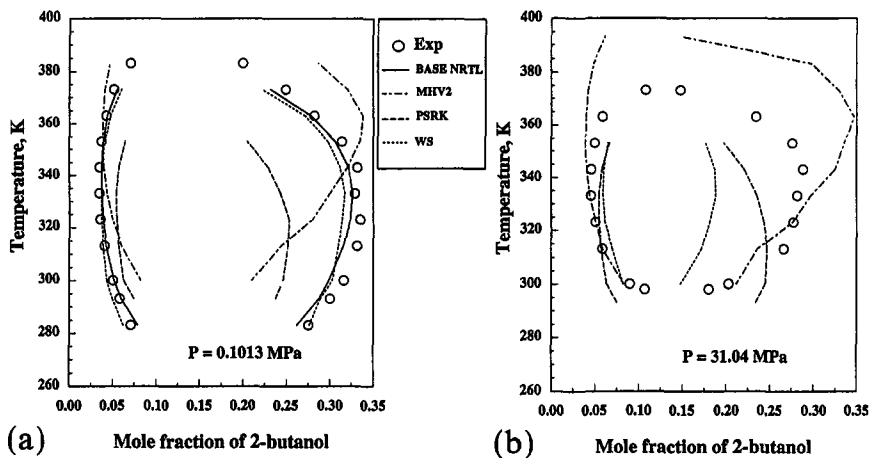

Fig. 7. (a) Reproducing the base model and experimental data [16] on LLE in 2-butanol-water system at 0.1013 MPa by commonly used methods with RKS EOS. (b) The same as for Fig. 6a at 30 MPa.

the use of linear dependence of b on compositions. The WS model provides satisfactory results after adjusting k_{12} to the atmospheric data ($k_{12} = 0.345$). Calculations at high pressures show the stronger degradation of phase splitting with increasing pressure as observed with the present approach.

5.1. Second Virial Coefficient Consideration

It was pointed out by Wong and Sandler [6] that the common way of incorporating ACM into an EOS violates correct composition dependence of the second virial coefficient. Such deficiency is true for parameter a_m of the present approach. We considered the simple way to correct this deficiency by adding the following term to the EOS:

$$\Delta p = -(a_0 - a_m)/V^2 \tag{19}$$

where

$$a_0 = \sum_i x_i \sum_j x_j (a_i a_j)^{1/2} (1 - k_{ij}) \tag{20}$$

In the low density region, the attractive term of the original EOS reduces to $-a_m/V^2$ which cancels the a_m/V^2 term introduced into Eq. (19). This leaves the $-a_0/V^2$ term which provides the correct composition dependence of a second virial coefficient. However, calculations for the systems described above have shown that including the correction (Eq. (19)) into the EOS has no practical significance.

6. CONCLUSION

1. A new approach for incorporation of the excess free energy from ACM into an EOS of the van der Waals type has been proposed. The approach connects any ACM with the EOS at some low but finite value of compressibility factor and results in an implicit mixing rule for parameter a of the EOS.

2. The approach can be reduced to the Huron–Vidal mixing rule by neglecting the contribution of the repulsive term of the EOS to the excess free energy. This simplification introduces inconsistency in the free energy calculation which explains the need to redetermine the base ACM parameters or the need to introduce additional adjustable parameters.

3. The new approach was tested on examples of VLE and LLE in binary systems which could not be described adequately by conventional mixing rules.

APPENDIX. ALGORITHM FOR SOLVING EQS. (6) AND (14)

The system of Eqs. (6) and (14) can be reduced to a nonlinear equation for $\alpha = a/(bRT)$ by using Eq. (15) and expressing $\varphi(v_f)$ as $\varphi(\alpha)$; actually $\varphi(v_f) = \varphi[v_f(\alpha)]$:

$$f(\alpha) = \sum_i x_i \alpha_i [1 - \varphi(\alpha_i)/c] - \alpha[1 - \varphi(\alpha)/c] - A_{ex}^{ACM}/(cRT) = 0 \qquad (A1)$$

Solution of Eq. (A1) can be obtained by

$$\alpha^{(n+2)} = \alpha^{(n+1)} + \Delta_\alpha^{(n+1)} \qquad (A2)$$

and

$$\Delta_\alpha^{(n+1)} = \Delta_\alpha^{(n)} f(\alpha^{(n+1)})/[f(\alpha^{(n)}) - f(\alpha^{(n+1)})] \qquad (A3)$$

$$\Delta_\alpha^{(0)} = \alpha^{(1)} - \alpha^{(0)} \qquad (A4)$$

where $\alpha^{(0)}$ is the zeroth approximation obtained from Eq. (4) and $\alpha^{(1)}$ is the result of the first "simple iteration" for Eq. (14) obtained by substituting $\alpha^{(0)}$ into Eq. (15), and Eq. (14).

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NOMENCLATURE

A	Helmholtz free energy
a	temperature dependent parameter of a cubic EOS
b	"covolume" parameter of a cubic EOS
c	constant in the equation for A
p	pressure
R	gas constant
r	ratio of the zeroth approximation for a/b to the actual a/b
T	temperature
V	molar volume
v	dimensionless volume: $v = V/b$
v_f	"free volume"
x_i	composition of component "i" in mixture
Z	compressibility factor

Greek Letters

α	dimensionless parameter: $\alpha = a/(bRT)$
$\varDelta$	departure function
φ	function of v_f defined by Eqs. (10) and (11)
Σ	summation

Superscripts

ACM	denotes value calculated by activity coefficient model
(0)	zeroth approximation
(1)	first approximation
(n)	nth approximation

Subscripts

ex	excess property
i, m	pure component and mixture property, respectively

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