

DETERMINATION OF THE BINARY CROSS VIRIAL COEFFICIENT IN THE WONG-SANDLER MIXING RULE FOR CUBIC EQUATIONS OF STATE

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The binary cross second virial coefficient in the mixing rule of Wong and Sandler (1992) can be determined analytically from pure component parameters and activity coefficients at infinite dilution. The modification allows to determine the binary interaction parameter without the additional minimization of excess Gibbs energy deviations. At low pressures, the accuracy of the modification is comparable to that of the original model.

High pressure phase equilibria were predicted by the modification of the Wong-Sandler mixing rule with Modified UNIFAC and ASOG group contribution methods.

Introduction

Mixing rules combining cubic equations of state with excess Gibbs energy models have recently attracted much research activity^{9, 12, 15}. An important feature of the newly developed models is that high pressure phase equilibria can be directly predicted from existing correlations of activity coefficients^{3, 4, 10}.

Wong and Sandler^{26, 27} (W-S) recently proposed a G^E mixing rule which reproduces correctly the quadratic composition dependence of the second virial coefficient. While being simple, the W-S model requires to evaluating the binary cross virial coefficient by an optimization technique.

The objective of this work is to investigate the possibility of determining the binary cross virial coefficient analytically. This modification should allow combining of the W-S mixing rule with group contribution methods, such as UNIFAC or ASOG, in a simple direct manner, without the use of the optimizing calculations.

1. Excess Gibbs Energy Mixing Rules

Huron and Vidal¹² (H-V) were the first to demonstrate that simple and flexible mixing rules can be obtained by combining cubic equations of state (EOS) with G^E models at infinite pressure. The derivation of the H-V mixing rules requires the linear mixing rule for the EOS size parameter b ,

$$b = \sum x_i b_i \quad (1)$$

Because of its simplicity, Eq. (1) was also employed in subsequent zero pressure modifications of the H-V mixing rules^{9, 15, 16}.

Orbey *et al.*²⁰ and others have pointed out that the

Huron-Vidal type mixing models do not give the quadratic composition dependence of the second virial coefficient required by statistical mechanics.

To overcome this deficiency, Wong and Sandler²⁶ developed a new model based on the following assumptions:

(i) The composition dependence of the combined EOS mixture parameter a/b is given through the expression for the excess Helmholtz energy at infinite pressure A^E .

$$\frac{a}{b} = \sum x_i \frac{a_i}{b_i} + \frac{1}{q} A^E (P = \infty) \quad (2)$$

where q is a constant dependent on EOS.

(ii) EOS parameters a and b are related through the expression for the second virial coefficient B ,

$$B = b - \frac{a}{RT} \quad (3)$$

(iii) B is quadratic in composition,

$$B(x) = \sum \sum x_i x_j B_{ij} \quad (4)$$

where B_{ij} is the cross second virial coefficient. Wong and Sandler²⁶ expressed the composition independent B_{ij} as

$$B_{ij} = \frac{(B_{ii} + B_{jj})}{2} (1 - k_{ij}) \quad (5)$$

with k_{ij} being a binary interaction parameter ($k_{ij} = k_{ji}$).

To incorporate activity coefficient correlations determined at low pressures, Wong *et al.*²⁷ used the approximation

$$A^E (P = \infty) \approx G^E (P = \text{low}) \quad (6)$$

which enables us to solve Eqs. (2)-(5) for EOS mixture parameters a and b . The initial difference between the excess Gibbs energy of the correlation and the excess Gibbs energy given by the EOS at low pressures is then compensated by adjusting k_{ij} values until a minimum of the

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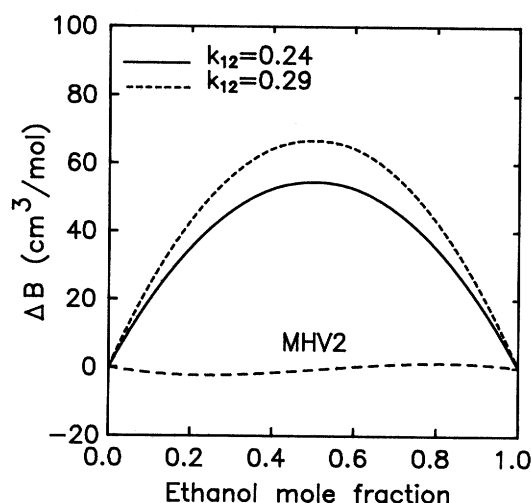


Fig. 1 ΔB composition dependence by Wong-Sandler and MHV2 mixing rules for SRK EOS. Ethanol (1)-Water (2), 343 K. k_{ij} determined at infinite dilutions by Eq. (18): $k_{ij}(i=2) = 0.29$; $k_{ij}(i=1) = 0.24$. Optimization by Wong *et al.*²⁷: $k_{ij} = 0.24$.

difference is found.

2. Implications of the Wong-Sandler Mixing Rule

For isothermal binary systems, the quadratic composition dependence of B implies

$$B(x) = x_1^2 B_{11} + 2x_1 x_2 B_{12} + x_2^2 B_{22} \quad (7)$$

where B_{12} is the binary cross second virial coefficient.

Consequently, the deviation function

$$\Delta B = B - x_1 B_{11} - x_2 B_{22} \quad (8)$$

has the following infinite dilution slopes

$$\left(\frac{\Delta B}{x_1 x_2}\right)_{x_i=0} = \left(\frac{d\Delta B}{dx_1}\right)_{x_i=0} = 2(B_{12})_{x_i=0} - B_{11} - B_{22} \quad (9)$$

If the binary cross virial coefficient B_{12} is to be composition independent, it must hold

$$(B_{12})_{x_1=0} = (B_{12})_{x_2=0} \quad (10)$$

The ΔB composition dependence of an EOS which satisfies Eq. (7) must therefore have a regular parabolic behavior and its infinite dilution limits must have identical slopes.

Figure 1 illustrates the ΔB composition dependence predicted by the W-S mixing rule for the system ethanol-water at 343 K. Figure 1 also shows the performance of the MHV2 mixing rule of Michelsen¹⁶ with the linear mixing rule for the EOS parameter b . The MHV2 mixing rule violates the second virial coefficient condition.

The binary cross virial coefficient B_{12} can be alternatively expressed in a dimensionless form convenient for numerical evaluations. Eq. (5) gives

$$k_{12} = 1 - \frac{2B_{12}}{(B_{11} + B_{22})} \quad (11)$$

The binary interaction parameter k_{ij} of the W-S

mixing rule is not a fully independent parameter. By construction, it is closely related to the EOS second virial coefficient B , which itself is a function of activity coefficients through Eqs. (2)-(3). From this it follows reversely that if a correlation of activity coefficients for a given mixture is available, it is possible to determine the cross second virial coefficient B_{ij} of the W-S mixing rule

3. Determination of B_{ij} at Infinite Dilution

As shown in Section 2, the relation between B_{ij} and EOS takes the simplest form at infinite dilutions. In particular, the cross second virial coefficient B_{ij} then becomes a function of only pure component parameters of EOS and activity coefficients at infinite dilution.

A large base of activity coefficient correlations is now available in the DECHEMA Series⁶) and by G^E group contribution methods. The present method aims to make direct use of these correlations in the W-S mixing rule.

Our development is based on the Soave-Redlich-Kwong (SRK) EOS²²),

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \quad (12)$$

and can be readily extended to other cubic EOS.

The EOS activity coefficient of component i at infinite dilution in a binary system of components i - j is

$$\ln(\gamma_i^{\text{EOS}}) = \ln \bar{\phi}_i^{\infty} - \ln \phi_i \quad (13)$$

where the fugacity coefficient at infinite dilution can be expressed as

$$\begin{aligned} \ln \bar{\phi}_i^{\infty} = & -\ln(z_j - \beta_j) + \left[\left(\frac{\bar{b}_i}{b_j} \right)_{x_i=0} \right] (z_j - 1) - \\ & - \delta_i \ln \left(1 + \frac{\beta_j}{z_j} \right) \end{aligned} \quad (14)$$

and the fugacity coefficient of pure component is given by

$$\ln \phi_i = -\ln(z_i - \beta_i) + (z_i - 1) - \alpha_i \ln \left(1 + \frac{\beta_i}{z_i} \right) \quad (15)$$

where

$$z_i = \frac{P v_i}{RT}, \quad \alpha_i = \frac{a_i}{RT b_i}, \quad \beta_i = \frac{P b_i}{RT}$$

From the W-S mixing rule it follows that:

$$\left(\frac{\bar{b}_i}{b_j} \right)_{x_i=0} = \frac{2B_{ij}}{B_{jj}} - \frac{(1 - \delta_i)}{(1 - \alpha_j)} \quad (16)$$

and

$$\delta_i = \alpha_i + \frac{\ln(\gamma_i^{\text{model}})}{q}, \quad q = -\ln(2)$$

If the EOS activity coefficient at infinite dilution is matched with a G^E correlation, $(\gamma_i^{\text{EOS}})^{\infty} = (\gamma_i^{\text{model}})^{\infty}$, the binary cross virial coefficient B_{ij} can be expressed from Eqs. (13)-(16) as

Table 1. VLE calculations of isothermal binary systems by Wong-Sandler mixing rule

System	T [K]	N _d	This work Eqs. (18) or (19)				Optimization Wong <i>et al.</i> ²⁷⁾				G ^E model Ref. ^b
			$\Delta P/P$	Δy	$\Delta G^E/G^E$	k_{ij}	$\Delta P/P$	Δy	$\Delta G^E/G^E$	k_{ij}	
Ethanol (1) -Water (2)	343	13	1.4	0.4	2.9	0.24	1.4	0.4	2.9	0.24	W+1)
						18/1					I/1a/174
Chloroform (1)-Acetone (2)	323	15	0.2	0.1	1.9	-0.11	0.3	0.1	1.5	-0.12	RK-2)
						18/2					
Benzene(1)- Hexafluoro- benzene (2)	313	10	0.3	0.3	27.0	0.018	0.3	0.3	23.0	0.015	RK±3)
						19					
Chloroform (1)-Ethanol (2) ^c	318	25	1.4	0.8	13.0	0.13	2.1	0.9	10.0	0.09	RK+4)
						19					
Acetone (1) -Water (2)	333	9	5.7	1.4	4.2	0.24	4.1	1.3	3.3	0.23	W+1)
						18/1					I/1a/188
Methanol (1) -Benzene (2)	328	9	4.3	3.5	9.3	0.26	4.3	3.1	6.4	0.32	W+1)
						18/2					I/2a/217
Methanol (1) -Hexane (2)	333	28	6.2	4.4	8.8	0.40	6.3	4.2	8.8	0.41	W+1)
						18/1					I/2c/220

^aEq specifies Eq. (18) or (19) and *i* identifies component in the infinite dilution of which k_{ij} was determined. ^bReferences in Tables 1 and 2 specify: G^E model (W - Wilson, NRTL, RK - Redlich-Kister), type of G^E composition dependence (+ positive maximum, - negative maximum, ± sigmoid) and data reference: 1) Gmehling and Onken⁶⁾; numbers correspond to volume/part/page, 2) Goral *et al.*⁷⁾, 3) Gaw and Swinton⁵⁾, 4) Scatchard and Raymond²⁾. ^cSystem with inflection point on G^E composition dependence.

$$\frac{\Delta P}{P} = \frac{1}{N_d} \sum_{k=1}^{N_d} \left[\frac{P_k^{cal} - P_k^{exp}}{P_k^{exp}} \right] \quad \Delta y = \frac{1}{N_d} \sum_{k=1}^{N_d} |y_{1,k}^{cal} - y_{1,k}^{exp}|$$

$$B_{ij} = \frac{B_{ij}}{2} \left[\frac{(1 - \delta_i)}{(1 - \alpha_j)} + \frac{\ln(\gamma_i^{\infty})^{model} + \ln \phi_i + \ln(z_j - \beta_j) + \delta_i \ln \left(1 + \frac{\beta_j}{z_j} \right)}{(z_j - 1)} \right] \quad (17)$$

The alternative of B_{ij} in the form of k_{ij} is given by Eq. (11).

As shown in Section 2, the feature of the W-S mixing model is that the k_{ij} values provided by Eq. (17) for both activity coefficients at infinite dilution should be identical. In most cases, however, it is found that the match of the W-S mixing rule with a low pressure G^E correlation gives two distinct values of k_{ij} (Fig. 1). While both interaction parameters can be used with the W-S mixing rule, only one of them usually gives a considerably better description of highly nonideal systems.

At low pressures, the excess Gibbs energy expression usually plays a dominant role in G^E mixing rules. In the following, we give an empirical rule which we have found useful for selecting the appropriate value of k_{ij} in low pressure region:

(i) For binary systems with components of different values of activity coefficients at infinite dilution (asymmetrical systems), the component with higher value of the activity coefficient at infinite dilution should be preferred, *i.e.*

$$k_{ij} = (k_{ij})_{x_{i=0}} \quad \text{for } \gamma_i^{\infty} > \gamma_j^{\infty} \quad (18)$$

(ii) For binary systems with low and comparable

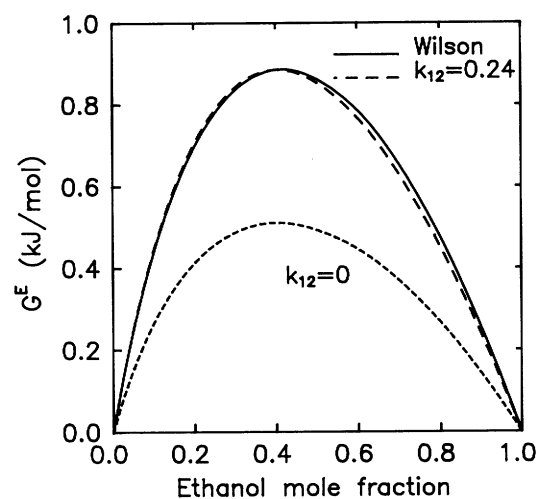


Fig. 2 Excess Gibbs energy prediction by Wong-Sandler mixing rule. Ethanol (1)-Water (2), 343 K. Wilson equation parameters from Gmehling and Onken⁶⁾ I/1a/174. Predictions by Eq. (18) with $i = 1$ and optimization by Wong *et al.*²⁷⁾ are identical; $k_{ij} = 0.24$.

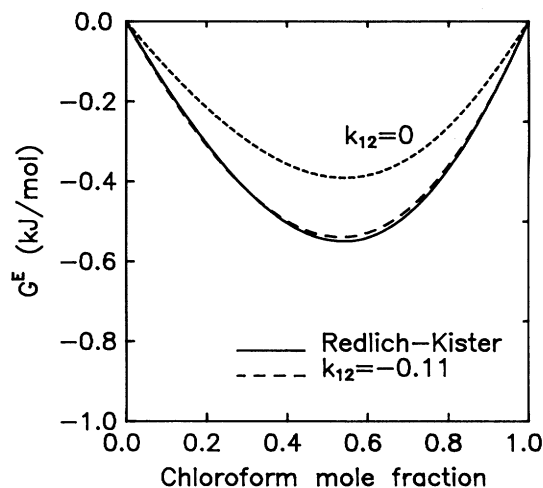


Fig. 3 Excess Gibbs energy prediction by Wong-Sandler mixing rule. Chloroform (1)-Acetone (2), 323 K. Redlich-Kister equation parameters from Goral *et al.*⁷⁾ Eq. (18) with $i = 1$; $k_{ij} = -0.11$; optimization by Wong *et al.*²⁷⁾; $k_{ij} = -0.12$. Differences in the predictions are undistinguishable in the figure.

values of activity coefficients at infinite dilution (symmetrical systems), k_{ij} can be taken as the average of its infinite dilution values, *i.e.*

$$k_{ij} = \frac{(k_{ij})_{x_{i=0}} + (k_{ij})_{x_{j=0}}}{2} \quad \text{if } \gamma_i^{\infty} \approx \gamma_j^{\infty} \quad (19)$$

In practice, however, there is little difference when using Eq. (18) even for symmetrical, nearly ideal systems. We therefore recommend using Eq. (19) only in the rare cases when the k_{ij} values have opposite signs.

3. Results and Discussion

3.1. Low pressure calculations

The proposed modification of the W-S mixing rule

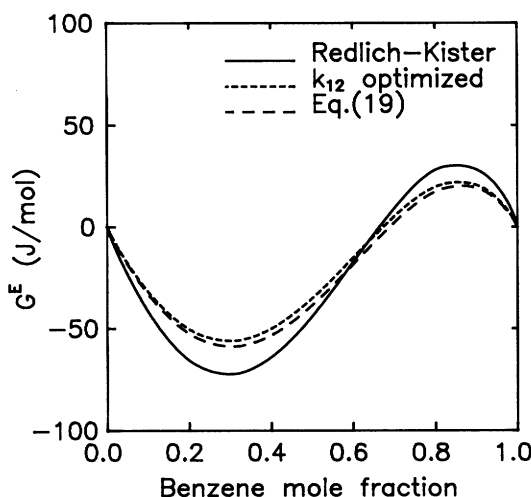


Fig. 4 Excess Gibbs energy prediction by Wong-Sandler mixing rule. Benzene (1)-Hexafluorobenzene (2), 313 K. Redlich-Kister equation parameters from Gaw and Swinton⁵.

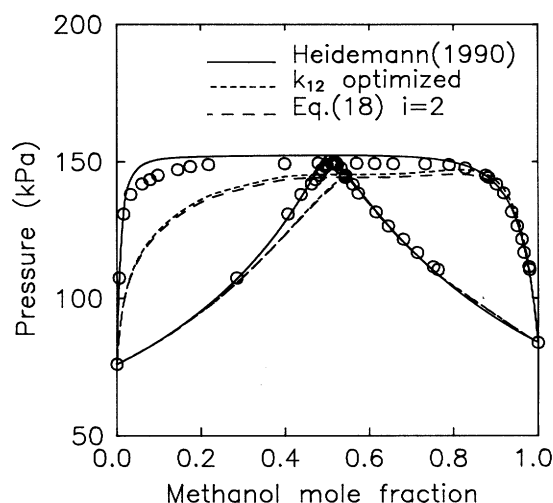


Fig. 5 VLE prediction by mixing rules of Heidemann and Kokal⁹; Wong and Sandler²⁶. Methanol (1)-Hexane (2), 333 K. Wilson equation parameters and experimental data from Gmehling and Onken⁶ I/2c/220.

Table 2. VLE calculations of isobaric binary systems by Wong-Sandler mixing rule ($P = 101.3$ kPa)

System	T [K]	N_d	This work Eqs. (18) or (19)				Optimization Wong <i>et al.</i> ²⁷				G^E model Ref. ^b
			$\Delta T/T$ [$\times 100$]	Δy	$\Delta G^E/G^E$ [$\times 100$]	k_{ij} Eq/i^a	$\Delta T/T$ [$\times 100$]	Δy	$\Delta G^E/G^E$ [$\times 100$]	k_{ij}	
Ethanol (1) -Water(2)	351 373	15	0.5	0.6	2.6	0.22	0.4	0.5	2.4	0.23	W+ 1) I/1a/154
Acetone (1) -Water (2)	329 373	19	2.0	0.7	4.7	0.26	1.7	0.9	4.3	0.28	W+ 1) I/1a/237
Methanol (1) -Benzene (2)	338 350	18	1.7	2.3	7.9	0.26	1.2	2.2	6.6	0.30	NRTL+ 1) I/2a/211
2-Butanone (1)-Water (2)	347 373	33	1.9	2.6	9.1	0.43	1.9	2.6	9.1	0.43	RK+ ^b 5)

^aData reference: see Table 1., 5) Moon¹⁷. ^bSystem with liquid immiscibility.

$$\frac{\Delta T}{T} = \frac{1}{N_d} \sum_{k=1}^{N_d} \left[\frac{T_k^{cal} - T_k^{exp}}{T_k^{exp}} \right] \quad \frac{\Delta G^E}{G^E} = \frac{1}{N_d} \sum_{k=1}^{N_d} \left[\frac{G_k^{E(cal)} - G_k^{E(exp)}}{G_k^{E(exp)}} \right]$$

for SRK EOS has been applied to a variety of systems used in the previous testing G^E mixing rules at moderate temperatures. The procedure and data selection have been given elsewhere¹³. The parameters of G^E equations were mostly taken from the DECHEMA Series⁶. The database was extended on some systems showing anomalous composition dependence of the excess Gibbs energy¹⁸.

The results in **Table 1** and **Figs. 2-4** demonstrate that for isothermal binary systems the proposed simple modification can produce the k_{ij} parameters with comparable values to the optimization method suggested by Wong *et al.*²⁶

Table 2 gives results of the calculation for isobaric systems at atmospheric pressure. For systems with varying temperature and for predicting high pressure phase equilibria, the evaluation of k_{ij} was fixed at the normal boiling temperature of the more volatile component in binary systems.

It should be noted that in the low pressure region

Table 3. VLE calculations with Wong-Sandler mixing rule for SRK EOS and group contribution methods

System Eq/i^a	T [K]	N_d	ASOG				Modified UNIFAC			
			$\Delta P/P$ [$\times 100$]	Δy	$\Delta G^E/G^E$ [$\times 100$]	k_{ij}	$\Delta P/P$ [$\times 100$]	Δy	$\Delta G^E/G^E$ [$\times 100$]	k_{ij}
Ethanol (1) -Water (2) ¹	343 423 473 523 548 573	13 17 17 18 13 9	2.6 3.5 4.8 4.5 4.9 5.0	0.4 0.9 2.1 1.4 2.3 2.5	3.7 5.8 6.9 -	0.22	0.8 2.4 2.2 2.4 1.7 1.2	0.5 0.4 1.1 0.6 1.6 2.1	3.7 2.4 9.2 -	0.24
Acetone (1) -Water (2) ²	333 373 423 473 523	9 22 17 25 17	6.2 2.1 2.7 2.2 2.8	2.7 1.2 0.5 0.6 0.6	2.5 6.8 14. 19. -	0.26	4.1 1.9 3.3 3.3 5.2	2.0 0.9 0.6 0.5 0.8	4.0 8.9 15. 17. -	0.25
Methanol (1) -Benzene (2) ³	328 373 393 453 473 493	9 10 10 10 10 10	5.2 5.8 5.8 12. 15. -	3.5 2.2 2.4 4.5 5.8 -	5.7 6.8 9.2 27. 56. -	0.32 0.30 ^c 0.29 ^c 0.20 ^c 0.11 ^c -	3.6 2.0 2.3 3.0 3.4 3.2	3.2 1.8 1.6 2.0 2.3 1.9	7.5 5.3 5.7 6.6 9.1 50.	0.28 0.32 ^c 0.34 ^c 0.41 ^d 0.41 ^d 0.41 ^d
Methanol (1) -Water (2) ²	298 373 423 473 523	13 16 14 15 10	2.2 2.3 0.6 1.5 1.6	0.9 1.3 1.2 1.1 1.4	8.3 3.8 6.4 18. -	0.077	1.8 2.6 1.2 1.7 5.3	0.8 1.5 1.4 1.4 2.2	14. 5.6 6.5 5.2 -	0.096
Acetone (1) -Methanol (2) ²	373 423 473	14 15 10	0.8 3.3 6.5	1.2 2.3 3.9	13. 87. 62.	0.091	1.7 1.3 2.8	1.1 1.7 2.9	12. 20. 9.3	0.099

^aSee Table 1. Data reference: 1)Barr-David and Dodge¹¹; 2)Griswold and Wong⁹; 3)Butcher and Medani²¹. ^bIncorrect temperature dependence of ASOG group parameters. ^c k_{ij} determined at system temperature. Group parameters strongly temperature dependent. ^dEq. (19).

the W-S mixing rule produces worse results than the mixing rule of Heidemann-Kokal⁹ and the MHV2 model by Michelsen¹⁶ tested in our previous work¹³. Figures 2-4 show that the adjustment of k_{ij} in the W-S mixing rule can not provide a perfect correspondence between the excess Gibbs energy calculated from the EOS and G^E correlation.

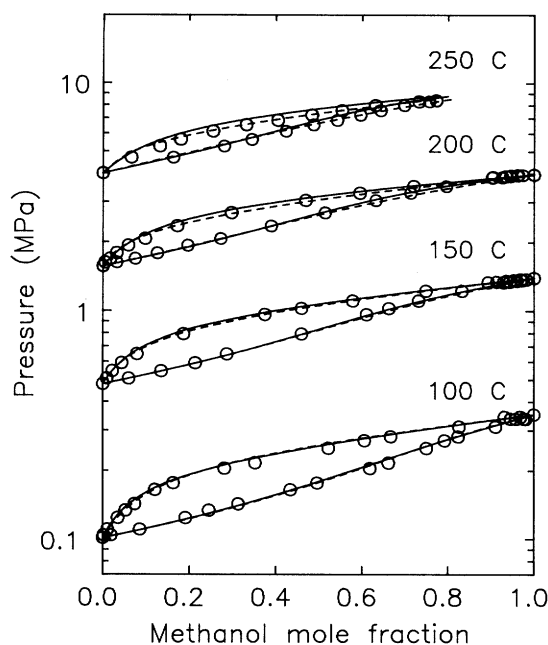


Fig. 6 High pressure VLE predictions by Wong-Sandler mixing rule with group contribution methods. Methanol (1)-Water (2). ASOG (dotted line), $k_{ij} = 0.077$; Modified UNIFAC (solid line), $k_{ij} = 0.096$. k_{ij} determined by Eq. (18) with $i = 1$ at 338 K (normal boiling temperature of methanol). Experimental data by Griswold and Wong⁸⁾.

The impact to the limitation of the W-S mixing rule to correctly follow the underlying G^E model is particularly notable in case of highly nonideal systems like the methanol-hexane in **Fig. 5** and 2-butanone-water in Table 2. The proposed modification cannot overcome this limitation, which is inherent in the W-S mixing rule.

A very recent proposal by Huang and Sandler¹¹⁾ for determining k_{ij} by equating G^E (EOS) = G^E (model) in the middle of composition has similar features to our treatment. Despite their method it does not avoid the optimization, nor can it correctly account for highly asymmetrical systems.

3.2. High pressure calculations with group contribution methods

It is of engineering interest to test the combination of the W-S mixing rule with existing G^E group contribution methods. Because of their built-in temperature dependence, the Modified UNIFAC¹⁴⁾ and ASOG²⁴⁾ methods appear to be particularly suitable for the prediction of phase equilibria in a wide range of temperatures.

Table 3 summarizes the calculations by the W-S mixing rule with the group contribution methods for systems containing mostly polar components. From **Table 3** and **Fig. 6** it can be seen that both group contribution models perform comparably, although a marked difference in some cases (e.g., the methanol-benzene system) calls for improving the temperature dependence of the ASOG group interaction parameters.

A comparison of **Table 3** with the MHV predictions of Dahl and Michelsen³⁾ and Tochigi *et al.*²³⁾ shows that

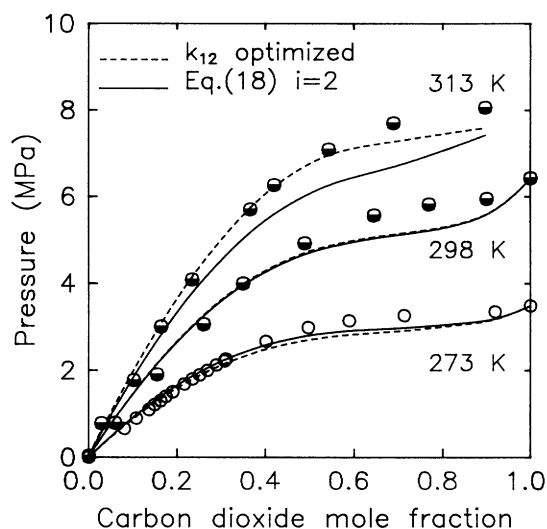


Fig. 7 High pressure VLE predictions by Wong-Sandler mixing rule with Modified UNIFAC. Carbon dioxide (1)-Methanol (2). Dotted line: k_{ij} by minimization of $\Delta P/P$ for each isotherm: k_{ij} (273 K) = 0.21, k_{ij} (298 K) = 0.24, k_{ij} (313 K) = 0.30. Solid lines: $k_{ij} = 0.24$ determined by Eq. (18) ($i = 2$) at the normal freezing temperature of CO₂, 217 K. Experimental data by Weber *et al.*²⁵⁾ (273 K); Ohgaki and Katayama¹⁹⁾ (298, 313 K).

in the high pressure region the W-S mixing rule produces essentially similar results.

Figure 7 shows the prediction of the system CO₂-Methanol by the W-S mixing rule with the parameters of the Modified UNIFAC⁴⁾. For this system any minimization of excess Gibbs energy deviations near the critical region is meaningless. **Figure 7** demonstrates that at subcritical temperatures the proposed simple modification can provide a k_{ij} value comparable to the minimization of relative pressure deviations. In the supercritical region the prediction with temperature independent k_{ij} necessarily deteriorates. However, the proposed method can still give a good first estimate of the binary interaction parameter of the W-S mixing rule.

Conclusion

For the prediction of high pressure phase equilibria with group contribution methods like the Modified UNIFAC and ASOG, the proposed modification can provide at least a good estimate of the W-S mixing rule parameter k_{ij} . It appears especially useful for the prediction in the critical region where a wrong initialization of the optimization can lead to a failure of the calculation.

Nomenclature

a	= energy parameter of equation of state	[Pa(m ³ /mol) ²]
A^E	= molar excess Helmholtz energy	[J/mol]
b	= size parameter of equation of state (covolume)	[m ³ /mol]
\bar{b}_i	= partial molar value of b	[m ³ /mol ²]
B	= second virial coefficient	[m ³ /mol]
G^E	= molar excess Gibbs energy	[J/mol]
k_{ij}	= binary interaction parameter of B	[-]

N_d	= number of data points	[-]
P	= pressure	[Pa]
R	= gas constant	[J/(mol K)]
T	= absolute temperature	[K]
v	= molar volume	[m ³ /mol]
x	= mole fraction	[-]
y	= mole fraction in the vapor phase	[-]
z	= compressibility factor, $z = Pv/RT$	[-]

α	= combined parameter of equation of state; $\alpha = a/RTb$	[-]
β	= Pb/RT ; Eq. (17)	[-]
γ	= activity coefficient	[-]
δ	= combined parameter; Eq. (17)	[-]
ΔB	= deviation function of B ; Eq. (8)	[m ³ /mol]
ϕ_i	= fugacity coefficient in solution	[-]
ϕ_i	= fugacity coefficient of pure component	[-]

<Subscripts>

i, j	= component index
k	= datapoint index

<Superscripts>

EOS	= calculated from equation of state
exp	= experimental value
$model$	= given by a G^E correlation of experimental data
∞	= infinite dilution

Literature Cited

- 1) Barr-David, F. and B.F. Dodge: *J. Chem. Eng. Data*, **4**, 107-121 (1959)
- 2) Butcher, K.L. and M.S. Medani: *J. Appl. Chem.*, **18**, 100-107 (1968)
- 3) Dahl, S. and M.L. Michelsen: *AIChE J.*, **36**, 1829-1836 (1990)
- 4) Dahl, S., A. Fredenslund and P. Rasmussen: *Ind. Eng. Chem. Res.*, **30**, 1936-1945 (1991)
- 5) Gaw, W.J. and F.L. Swinton: *Trans. Faraday Soc.*, **64**, 2023-2034 (1968)
- 6) Gmehling, J. and U. Onken: "Dechema Chemistry Data Series", DECHEMA, Frankfurt am Main, FRG (1977 af.)
- 7) Goral, M., G. Kolasinska, P. Oracz and S. Warycha: *Fluid Phase Equilib.*, **89**, 89-117 (1985)
- 8) Griswold, J. and S.Y. Wong: *Chem. Eng. Prog. Symp. Ser.*, **48**, 18-34 (1952)
- 9) Heidemann, R.A. and S.L. Kokal: *Fluid Phase Equilib.*, **56**, 17-37 (1990)
- 10) Holderbaum, T. and J. Gmehling: *Fluid Phase Equilib.*, **70**, 251-265 (1991)
- 11) Huang, H. and S.I. Sandler: *Ind. Eng. Chem. Res.*, **32**, 1498-1503 (1993)
- 12) Huron, M.-J. and J. Vidal: *Fluid Phase Equilib.*, **3**, 255-271 (1979)
- 13) Kolář, P. and K. Kojima: *J. Chem. Eng. Japan*, **26**, 165-171 (1993)
- 14) Larsen, B.L., P. Rasmussen and A. Fredenslund: *Ind. Eng. Chem. Res.*, **26**, 2274-2286 (1987)
- 15) Michelsen, M.L.: *Fluid Phase Equilib.*, **60**, 47-58 (1990)
- 16) Michelsen, M.L.: *Fluid Phase Equilib.*, **60**, 213-219 (1990)
- 17) Moon H.M.: PhD Dissertation, Nihon Univ., Tokyo, Japan (1989)
- 18) Novák, J.P., J. Matouš and J. Pick: "Liquid-Liquid Equilibria", Elsevier, Amsterdam, The Netherlands (1987)
- 19) Ohgaki, K. and T. Katayama: *J. Chem. Eng. Data*, **21**, 53-55 (1976)
- 20) Orbey, H., S.I. Sandler and D.S.H. Wong: *Fluid Phase Equilib.*, **85**, 41-54 (1993)
- 21) Scatchard, G. and C.L. Raymond: *J. Am. Chem. Soc.*, **60**, 1278-1287 (1938)
- 22) Soave, G.: *Chem. Eng. Sci.*, **27**, 1197-1203 (1972)
- 23) Tochigi, K., D. Tiegs, J. Gmehling and K. Kojima: *J. Chem. Eng. Japan*, **23**, 453-463 (1993)
- 24) Tochigi, K., T. Iizumi, P. Kolář and K. Kojima: *J. Japan Petrol. Inst.*, **36**, 398-401 (1993)
- 25) Weber, W., S. Zeck and H. Knapp: *Fluid Phase Equilib.*, **18**, 253-278 (1984)
- 26) Wong, D.S.H. and S.I. Sandler: *AIChE J.*, **38**, 671-680 (1992)
- 27) Wong, D.S.H., H. Orbey and S.I. Sandler: *Ind. Eng. Chem. Res.*, **31**, 2033-2039 (1992)