

# A Mixing Rule To Incorporate Solution Model into Equation of State

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A mixing rule is developed to incorporate solution model in equation of state (EOS) to extend the EOS to highly nonideal mixtures. To obtain the mixture parameter  $a$  of the EOS, the excess free energy of the solution model is matched to that of the EOS at a molar volume equal to a fixed multiple of the excluded volume  $b$ , such that all of the mixed liquids are at a low pressure (by the EOS). The mixing rule is applicable to cubic EOS as well as to noncubic perturbation type EOS, for which the zero-pressure-based or infinite pressure-based mixing rules are not applicable. A wealth of solution model parameters that have been fitted to low-pressure data are made useful by means of the mixing rule for phase equilibrium calculations at elevated pressures. Examples are presented of the use of the UNIFAC model with previously reported parameters and the Wang–Chao–Wilson model using newly fitted parameters incorporated into the Peng–Robinson EOS and the chain-of-rotators group contribution EOS.

## Introduction

Equations of state are widely used for the representation of fluid phase equilibria. The advantage of the equation of state method is the applicability over wide ranges of temperature and pressure to mixtures of diverse components, from the light gases to heavy liquids. Since the same equation of state is applied to the various phases at equilibrium, a consistent description is obtained that is self-sufficient and convenient.

Cubic equations of state, which are the most widely used with the van der Waals mixing rules, are, however, limited to nonpolar fluids. The van der Waals mixing rules are incapable of representing the highly nonideal mixture behavior of polar or associating fluids. A number of mixing rules have been proposed to extend the equations to highly nonideal mixtures with varying degrees of success. We mention here only the development that was initiated by Huron and Vidal (1979) that led to the present work. Huron and Vidal proposed to match the excess free energy of an equation of state to that of a solution model at a specified state and to solve for the van der Waals attractive parameter  $a$  from the equation.  $a$  obtained in this way is the mixing rule. By using this  $a$ , the equation of state reproduces the solution model at the specified state. As the state is varied from that specified, the  $G^E$  of the EOS changes with the volumetric properties of the EOS, thus accomplishing the objective of incorporating the solution model in the EOS.

Huron and Vidal matched the  $G^E$  of the solution model to that of the EOS at the state of infinite pressure. They assumed that  $G^E$  at infinite pressure can be represented by the same solution models that describe low-pressure solutions, but the parameters of the model must now be fitted to experimental data. Previously reported parameter values fitted to low-pressure data are not useful for the new equation.

To make possible the use of solution model parameters fitted to low-pressure data, Mollerup (1986) suggested matching the  $G^E$  of a solution model with that of an EOS at low pressure, which may be either the zero pressure or a suitably fixed ( $b/v$ ). The zero-pressure approach was developed by Heidemann and Kokal (1990), Michelsen (1990a,b), and Dahl and Michelsen (1990). The volume of the zero-pressure liquid is obtained by solving the EOS as part of the phase equilibrium calculations. A difficulty of the method is that cubic EOS zero-pressure liquid exists at suitably

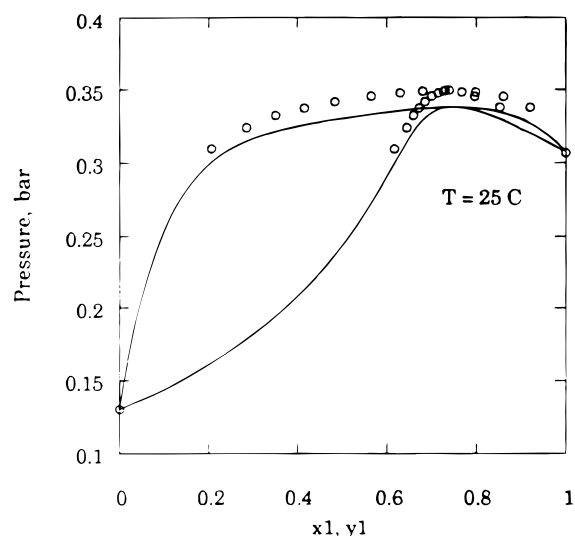


Figure 1. Acetone (1)–cyclohexane (2) vapor–liquid equilibrium using the PRSV EOS with UNIFAC. Circles represent data taken from Hirata and Ohe (1975) and lines show predictions.

Table 1. Molecular Parameters for the Chain-of-Rotators Group Contribution Equation of State

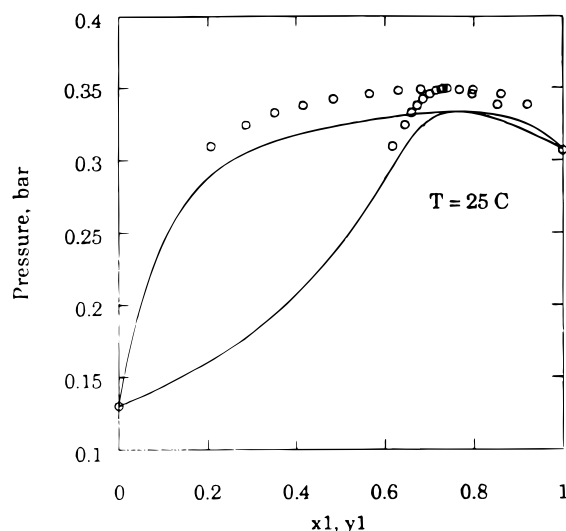
	$a_1$ (bar· cm <sup>6</sup> /mol <sup>2</sup> )	$a_2 \times 10^3$ (K <sup>-1</sup> )	$b_1$ (cm <sup>3</sup> /mol)	$b_2 \times 10^3$ (K <sup>-1.5</sup> )	$c$
<i>n</i> -hexane	95 898 413.8	2.5830	240.85	0.057 98	4.92
<i>n</i> -heptane	124 585 153.0	2.4916	277.22	0.051 96	5.65
cyclohexane	80 357 822.4	2.2622	202.63	0.051 83	4.38
benzene	67 006 487.4	2.1938	171.11	0.048 43	1.80
<i>p</i> -xylene	116 943 328.1	2.0595	243.08	0.040 39	3.80
acetone	51 428 343.1	2.3209	134.06	0.048 31	2.70
butanone	68 531 222.3	2.2305	167.20	0.046 35	3.42
ethanol	72 768 956.5	3.4457	126.55	0.063 89	2.32
1-propanol	102 892 982.4	3.4461	164.56	0.062 12	3.05
water	17 964 353.7	1.9254	37.04	0.037 69	0

low temperatures, but ceases to exist at higher temperatures, in which case an extrapolation has to be made to obtain a hypothetical zero-pressure liquid. For noncubic EOS, the zero-pressure liquid volume cannot be given in an analytical form, and the zero-pressure method becomes inapplicable. The zero-pressure mixing rules have been found to make good use of  $G^E$  parameters of low-pressure solutions.

Wong and Sandler (1992) and Wong, Orbey, and Sandler (1992) incorporated the second virial coefficient as well as solution model into the mixing rule obtained by identifying the excess Helmholtz free energy  $A^E$  of a

**Table 2. Deviation of Saturated Pressure and Vapor Composition**

mixture	temp (°C)	data points	PRSV				chain-of-rotators			
			UNIFAC		Wang–Chao–Wilson		UNIFAC		Wang–Chao–Wilson	
			$\Delta P$ (%)	$\Delta y$	$\Delta P$ (%)	$\Delta y$	$\Delta P$ (%)	$\Delta y$	$\Delta P$ (%)	$\Delta y$
Polar + Nonpolar										
acetone–cyclohexane	25	12	8.319	0.0200	0.876	0.0076	8.630	0.0209	0.729	0.0065
butanone– <i>n</i> -heptane	25	16	0.757	0.0086			1.327	0.0071		
Hydrogen-Bonding Mixtures										
ethanol–water	150	17	1.318	0.0050			1.244	0.0066		
	200	17	2.264	0.0082			1.192	0.0029		
	250	18	3.968	0.0064			1.571	0.0042		
	275	13	7.541	0.0114			2.161	0.0186		
	300	9	3.974	0.0077			2.635	0.0270		
	325	7	3.971	0.0082			2.700	0.0390		
	350	4	21.27	0.0278			9.603	0.0991		
acetone–water	100	22	4.963	0.0178			4.860	0.0164		
	150	17	4.249	0.0217			1.901	0.0121		
	200	25	6.872	0.0195			1.345	0.0107		
	250	17	10.257	0.0095			1.847	0.0097		
Hydrogen-Bonding + Nonpolar										
<i>n</i> -hexane–ethanol	35	9	3.003	0.0121	1.788	0.0127	4.693	0.0211	2.941	0.0099
	45	9	3.735	0.0139	1.570	0.0184	5.761	0.0291	1.638	0.0097
benzene–1-propanol	40	10	2.771	0.0244	5.952	0.0118	3.654	0.0369	7.745	0.0130
Paraffin + Aromatic										
<i>n</i> -hexane–benzene	25	9	3.992	0.0079			2.281	0.0085		
<i>n</i> -heptane– <i>p</i> -xylene	25	14	0.806	0.0050			2.785	0.0122		
	40	13	0.939	0.0058			3.224	0.0108		
	55	13	1.244	0.0067			3.605	0.0100		

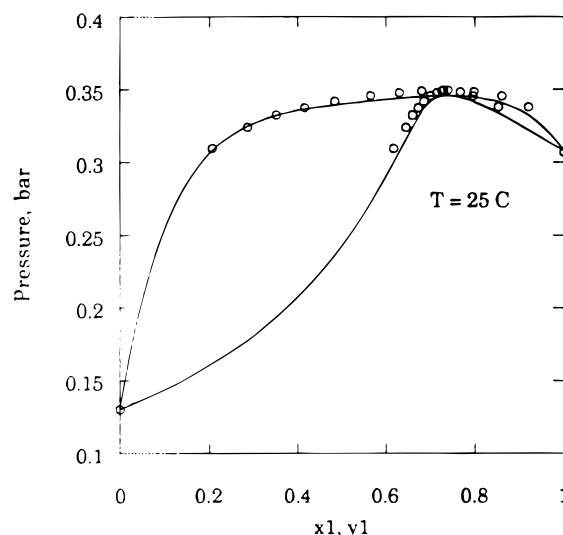
**Figure 2.** Acetone (1)–cyclohexane (2) vapor–liquid equilibrium using the chain-of-rotators EOS with UNIFAC. Circles represent data taken from Hirata and Ohe (1975) and lines show predictions.

solution model with that of an EOS at infinite pressure. Low-pressure solution model parameters are found to be useful in this mixing rule because of the insensitivity of  $A^E$  to pressure.

In this work, we match the excess free energy of the solution model to that of the EOS for low-pressure liquids at a molar volume equal to a fixed multiple of the excluded volume  $b$ . The method is (1) simple to implement by not requiring a zero-pressure liquid volume either by EOS calculation or by extrapolation; (2) free of dependence on a hypothetical state of infinite pressure; (3) capable of expressing the quadratic composition dependence of the second virial coefficient; and (4) applicable to a broader class of EOS.

### Mixing Rules for a Cubic EOS

We present the derivation and new mixing rules for the Peng–Robinson equation as an example of cubic

**Figure 3.** Acetone (1)–cyclohexane (2) vapor–liquid equilibrium using the PRSV EOS with the Wang–Chao–Wilson model. Circles represent data taken from Hirata and Ohe (1975) and lines show correlations. Wang–Chao–Wilson constants:  $(g_{21} - g_{11}) = 815.33$  J/mol;  $(g_{12} - g_{22}) = 476.58$  J/mol.

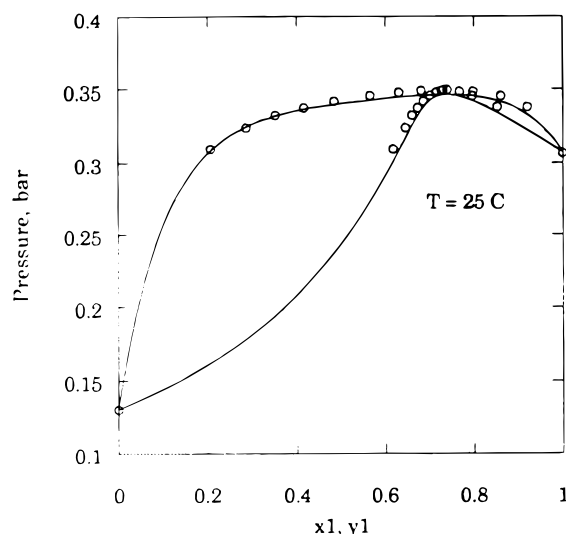
EOS. The Peng–Robinson (1976) equation is

$$P = \frac{RT}{v - b} - \frac{a}{v^2 + 2bv - b^2} \quad (1)$$

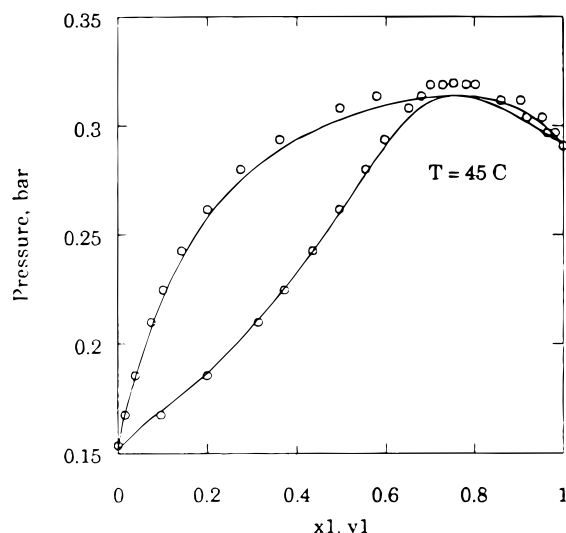
The fugacity coefficient obtained from eq 1 is

$$\ln \phi = \ln \left( \frac{v}{v - b} \right) + \frac{a}{2\sqrt{2}bRT} \ln \left[ \frac{v + b(1 - \sqrt{2})}{v + b(1 + \sqrt{2})} \right] + \frac{z - 1 - \ln z}{z} \quad (2)$$

The excess Gibbs energy is given by the fugacity coefficients in general by



**Figure 4.** Acetone (1)-cyclohexane (2) vapor-liquid equilibrium using the chain-of-rotators EOS with the Wang-Chao-Wilson model. Circles represent data taken from Hirata and Ohe (1975) and lines show correlations. Wang-Chao-Wilson constants:  $(g_{11} - g_{12}) = 987.79$  J/mol;  $(g_{12} - g_{22}) = 487.60$  J/mol.



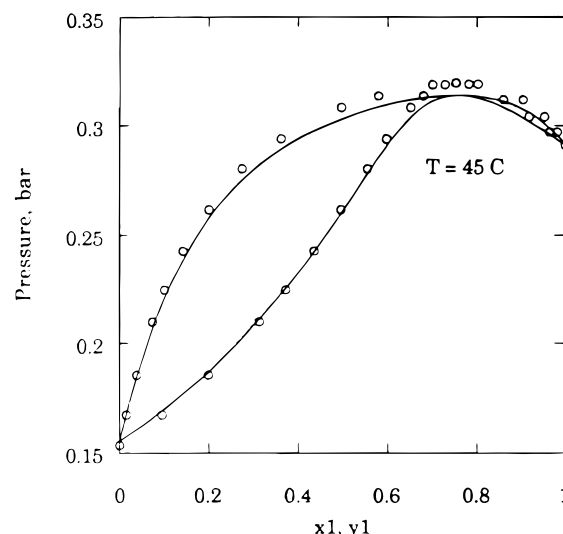
**Figure 5.** Butanone (1)-*n*-heptane (2) vapor-liquid equilibrium using the PRSV EOS with UNIFAC. Circles represent data taken from Takeo, Nishii, Nitta, and Takayama (1979) and lines show predictions.

$$G^E = RT(\ln \phi - \sum_{i=1}^n x_i \ln \phi_i^*) \quad (3)$$

where  $\phi_i^*$  denotes fugacity coefficients of pure component  $i$  and  $\phi$  denotes that of the mixture. Substitution of eq 2 into 3 gives the excess Gibbs energy of a Peng-Robinson fluid mixture:

$$\begin{aligned} \frac{G^E}{RT} = & \ln\left(\frac{v}{v-b}\right) - \sum x_i \ln\left(\frac{v_i^*}{v_i^* - b_i}\right) + \frac{a}{2\sqrt{2}bRT} \times \\ & \ln\left[\frac{v + b(1 - \sqrt{2})}{v + b(1 + \sqrt{2})}\right] - \frac{1}{2\sqrt{2}RT} \sum x_i (a/b_i) \times \\ & \ln\left[\frac{v_i^* + b_i(1 - \sqrt{2})}{v_i^* + b_i(1 + \sqrt{2})}\right] + \frac{P}{RT}(v - \sum x_i v_i^*) - \\ & \ln v + \sum x_i \ln v_i^* \quad (4) \end{aligned}$$

where the superscript \* indicates a pure component.



**Figure 6.** Butanone (1)-*n*-heptane (2) vapor-liquid equilibrium using the chain-of-rotators EOS with UNIFAC. Circles represent data taken from Takeo, Nishii, Nitta, and Takayama (1979) and lines show predictions.

The mixing process described by eq 4 is now set to take place for liquids at a molar volume equal to a common constant multiple of its excluded volume, i.e., at  $v_i^* = kb_i$  and  $v = kb$ . The constant factor  $k$  is found from the examination of a large number of fluids. The saturated liquid volumes of the fluids at pressures of 0.5, 1.0, and 2.0 bars are calculated with the EOS, and the  $k$  values corresponding to these volumes are found. An average  $k$  value in the middle range is selected so that, at this value of  $k$ , all fluids are at a low-pressure liquid state. To use such a common  $k$  in  $v_i^* = kb_i$  and  $v = kb$  in eq 4 is to approximate the isobaric mixing process that defines  $G^E$  with the mixing of low-pressure fluids at different pressures. The temperature is kept constant in the mixing process. Since Gibbs energy is insensitive to pressure for low-pressure liquids, the  $G^E$  of mixing of low-pressure liquids is a good approximation of the  $G^E$  of a rigorously isobaric mixing process. Our search shows that  $k = 1.15$  is suitable for Peng-Robinson fluids. A value of  $k$  must be determined for each EOS.

By using  $v_i^* = kb_i$  and  $v = kb$ , eq 4 is simplified to give

$$\frac{G^E}{RT} = \frac{1}{2\sqrt{2}RT} \ln\left(\frac{k+1-\sqrt{2}}{k+1+\sqrt{2}}\right) [a/b - \sum x_i (a/b_i)] - \ln b + \sum x_i \ln b_i \quad (5)$$

To incorporate a solution model into the EOS, the  $G^E$  of the EOS in eq 5 is set to be equal to that of the solution model. Upon solving for  $a/b$ , we obtain

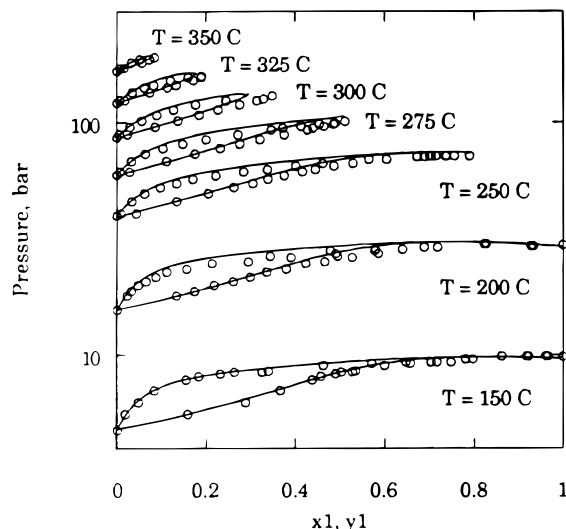
$$a/b = \frac{2\sqrt{2}RT}{\ln\left(\frac{k+1-\sqrt{2}}{k+1+\sqrt{2}}\right)} \left( \frac{G_{sm}^E}{RT} + \ln b - \sum x_i \ln b_i \right) + \sum x_i (a/b_i) \quad (6)$$

The subscript of  $G_{sm}^E$  in eq 6 emphasizes that it is the solution model.

The classical mixing rule for  $b$  is

$$b = \sum x_i b_i \quad (7)$$

Equations 6 and 7 make a set of mixing rules for  $a$  and  $b$ .



**Figure 7.** Ethanol (1)-water (2) vapor-liquid equilibrium using the PRSV EOS with UNIFAC. Circles represent data taken from Barr-David and Dodge (1959) and lines show predictions.

The fugacity coefficient obtained from the mixing rules is

$$RT \ln \phi_i = -\ln \left( \frac{P(v-b)}{RT} \right) + \frac{b_i}{b} (z-1) + \frac{a}{2\sqrt{2}RT} \left( \frac{1}{na} \frac{\partial n^2 a}{\partial n_i} - \frac{b_i}{b} \right) \ln \left( \frac{v+b(1-\sqrt{2})}{v+b(1+\sqrt{2})} \right) \quad (8)$$

with

$$\frac{1}{na} \left( \frac{\partial n^2 a}{\partial n_i} \right) = (b_i/b) + (b/a) \{ K[-\ln \gamma_i + \ln(b/b) + 1 - (b_i/b)] + (a_i/b_i) \} \quad (9)$$

and

$$K = \frac{-2\sqrt{2}RT}{\ln \left( \frac{k+1-\sqrt{2}}{k+1+\sqrt{2}} \right)} \quad (10)$$

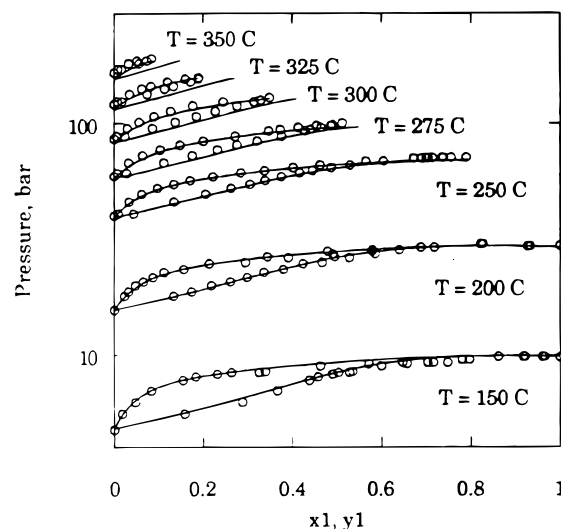
To incorporate the second virial coefficient in the mixing rule, we obtain the excess Helmholtz energy  $A^E$  for Peng-Robinson fluids at the specified low-pressure liquid states with  $v_i = kb_i$  and  $v = kb$  and set it equal to a solution model.

$$A_{sm}^E = \frac{-1}{2\sqrt{2}} \ln \left( \frac{k+1+\sqrt{2}}{k+1-\sqrt{2}} \right) \left( (a/b) \sum_i x_i (a_i/b_i) \right) \quad (11)$$

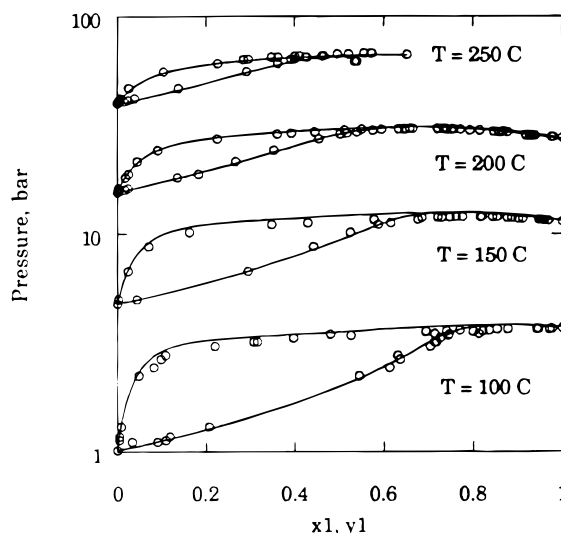
The second virial coefficient for Peng-Robinson fluid is

$$b - (a/RT) = \sum_i x_i x_j (b_{ij} - (a_{ij}/RT)) \quad (12)$$

Elimination of  $a$  from eqs 11 and 12 gives the mixing



**Figure 8.** Ethanol (1)-water (2) vapor-liquid equilibrium using the chain-of-rotators EOS with UNIFAC. Circles represent data taken from Barr-David and Dodge (1959) and lines show predictions.



**Figure 9.** Acetone (1)-water (2) vapor-liquid equilibrium using the PRSV EOS with UNIFAC. Circles represent data taken from Griswold and Wong (1952) and lines show predictions.

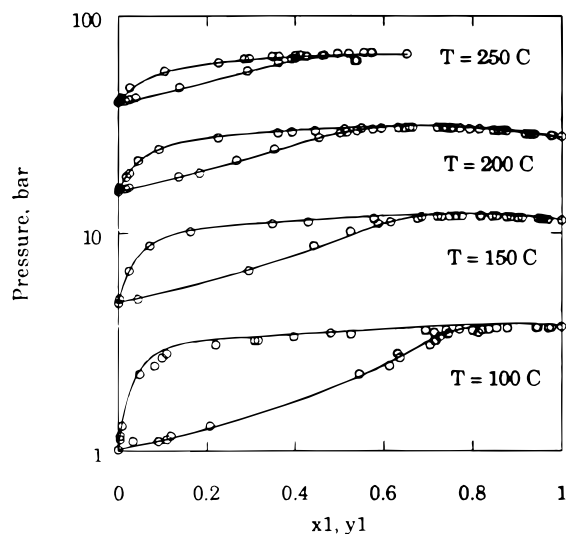
rule for  $b$

$$b = \frac{\sum_i \sum_j x_i x_j (b_{ij} - (a_{ij}/RT))}{1 + \frac{1}{RT} \left( \frac{2\sqrt{2}A_{sm}^E}{\ln \left( \frac{k+1+\sqrt{2}}{k+1-\sqrt{2}} \right)} - \sum_i x_i (a_i/b_i) \right)} \quad (13)$$

Substitution of eq 13 into eq 11 gives the mixing rule for  $a$ :

$$a = b \left( -\frac{2\sqrt{2}A_{sm}^E}{\ln \left( \frac{k+1+\sqrt{2}}{k+1-\sqrt{2}} \right)} + \sum_i x_i (a_i/b_i) \right) \quad (14)$$

Equations 13 and 14 make up the set of mixing rules that also expresses the quadratic composition dependence of the second virial coefficient.



**Figure 10.** Acetone (1)-water (2) vapor-liquid equilibrium using the chain-of-rotators EOS with UNIFAC. Circles represent data taken from Griswold and Wong (1952) and lines show predictions.

### Mixing Rules for a Noncubic EOS

The derivation and mixing rules for the chain-of-rotators EOS are presented here to show the application to a noncubic EOS. The chain-of-rotators group contribution EOS (Pulst et al., 1989) is a COR equation for which parameter values have been reported for a number of groups and molecules. Although called a group contribution equation, it is useful with molecular parameters just as well as with group parameters. In this work the equation will be used solely with molecular parameters and will be referred to in the following simply as a COR equation. This equation is

$$\frac{Pv}{RT} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} + \frac{c(\alpha - 1) \left( \frac{3y + 3\alpha y^2 - (\alpha + 1)y^3}{(1 - y)^3} \right) - \frac{a}{RT(v + b)}}{2} \quad (15)$$

where  $y = b/4v$  is a reduced density, also called the packing fraction,  $c$  is the degrees of rotational freedom, and  $\alpha = 1.078$  is the nonsphericity constant. The fugacity coefficient  $\phi$  obtained from eq 15 is

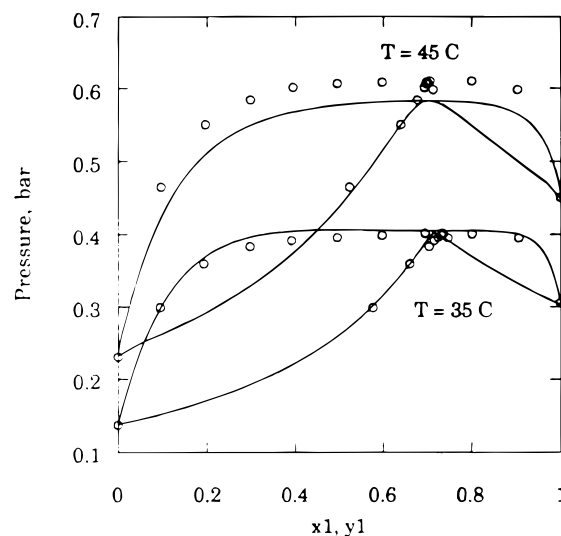
$$\ln \phi = \frac{y(4 - 3y)}{(1 - y)^2} + \frac{c(\alpha - 1)}{2} \left[ \frac{(\alpha + 4)y - 3y^2}{(1 - y)^2} + (\alpha + 1) \ln(1 - y) \right] - \frac{a}{bRT} \ln(1 + 4y) + z - 1 - \ln z \quad (16)$$

The excess Gibbs energy is obtained by substituting eq 16 into eq 3 for the mixture and the components. The equation is long, but is much simplified when the molar volumes are set as  $v_i = kb_i$  and  $v = kb$ . We have found that with  $k = 0.6$  the fluids are low-pressure liquids. The equation is further simplified with the adoption of linear mixing rules for  $b$  and  $c$ :

$$b = \sum x_i b_i \quad (17)$$

$$c = \sum x_i c_i \quad (18)$$

leading to



**Figure 11.** *n*-Hexane (1)-ethanol (2) vapor-liquid equilibrium using the PRSV EOS with UNIFAC. Circles represent data taken from Hirata and Ohe (1975) and lines show predictions.

$$G^E = \ln(1 + 1/k) \left[ -\frac{a}{b} + \sum x_i \left( \frac{a}{b_i} \right) \right] + RT \left[ \sum x_i \ln b_i - \ln b \right] \quad (19)$$

Upon setting the  $G^E$  of the low-pressure COR liquids of eq 19 equal to that of solution model  $G_{sm}^E$ , we obtain the mixing rule for  $a$  that incorporates the solution model:

$$a = b \left[ \frac{RT}{\ln(1 + 1/k)} \left( \frac{G_{sm}^E}{RT} + \sum x_i \ln b_i - \ln b \right) + \sum x_i \left( \frac{a}{b_i} \right) \right] \quad (20)$$

where  $k = 0.6$ . Equations 17, 18, and 20 make up a set of mixing rules for the COR equation.

The fugacity coefficient for a mixture component  $i$  obtained from the COR EOS with the mixing rules is

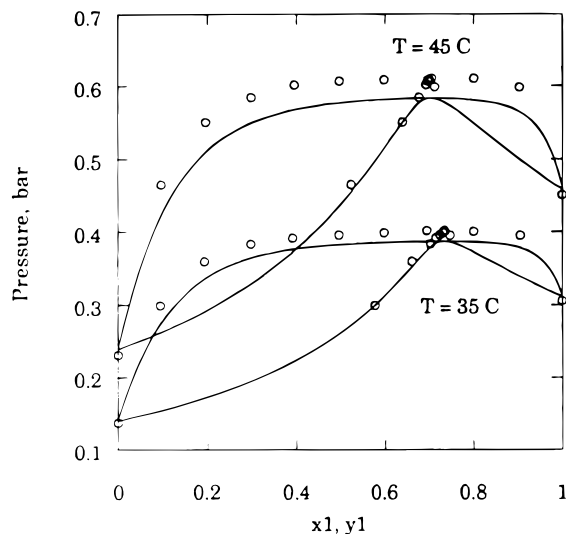
$$\ln \phi_i = \frac{y(4 - 3y)}{(1 - y)^2} + \frac{c_i(\alpha - 1)}{2} \left[ \frac{(\alpha + 4)y - 3y^2}{(1 - y)^2} + (\alpha + 1) \ln(1 - y) \right] + (b_i/b)(z - 1) - \ln z - \frac{\ln(1 + 4y)}{RT} \left[ \frac{a}{b_i} + \frac{RT}{\ln(1 + 1/k)} (-\ln \gamma_i + \ln(b/b_i) + 1 - (b_i/b)) \right] \quad (21)$$

where  $\gamma_i$  is the activity coefficient given by the solution model.

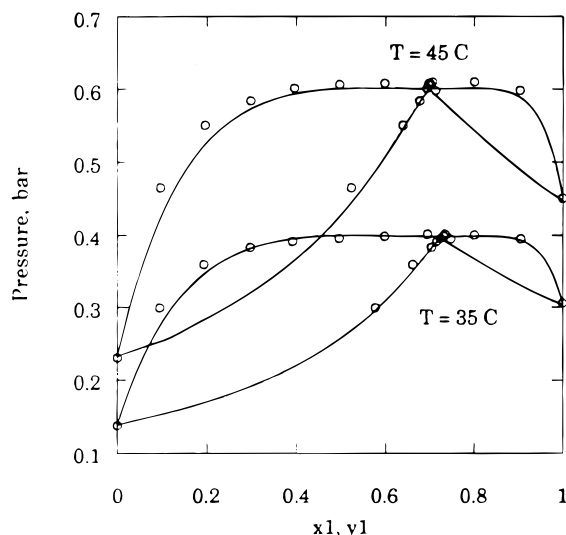
The quadratic form of the second virial coefficient can be incorporated into the mixing rules by using the excess Helmholtz energy  $A^E$  in place of  $G^E$  and by not using the linear mixing rule for  $b$ , eq 17, in the derivation.

### Vapor-Liquid Equilibria

In Figures 1-23, we present vapor-liquid equilibrium calculations by using the mixing rules of this work to incorporate the UNIFAC and Wang-Chao-Wilson (1983) solution models in the Peng-Robinson and COR EOS. Comparison is made with experimental data on the figures.



**Figure 12.** *n*-Hexane (1)-ethanol (2) vapor-liquid equilibrium using the chain-of-rotators EOS with UNIFAC. Circles represent data taken from Hirata and Ohe (1975) and lines show predictions.

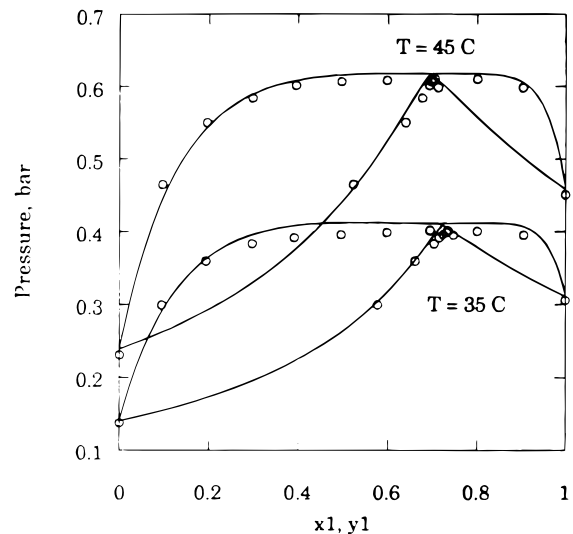


**Figure 13.** *n*-Hexane (1)-ethanol (2) vapor-liquid equilibrium using the PRSV EOS with the Wang-Chao-Wilson model. Circles represent data taken from Hirata and Ohe (1975) and lines show correlations. Wang-Chao-Wilson constants:  $(g_{21} - g_{11}) = 40.73$  J/mol;  $(g_{12} - g_{22}) = 2095.26$  J/mol.

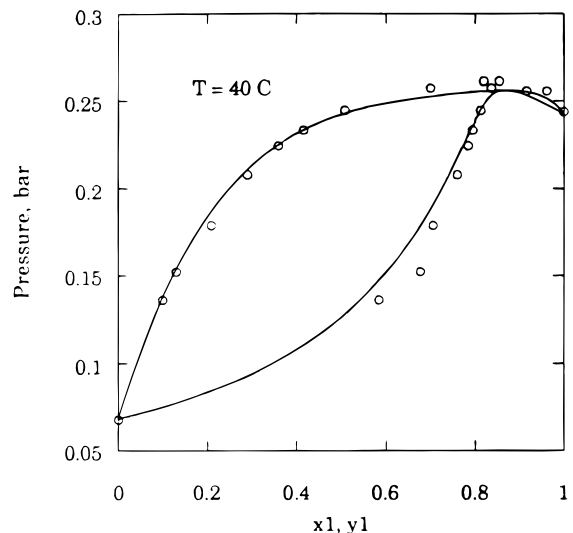
The UNIFAC-based calculations demonstrate the use of previously reported solution model parameters. On the other hand, parameters of the Wang-Chao-Wilson solution model incorporated in the EOS are determined here to fit low-pressure experimental data. The method of Marquardt (1963) is employed to search for parameter values that minimize the sum of squares of the percent deviations of calculated equilibrium ratios. The Wang-Chao-Wilson model examples demonstrate the proposed method where solution model parameters are to be fitted.

The Peng-Robinson EOS calculations make use of the fugacity coefficient expression of eq 8 based on the mixing rules of eqs 6 and 7. The EOS parameters for polar components are taken from Stryjek and Vera (1986).

The COR EOS calculations make use of the fugacity coefficient expression of eq 21 based on the mixing rules of eqs 17, 18, and 20. The EOS parameters  $a$  and  $b$  for



**Figure 14.** *n*-Hexane (1)-ethanol (2) vapor-liquid equilibrium using the chain-of-rotators EOS with the Wang-Chao-Wilson model. Circles represent data taken from Hirata and Ohe (1975) and lines show correlations. Wang-Chao-Wilson constants:  $(g_{21} - g_{11}) = 81.79$  J/mol;  $(g_{12} - g_{22}) = 2352.02$  J/mol.



**Figure 15.** Benzene (1)-1-propanol (2) vapor-liquid equilibrium using the PRSV EOS with UNIFAC. Circles represent data taken from Hirata and Ohe (1975) and lines show predictions.

the components are temperature-dependent, according to

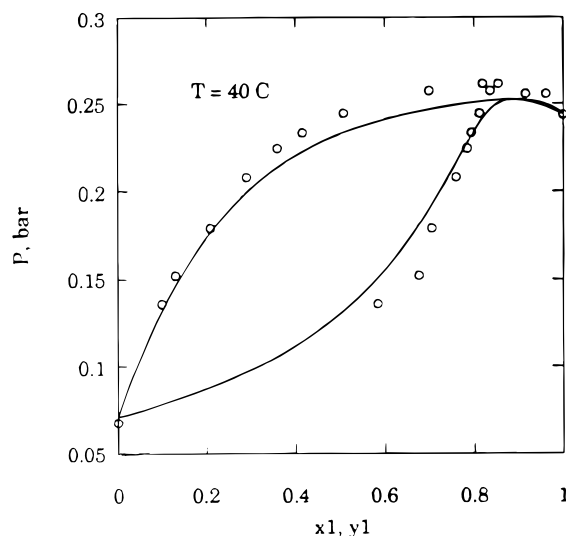
$$a = a_1 \exp(-a_2 T) \quad (22)$$

$$b = b_1 \exp(-b_2 T^{1.5}) \quad (23)$$

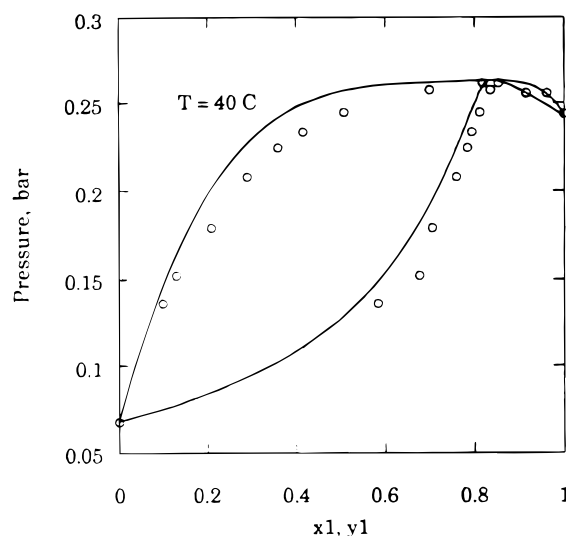
The constants  $a_1$ ,  $a_2$ ,  $b_1$ , and  $b_2$  of eqs 22 and 23 and  $c$ , the degrees of rotational freedom of the components used in this work, are presented in Table 1.

Equation 22 for  $a$  and eq 23 for  $b$  are modifications of the equations of Pults et al. (1989). The modification has been made to extend the equations to polar and associating substances and for improved accuracy. An extended table for the new equation parameters  $a_1$ ,  $a_2$ ,  $b_1$ ,  $b_2$ , and  $c$  for a large number of substances will be reported elsewhere (Novenario and Chao, 1996).

Figures 1-4 show calculated isothermal  $P$ - $x$ - $y$  diagrams in comparison with experimental data for mixtures of acetone + cyclohexane. The four figures show the calculations by PRSV EOS + UNIFAC, COR EOS + UNIFAC, PRSV EOS + Wang-Chao-Wilson and



**Figure 16.** Benzene (1)-1-propanol (2) vapor-liquid equilibrium using the chain-of-rotators EOS with UNIFAC. Circles represent data taken from Hirata and Ohe (1975) and lines show predictions.

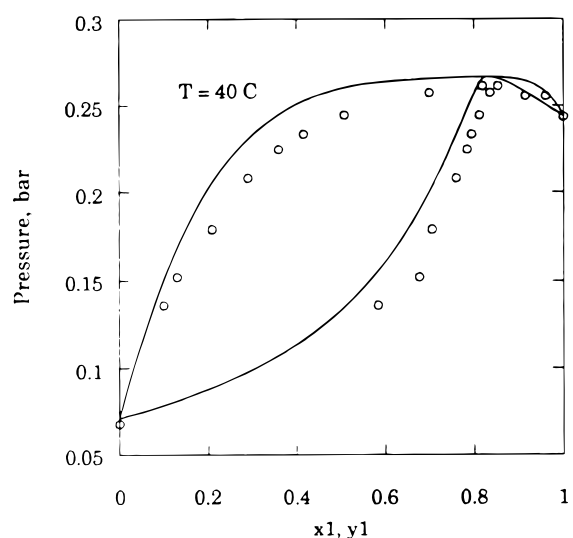


**Figure 17.** Benzene (1)-1-propanol (2) vapor-liquid equilibrium using the PRSV EOS with the Wang-Chao-Wilson model. Circles represent data taken from Hirata and Ohe (1975) and lines show correlations. Wang-Chao-Wilson constants:  $(g_{21} - g_{11}) = -60.98$  J/mol;  $(g_{12} - g_{22}) = 1626.73$  J/mol.

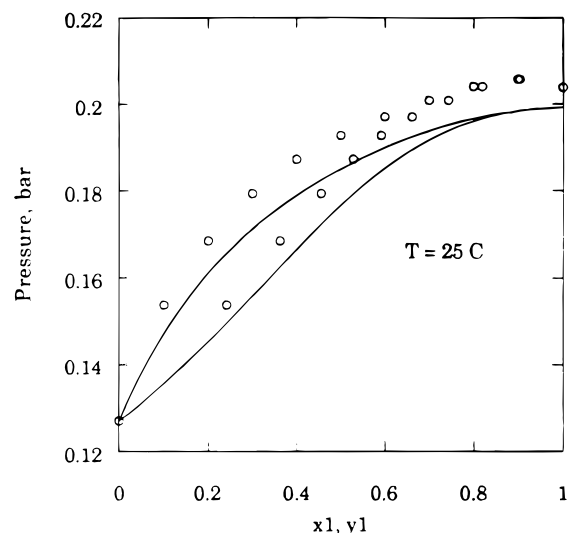
COR EOS + Wang-Chao-Wilson, respectively. Figures 5 and 6 show isothermal  $P$ - $x$ - $y$  diagrams for butanone +  $n$ -heptane, both calculated with the UNIFAC model incorporated in one of the EOS.

Both mixtures in Figures 1-6 are at low pressures. The calculations demonstrate that the effectiveness of the solution models for the representation of vapor-liquid equilibrium of highly nonideal solutions is preserved when the models are incorporated in an EOS by the method of this work. Vapor pressure and second virial coefficient are not required for the calculation. The advantage of the EOS being self-sufficient for the description of phase equilibrium is extended to nonideal solutions.

Figures 7-10 present calculated isothermal  $P$ - $x$ - $y$  diagrams of ethanol + water and acetone + water mixtures at a number of temperatures. The range of pressures is very wide, from about ambient up to about 100 bars. The calculation is made with the UNIFAC model incorporated in the PRSV and the COR EOS. Both mixtures are strongly hydrogen-bonded.



**Figure 18.** Benzene (1)-1-propanol (2) vapor-liquid equilibrium using the chain-of-rotators EOS with the Wang-Chao-Wilson model. Circles represent data taken from Hirata and Ohe (1975) and lines show correlations. Wang-Chao-Wilson constants:  $(g_{21} - g_{11}) = -37.15$  J/mol;  $(g_{12} - g_{22}) = 1726.20$  J/mol.



**Figure 19.**  $n$ -Hexane (1)-benzene (2) vapor-liquid equilibrium using the PRSV EOS with UNIFAC. Circles represent data from Smith and Robinson (1970) and lines show predictions.

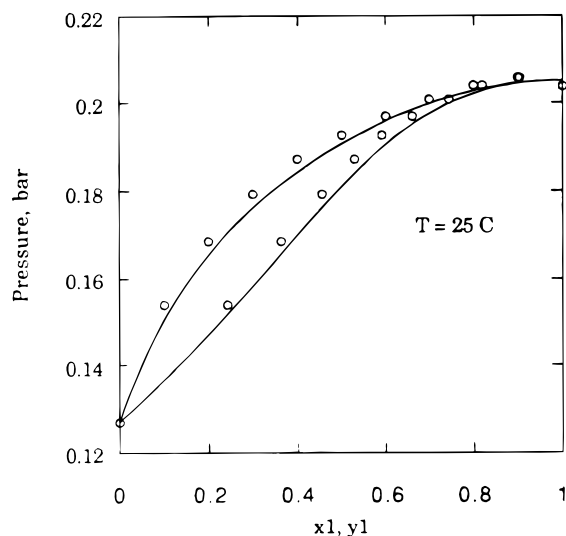
Two highly nonideal mixtures of a hydrogen-bonding component + a nonpolar component are shown in Figures 11-18. Mixtures of  $n$ -hexane + ethanol are shown in the first four figures, followed by mixtures of benzene + 1-propanol in the next four figures. Calculations by the four combinations of an EOS and a solution model are displayed for each mixture.

The last examples are two mixtures of paraffin + an aromatic hydrocarbon. Figures 19-22 show mixtures of  $n$ -hexane + benzene and  $n$ -heptane +  $p$ -xylene calculated by the UNIFAC model incorporated in either EOS.

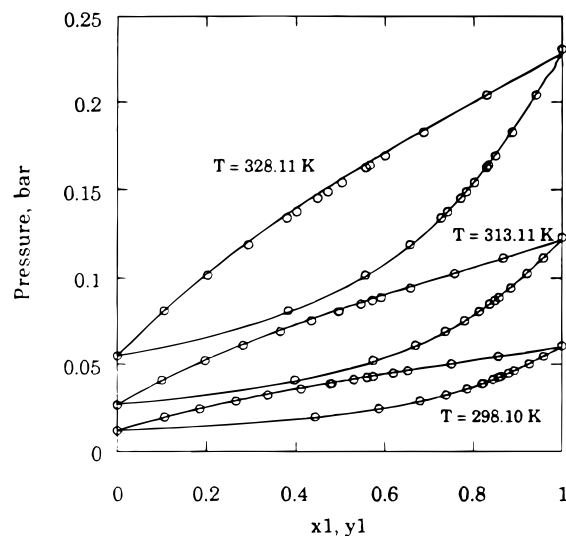
Table 2 presents a summary comparison of the calculations with data. The average absolute percent deviation in pressure and the average absolute deviation in  $y$  are shown for each isotherm of the mixtures that are selected as examples.

## Discussion and Conclusions

A method of incorporating solution model into EOS is developed to apply to cubic as well as to some



**Figure 20.** *n*-Hexane (1)-benzene (2) vapor-liquid equilibrium using the chain-of-rotators EOS with UNIFAC. Circles represent data from Smith and Robinson (1970) and lines show predictions.

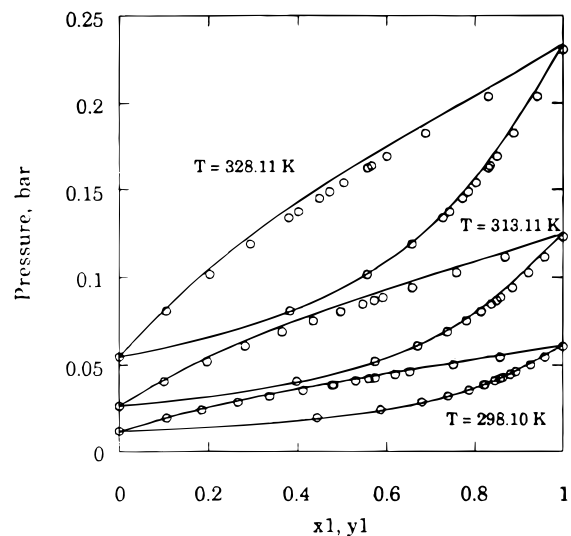


**Figure 21.** *n*-Heptane (1)-*p*-xylene (2) vapor-liquid equilibrium using the PRSV EOS with UNIFAC. Circles represent data from Mentzer, Greenkorn, and Chao (1982) and lines show predictions.

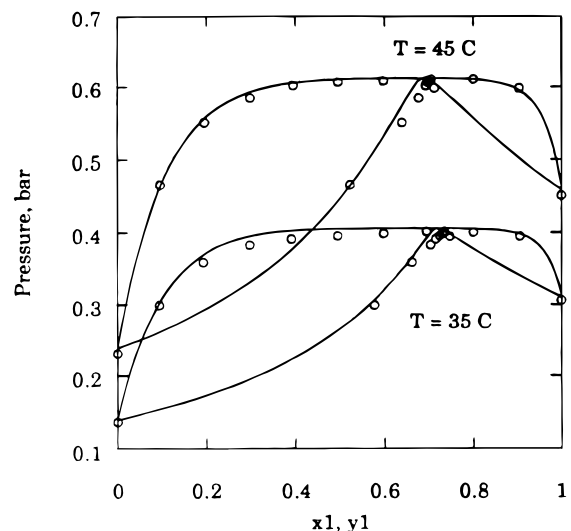
noncubic EOS. To obtain the mixture parameters of the EOS, the excess free energy of the solution model is identified as that of the EOS at a molar volume equal to  $b$  multiplied by a constant factor, which is selected from a search of saturated liquid volumes such that the liquids being mixed are at low pressures. The method is simple to implement by not requiring a zero-pressure liquid volume to be calculated as part of any EOS calculations. The method can be used to express the quadratic composition dependence of the second virial coefficient.

The examples show that the solution model parameters reported in the literature are useful in the method for the representation of vapor-liquid equilibria of highly nonideal solutions in the EOS calculations. The UNIFAC model and parameters are directly used in this method; any intermediate calculations with the UNIQUAC equations as required in the Wong-Orbey-Sandler (1992) method are avoided.

Examples of incorporating the Wang-Chao-Wilson solution model in EOS show that solution model parameters can be fitted to experimental data and then applied to the description of higher pressure vapor-liquid equilibria in this method.



**Figure 22.** *n*-Heptane (1)-*p*-xylene (2) vapor-liquid equilibrium using the chain-of-rotators EOS with UNIFAC. Circles represent data from Mentzer, Greenkorn, and Chao (1982) and lines show predictions.



**Figure 23.** *n*-Hexane (1)-ethanol (2) vapor-liquid equilibrium using the COR EOS with UNIFAC by setting  $k = 0.7$ . Circles represent data taken from Hirata and Ohe (1975) and lines show predictions.

In all of the calculations presented here, the liquid volume is set to be a constant factor ( $\equiv v/b$ ) multiplied by the excluded volume  $b$  at the standard state, where the solution model  $G^E$  is matched with that of the EOS. To use a constant  $k$  for all substances and mixtures in one equation of state is a convenience that leads to good results. Improved results can be obtained for some mixtures by using a slightly different value of this factor found by search for the mixture. Figure 23 shows an example of using  $k = 0.7$  in the COR EOS for mixtures of *n*-hexane + ethanol. Better results are obtained than in Figure 12. Finding a specific value of  $k$  for a mixture can be worthwhile in specialized applications.

## Nomenclature

- $A^E$  = molar excess Helmholtz free energy
- $a$  = attractive parameter
- $b$  = excluded volume parameter
- $a_i$  = attractive parameter of component  $i$
- $b_i$  = excluded volume parameter of component  $i$



$c$  = degrees of rotational freedom for the chain-of-rotators EOS

EOS = equation of state

$G^E$  = molar excess Gibbs free energy

$G_{sm}^E$  = molar excess Gibbs free energy from a solution model

$k$  = constant ratio of molar volume to excluded volume parameter

$P$  = pressure

$R$  = ideal gas constant

$T$  = temperature

$v$  = molar volume

$v_i$  = molar volume of component  $i$

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

$y$  = reduced density for the chain-of-rotators EOS

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

$\alpha$  = nonsphericity constant (=1.078) for the chain-of-rotators EOS

$\phi_i$  = fugacity coefficient of component  $i$  in a mixture

$\gamma_i$  = activity coefficient of component  $i$  in a mixture

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