High-Pressure Vapor-Liquid Equilibrium with a UNIFAC-Based Equation of State

Recent procedures developed by Heidemann (1990) and by Michelsen (1990a, b) enable us to formally incorporate excess Gibbs energy model parameters into a fully consistent equation of state, cith accurate reproduction of the behavior of the excess Gibbs energy model at atmospheric pressure.

This paper investigates the ability of the mixing rules proposed by Michelsen to predict high-pressure phase equilibrium, when used in combination with the parameter table of modified UNIFAC. Considering that a group contribution method is used for the excess Gibbs energy and that model parameters are extrapolated over a 200 K temperature interval, quite satisfactory results are obtained for the mixtures investigated.

Søren Dahl
Michael L. Michelsen
Institut for Kemiteknik
Technical University of Denmark
DK-2800 Lyngby, Denmark

Introduction

Although equation of state mixing rules, based on local composition concepts, were introduced more than a decade ago (Huron and Vidal, 1979), thermodynamically consistent equation of state models capable of directly incorporating existing model parameter tables for excess Gibbs energy models have not appeared until recently (Heidemann and Kokal, 1990; Michelsen, 1990a, b). Gupte et al. (1986) derived a mixing rule for the a parameter in the Van der Waals equation of state to extend the applicability of the UNIFAC group contribution method to the prediction of high-pressure equilibria. The predictions obtained using the approach of Gupte et al. (the UNIWAALS model) were generally satisfactory, but the matching procedure for the a parameter violated thermodynamic consistency, making the model incapable of generating a critical point. Later, Gani et al. (1989) modified UNIWAALS to correct the consistency problem. Unfortunately, the resulting procedure is exceedingly cumbersome, relating pressure and volume through a differential equation, rather than the customary cubic equation.

Mollerup (1986) originally suggested to match the question of state and the excess Gibbs energy model at zero pressure, and the procedures of Heidemann and Kokal (1990) and Michelsen (1990a, b) all follow this suggestion, leading to a density-independent mixing rule for the mixture a parameter. The approach of Michelsen emphasizes computational efficiency and essentially reduces the cost of deriving properties from the equation of state to that of the underlying excess Gibbs energy model.

The ability of an equation of state to directly utilize existing parameter tables for excess Gibbs energy models is advantageous particularly in connection with group contribution methods like UNIFAC (Fredenslund et al., 1977) or modified UNIFAC (Larsen et al., 1987). The performance of these models in low-pressure phase equilibrium prediction is well documented, with readily available large parameter tables (Larsen et al., 1987), which are not easily recorrelated, as the model parameters cannot be determined on a simple pairwise basis.

The availability of temperature-dependent parameters in modified UNIFAC, based on simultaneous correlation of phase equilibrium and excess enthalpy over a fairly wide temperature range, suggests that this model might be useful particularly in connection with extrapolation to high temperatures and pressures. The objective of this paper is to investigate the applicability of an equation of state, based on the mixing rules of Michelsen and the parameter tables of modified UNIFAC, for *the prediction of high-pressure vapor-liquid equilibrium* (VLE). In addition, we provide results obtained with the UNIQUAC model (Abrams and Prausnitz, 1975) using parameters estimated from low-temperature data.

Thermodynamic Model

All calculations are based on a modified Redlich-Kwong equation of state,

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

Table 1. Temperature Dependence of *a* Parameter (Eq. 5)

Compound	C1	C2	C3
Acetone	1.003	−0.456	0.662
Methanol	1.445	−0.815	0.249
Benzene	0.852	−0.491	1.197
Ethanol	1.365	0.726	−2.694
Water	1.087	−0.638	0.635

where the mixture b parameter is derived from the conventional linear mixing rule,

$$b = \sum_{i=1}^{c} z_i b_{ii} \tag{2}$$

using for the corresponding pure-component parameter

$$b_{ii} = 0.08664 \frac{RT_{ci}}{P_{ci}} \tag{3}$$

The pure component a parameter is given by

$$a_{ii} = 0.4286 \frac{R^2 T_{ci}^2}{P_{ci}} [f(T_{ri})]^2 \tag{4}$$

with (Mathias and Copeman, 1983)

$$f(T_r) = \begin{cases} 1 + C_1(1 - \sqrt{T_r}) + C_2(1 - \sqrt{T_r})^2 & \\ \quad + C_3(1 - \sqrt{T_r})^3 & T_r < 1 \\ 1 + C_1(1 - \sqrt{T_r}) & T_r > 1 \end{cases} \tag{5}$$

where constants C_1, C_2 and C_3, given in Table 1, are fitted to match the vapor pressure of the pure components.

The equation of state parameter a for a mixture is calculated by an expression for the mixture excess Gibbs energy, and the key steps leading to the mixing rule for this parameter are summarized as follows.

Huron and Vidal (1979) originally introduced excess Gibbs-energy-based mixing rules into equations of state, by formally matching the excess Gibbs energy of the equation of state at infinite pressure with an independently prescribed expression g^{E*} for the excess Gibbs energy. Their matching procedure yields the following mixing rule for the a parameter,

$$\left(\frac{a}{bRT}\right)_{\text{mix}} = \sum_{i=1}^{C} z_i \left(\frac{a_{ii}}{b_{ii}RT}\right) - \frac{1}{\ln 2} \frac{g^{E*}}{RT} \tag{6}$$

or more conveniently,

$$\alpha_{\text{mix}} = \sum_{i=1}^{C} z_i \alpha_{ii} - \frac{1}{\ln 2} \frac{g^{E*}}{\text{RT}} \tag{7}$$

where the a parameter is replaced by the dimensionless parameter $\alpha = a/bRT$.

The equation of state excess Gibbs energy at near atmospheric pressure, however, differs substantially from that at infinite pressure; therefore, existing parameter tables for g^E models, correlated from vapor-liquid equilibrium data at pressures below 5 bar, cannot be utilized directly with the Huron-Vidal mixing rule.

Table 2. VLE Results for MHV2 and Extrapolation Method with Modified UNIFAC Model

Model	SRK + Mod. UNIFAC			MHV2		EXTRP		MHV2		
Parameters				Table*		Table*		Gupte**		
System	T(K)	P(bar)	No. Dpts.†	$\Delta P/P$ (×100)	Δy	$\Delta P/P$ (×100)	Δy	$\Delta P/P$ (×100)	Δy	Ref.
Acetone (1)–water (2)	373	1.1–3.7	22	4.6	2.0	3.5	1.6	—		Griswold and Wong (1952)
	423	6.7–11.6	14	2.3	1.8	2.4	1.7	—		
	473	16.0–27.9	25	2.6	1.3	4.4	1.8	—		
	523	40.3–63.4	8	0.8	0.7	3.9	1.2	—		
Methanol (1)–benzene (2)	373	3.1–4.0	10	0.7	0.6	0.8	0.6	—		Butcher and Medani (1968)
	413	6.7–11.6	10	1.0	0.7	1.4	0.5	—		
	453	13.2–27.2	10	3.1	1.9	1.8	1.6	—		
	493	22.6–57.6	10	5.9	3.6	4.4	3.5	—		
Methanol (1)–water (2)	373	1.0–3.4	12	4.2	1.7	—		2.1	1.4	Griswold and Wong (1952)
	423	5.1–13.7	11	3.0	2.0	—		1.5	1.5	
	473	16.3–39.4	11	7.1	3.2	—		3.2	2.0	
	523	47.0–83.0	10	16.2	3.8	—		7.4	2.0	
Ethanol (1)–water (2)	423	5.6–9.9	17	3.3	0.8	2.8	0.7	—		Barr et al. (1959)
	473	17.9–29.5	17	2.8	2.1	3.0	2.1	—		
	523	40.8–69.2	12	3.7	2.7	3.9	2.9	—		
	598	124–155	6	1.4	0.9	3.3	1.7	—		
	623	170–185	3	0.5	0.1	1.9	0.4	—		
Acetone (1)–methanol (2)	373	3.5–3.7	14	2.7	1.2	—		—		Griswold and Wong (1952)
	423	11.7–14.1	15	0.7	1.7	—		—		
	473	29.5–39.9	10	2.1	3.1	—		—		
Average deviation, %				3.5	1.8	3.1	1.6	3.4	1.7	

*Modified UNIFAC parameters as given in Larsen et al. (1987).
**Parameters reestimated for the methanol-water system as given in Gupte et al. (1986).
†Data points.

Michelsen (1990b) repeated the matching procedure of Huron and Vidal, using a reference pressure of zero. This results in the implicit mixing rule

$$q(\alpha) = \sum_{i=1}^{C} z_i q(\alpha_{ii}) + \frac{g^{E*}}{RT} + \sum_{i=1}^{C} z_i \ln\left(\frac{b}{b_{ii}}\right) \qquad (8)$$

where the function $q(\alpha)$ is given by

$$q(\alpha) = -1 - \ln(u-1) - \alpha \ln\left(\frac{u+1}{u}\right) \qquad (9)$$

with

$$u = (v/b)_{P=0} = \frac{1}{2}\left(\alpha - 1 - \sqrt{\alpha^2 - 6\alpha + 1}\right) \qquad (10)$$

Equation 8 cannot be used for evaluation of the a (or α) parameter under all conditions, as the function $q(\alpha)$ is defined only for $\alpha > 3 + 2\sqrt{2}$. To reproduce the behavior of the underlying g^E model, however, an approximation for $q(\alpha)$, matching Eq. 9 in the range $10 < \alpha < 13$, was adequate. Outside this range, the approximation only has to establish a one-to-one relation between q and α, satisfying appropriate conditions of continuity. A variety of approximations were suggested, the simplest being the linear relation:

$$q(\alpha) \simeq q_0 + q_1\alpha \qquad (11)$$

Substitution of this expression into Eq. 8 results in the explicit mixing rule,

$$\alpha_{\text{mix}} = \sum_{i=1}^{C} z_i\alpha_{ii} + \frac{1}{q_1}\left[\frac{g^{E*}}{RT} + \sum_{i=1}^{C} z_i \ln\left(\frac{b}{b_{ii}}\right)\right] \qquad (12)$$

the recommended value of q_1 being -0.593.

The mixing rule of Eq. 12 is surprisingly similar to the original Huron-Vidal mixing rule and was, therefore, called the modified Huron-Vidal first order (MHV1). The mixing rule provides for a fair reproduction of the g^E model, but a much better match is obtained with $q(\alpha) \simeq q_0 + q_1\alpha + q_2\alpha^2$ yielding:

$$q_1\left(\alpha_{\text{mix}} - \sum_{i=1}^{C} z_i\alpha_{ii}\right) + q_2\left(\alpha_{\text{mix}}^2 - \sum_{i=1}^{C} z_i\alpha_{ii}^2\right) = \frac{g^{E*}}{RT} + \sum_{i=1}^{C} z_i \ln\left(\frac{b}{b_{ii}}\right) \qquad (13)$$

the modified Huron-Vidal second-order (MHV2) mixing rule. The recommended values of q_1 and q_2 are -0.478 and -0.0047, respectively. The derivation of fugacity coefficients from the MHV2 mixing rule is described in the Appendix.

Michelsen's original proposal (Michelsen, 1990a) is slightly different. A limiting lower value of α, α_{cut} is selected. Equations 9 and 10 were used to relate q and α for $\alpha > \alpha_{\text{cut}}$, whereas a parabolic extrapolation,

$$\alpha - \alpha_{\text{cut}} = K_1(q - q_{\text{cut}}) + K_2(q - q_{\text{cut}})^2 \qquad (14)$$

Table 3. VLE Results for MHV2 with UNIQUAC Model

Model	SRK + Original UNIQUAC and MHV2									
Parameters Estimated from				All Data Points		Low-Temp. Data Only		Individual Isoterms		
System	T(K)	P(bar)	No. Dpts.†	$\Delta P/P$ (×100)	Δy	$\Delta P/P$ (×100)	Δy	$\Delta P/P$ (×100)	Δy	Ref.
Acetone (1)–water (2)	373	1.1–3.7	22	1.5	0.6	1.5	0.7	1.5	0.5	Griswold and Wong (1952)
	423	6.7–11.6	14	0.5	0.9	0.5	0.9	0.8	0.7	
	473	16.0–27.9	25	2.7	1.1	2.8	1.2	0.7	0.3	
	523	40.3–63.4	8	3.4	1.0	3.6	1.1	0.6	0.4	
Methanol (1)–benzene (2)	373	3.1–4.0	10	1.4	0.7	2.0	1.7	0.8	0.7	Butcher and Medani (1968)
	413	6.7–11.6	10	2.7	0.8	6.7	2.5	0.7	0.5	
	453	13.2–27.2	10	5.9	1.7	10	3.3	0.8	1.4	
	493	22.6–57.6	10	7.4	3.4	11	4.3	3.2	3.3	
Methanol (1)–water (2)	373	1.0–3.4	12	2.7	1.0	2.4	1.1	1.1	1.0	Griswold and Wong (1952)
	423	5.1–13.7	11	1.5	1.4	1.3	1.3	0.9	1.0	
	473	16.3–39.4	11	1.5	1.2	2.0	1.4	0.8	1.0	
	523	47.0–83.0	10	3.6	1.3	4.8	1.5	0.5	0.7	
Ethanol (1)–water (2)	423	5.6–9.9	17	2.3	0.9	3.6	1.0	1.2	0.6	Barr et al. (1959)
	473	17.9–29.5	17	3.1	1.1	4.3	1.6	0.9	0.4	
	523	40.8–69.2	12	4.4	1.1	5.8	1.5	0.6	0.3	
	598	124–155	6	2.8	0.8	3.4	1.0	0.4	0.2	
	623	170–185	3	0.5	0.1	0.7	0.1	—	—	
Acetone (1)–methanol (2)	373	3.5–3.7	14	2.6	1.1	3.5	1.2	0.9	1.2	Griswold and Wong (1952)
	423	11.7–14.1	15	1.4	1.8	4.8	3.2	0.8	1.8	
	473	29.5–39.9	10	4.2	3.2	5.8	1.5	2.7	3.1	
Average deviation, %				2.7	1.2	3.9	1.6	1.0	0.9	

*Data points.

was used for $\alpha < \alpha_{cut}$ $[q_{cut} = q\ (\alpha_{cut})]$. Constants K_1 and K_2 are determined to yield continuity in the first and second derivatives of q at α_{cut}. Computationally, this procedure for evaluating the mixture parameter—the extrapolation method—is slightly more complex.

Any appropriate model for the excess Gibbs energy can be used in connection with the present mixing rules. In this paper, modified UNIFAC and UNIQUAC are used. For the modified UNIFAC model, we used the structural parameters R and Q from Larsen et al. (1987), and for the original UNIQUAC model molecular R and Q given as in Gmehling (1977).

Results

We investigated five binary mixtures, for which high-pressure VLE-data are available. Calculations with the modified UNIFAC were based on the parameter tables of Larsen et al. (1987), and for methanol-water the parameters of Gupte et al. (1986) were used. In addition to the MHV2, mixing rule calculations are also performed with the extrapolation method suggested earlier by Michelsen (1990a), using as spline point $v/b = 1.4$, corresponding to $\alpha_{cut} = 8.4$.

For comparison, calculations with UNIQUAC are included. In these examples, UNIQUAC interaction parameters are determined by estimating:

- A single set of parameters using all the experimental data points
- A single set of parameters from low-temperature data only (T below 373 K)
- UNIQUAC parameters for each isotherm.

Finally, equilibrium calculations based on the previously determined binary parameters for the ternary mixture methanol-water-acetone are performed.

The UNIQUAC parameter estimations are performed by minimizing the explicit objective function in all cases:

$$SSQ = \sum_{n=1}^{dtps} \sum_{i=1}^{2} \left[x_i \frac{\phi_i^l(T, P, x)}{\phi_i^v(T, P, y)} - y_i \right]^2 \tag{15}$$

using the experimental temperature, pressure and phase composition. This objective function is very easy to apply and corresponds quite closely to minimizing $(\Delta P/P)^2 + (\Delta y)^2$.

The purely predictive results obtained with modified UNIFAC and the MHV2 mixing rule are shown in Table 2 together with the results for selected mixtures using Michelsen's extrapolation method. Considering that all calculations are performed with parameters based solely on low-pressure data, the quality of the predictions is satisfactory, except for the methanol-water system. Not surprisingly, this mixture was improved with the parameters of Gupte et al. (1986), where high-pressure data were included in the estimation. The results obtained with the extrapolation method are largely equivalent to those obtained with the MHV2 mixing rule. In addition to modified UNIFAC, we have also investigated the original UNIFAC equation with temperature-independent parameters. Here, substantial improvement for the methanol-water system was noted, at the expense of a severe degradation for the other four mixtures.

Table 4. Molecular Interaction Parameters for UNIQUAC Used for MHV2

Parameters Estimated from				All Data Points		Low-Temp. Data Only		Individual Isoterms		
System	T (K)	P (bar)	No. Dpts.*	$a12$ (K)	$a21$ (K)	$a12$ (K)	$a21$ (K)	$a12$ (K)	$a21$ (K)	Ref.
Acetone(1)–water(2)	373	1.1–3.7	22	194	36	191	41	230	11	Griswold and Wong (1952)
	423	6.7–11.6	14					163	59	
	473	16.0–27.9	25					148	40	
	523	40.3–63.4	8					386	130	
Methanol(1)–benzene(2)	373	3.1–4.0	10	−19	465	−52	594	−42	533	Butcher and Medani (1968)
	413	6.7–11.6	10					−38	461	
	453	13.2–27.2	10					−65	455	
	493	22.6–57.6	10					−48	413	
Methanol(1)–water(2)	373	1.0–3.4	12	−120	180	−163	261	−299	539	Griswold and Wong (1952)
	423	5.1–13.7	11					−314	578	
	473	16.3–39.4	11					−366	648	
	523	47.0–83.0	10					−353	523	
Ethanol(1)–water(2)	423	5.6–9.9	17	−16	155	−8	164	−186	408	Barr et al. (1959)
	473	17.9–29.5	17					−241	470	
	523	40.8–69.2	12					−210	370	
	598	124–155	6					−409	682	
	623	170–185	3					—	—	
Acetone(1)–methanol(2)	373	3.5–3.7	14	184	−33	203	−38	178	−50	Griswold and Wong (1952)
	423	11.7–14.1	15					310	−127	
	473	29.5–39.9	10					331	−152	

*Data points.

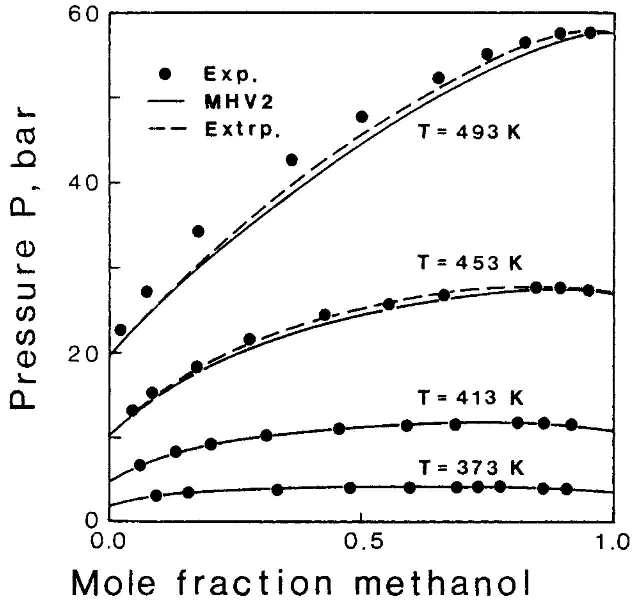

Figure 1. ***Px* diagram for methanol-benzene calculated using modified UNIFAC with MHV2 and with the extrapolation method.**

Experimental data of Butcher and Medani (1968).

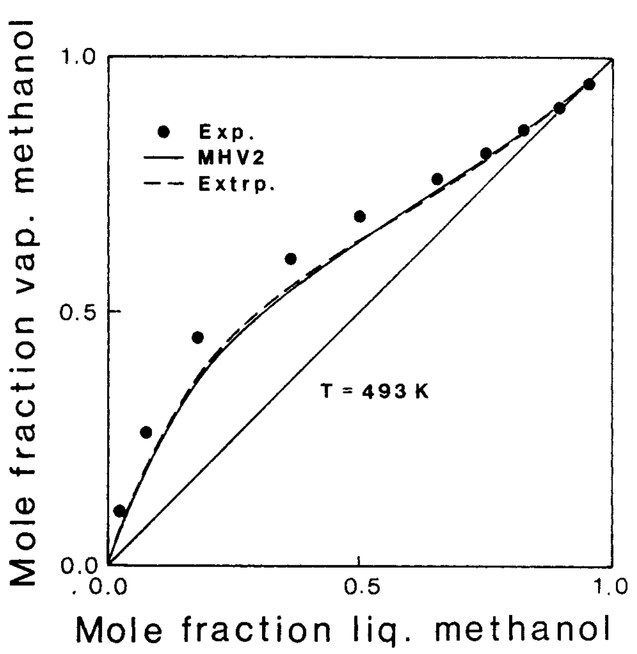

Figure 3. ***xy* diagram for methanol-benzene at 493 K calculated using modified UNIFAC with MHV2 and with the extrapolation rule.**

Experimental data of Butcher and Medani (1968).

In Table 3 are given results for the UNIQUAC method using a single pair of temperature-independent parameters for each binary system. When data for all the isotherms are included in the parameter estimation, average errors are decreased by about 30% as compared with the UNIFAC predictions. It is, however, worthwhile to note that quite satisfactory extrapolations are also obtained by using UNIQUAC parameters estimated solely from low-pressure data. Finally, very small errors obtained by fitting UNIQUAC parameters to each isotherm demonstrate that the MHV2 mixing rule is capable of describing the data well. The UNIQUAC parameters used for the calculations in Table 3 are listed in Table 4.

Figures 1-3 show experimental and calculated phase equilibrium for mixtures of methanol and benzene. Calculations are

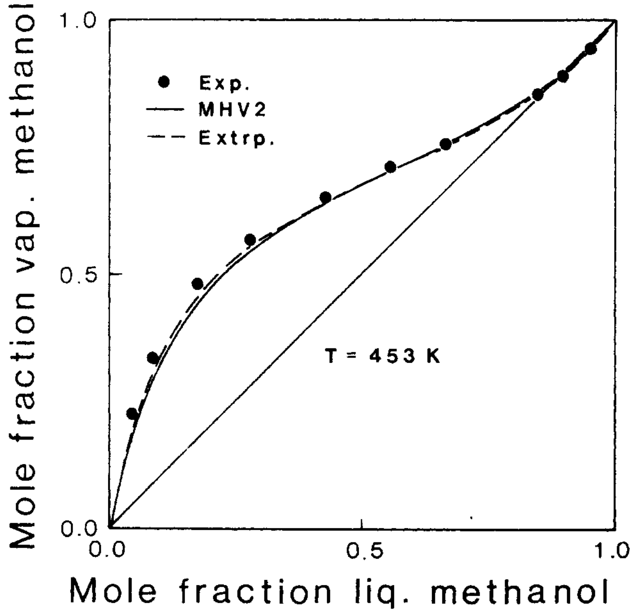

Figure 2. ***xy* diagram for methanol-benzene at 453 K calculated using modified UNIFAC with MHV2 and with the extrapolation rule.**

Experimental data of Butcher and Medani (1968).

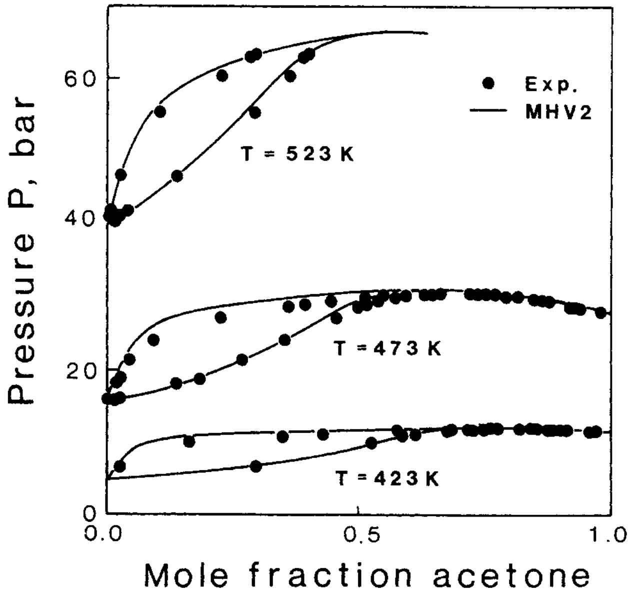

Figure 4. ***Pxy* diagram for acetone-water using modified UNIFAC with the MHV2 mixing rule.**

Experimental data of Griswold and Wong (1952).

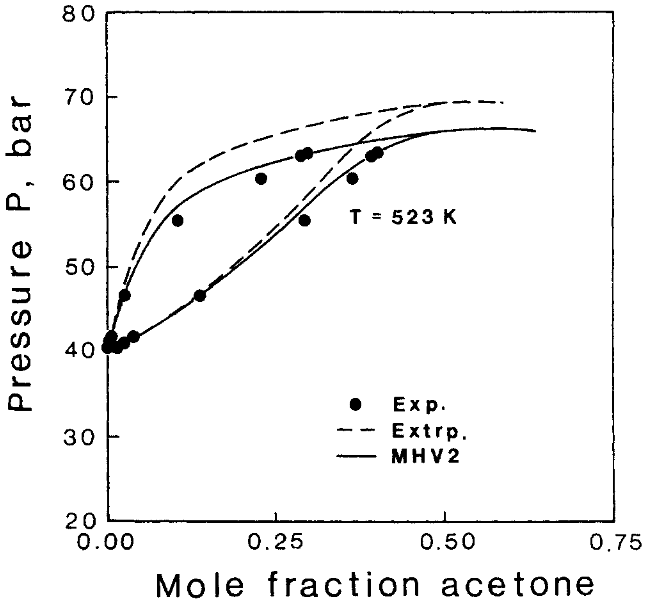

Figure 5. *Pxy* for acetone-water at 573 K modified UNIFAC with MHV2 and with the extrapolation method.

Experimental data of Griswold and Wong (1952).

performed with both the MHV2 mixing rule and the extrapolation rule suggested earlier by Michelsen (1990a). At lower temperatures, the predictions with the two mixing rules are of nearly identical quality, whereas the extrapolation method yields slightly better results at higher temperatures. Isotherms for acetone-water are shown in Figures 4-5, the MHV2 mixing rule being markedly superior at 523 K. Figure 6 shows isotherms for ethanol-water calculated with the modified UNIFAC and MHV2 over a very wide temperature range. The agreement between calculated and experimental data is excellent at low as well as at very high temperatures, whereas some deviation is observed at 523 K. Figure 7 illustrates methanol-water predictions with the modified UNIFAC, compared with the UNIQUAC using adjusted parameters for each isotherm. The individual isotherms are very well represented with the MHV2 mixing rule, but the predictions based on the modified UNIFAC tables were clearly overshot.

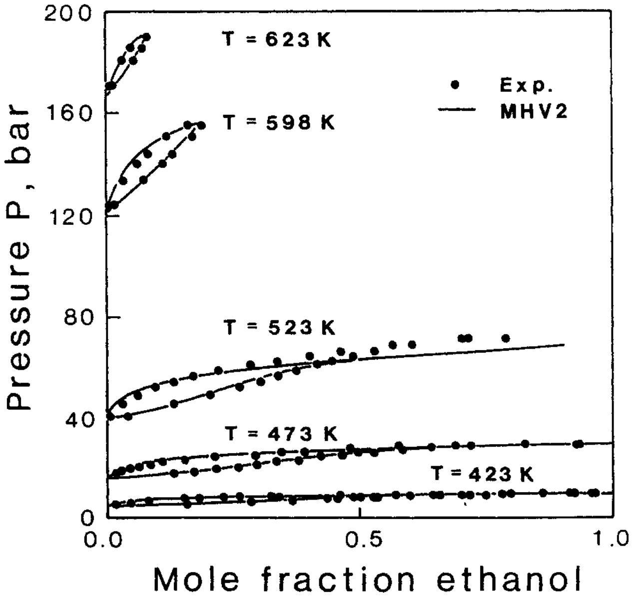

Figure 6. *Pxy* diagram for ethanol-water using modified UNIFAC with the MHV2 mixing rule.

Experimental data of Barr et al. (1959).

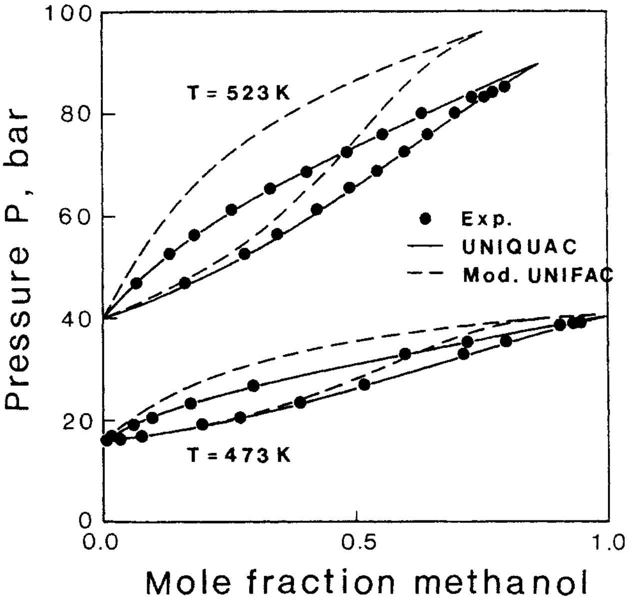

Figure 7. *Pxy* diagram for methanol-water with the MHV2 mixing rule and modified UNIFAC compared to UNIQUAC, using adjusted parameters for each isotherm.

Experimental data of Griswold and Wong (1952).

Table 5 shows equilibrium calculations for the ternary mixture acetone-methanol-water, based on the UNIFAC parameter tables as well as on the previously determined UNIQUAC parameters. It is noted that independent of the approach used, no visible degradation occurs in extending predictions to the ternary mixture. A more extensive investigation of the behavior of the model in multicomponent high-pressure phase equilibrium would evidently be desirable, but very few experimental data for such mixtures containing polar components are available.

Discussion and Conclusion

Our objective was to determine whether formal incorporation of the parameter tables of modified UNIFAC into a fully consistent equation of state was feasible and capable of yielding predictions of comparable quality to those of modified UNIFAC at low pressures. Based on the rather limited amount of high-pressure data available, the answer is confirmative, with minor, but important, reservations. Rather inaccurate results obtained for the methanol-water mixture may appear surprising, since the methanol-water interaction parameters in the modified UNIFAC have been determined independent of other group-interaction parameters, as both molecules are treated as

Table 5. Prediction of High-Pressure VLE for the System of Acetone(1)–Methanol(2)–Water(3): Experimental Data Griswold and Wong (1952)

Model	SRK and MHV2 +		UNIFAC		UNIFAC		UNIQUAC		UNIQUAC		UNIQUAC	
Parameters Estimated from			Parameter Table*		Parameter Table**		All Data Points		Low-Temp. Data Only		Individual Isoterms	
T (K)	P (bar)	No. Dpts.†	$\Delta P/P$ (×100)	Δy	$\Delta P/P$ (×100)	Δy	$\Delta P/P$ (×100)	Δy	$\Delta P/P$ (×100)	Δy	$\Delta P/P$ (×100)	Δy
373	1.2–3.9	51	7.6	3.0	5.6	2.7	2.4	2.1	2.8	2.3	3.4	1.9
523	47.5–82.0	57	8.5	2.1	4.4	1.5	6.0	1.5	7.0	1.6	1.6	1.2

*Modified UNIFAC parameters as given in Larsen et al. (1987).
**Methanol-water parameters from Gupte et al. (1986).
†Data points.

single groups. One explanation might be that this limited the temperature interval, over which the model parameters were correlated in the modified UNIFAC, as compared with groups that form part of a multitude of molecules. The methanol-water parameters for the modified UNIFAC are shown in Figure 8, and it is clear that the use of three terms to represent the temperature dependence over a limited temperature interval entails a risk of "overcorrelating," when a temperature extrapolation by 150 K or more is performed. Evidently, the possiblity of erroneous extrapolation for other mixtures cannot be excluded, and in particular group interactions exhibiting very strong temperature dependence warrants caution.

When judged on the basis of the mixtures investigated in this work, however, the overall performance of the modified UNIFAC is far superior to that of the original UNIFAC and quite acceptable in light of the inherent limitations of a group-contribution method.

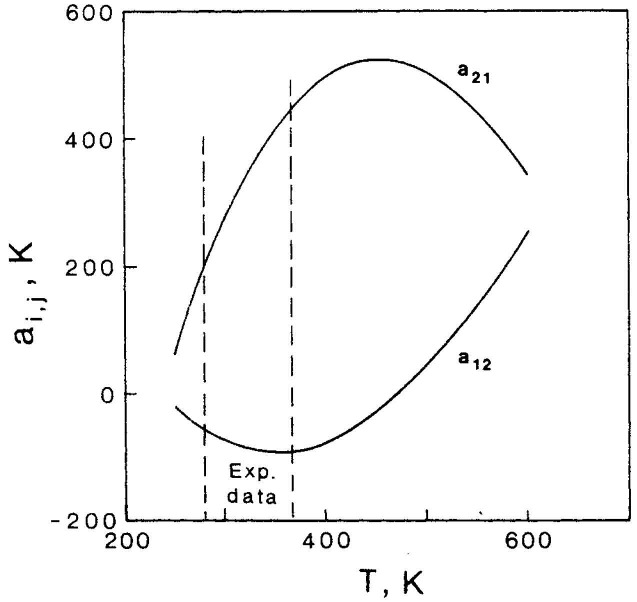

Figure 8. Modified UNIFAC interaction parameters for methanol-water as a function of temperature.

These parameters were estimated in the interval $T_{min} = 278$ K to $T_{max} = 366$ K.

Acknowledgment

We would like to thank Peter Rasmussen of the Technical University of Denmark for many helpful discussions.

Appendix: Calculation of Fugacity Coefficients

The fugacity coefficient expression is most easily derived in terms of the mixture parameter α, substituting $a = \alpha bRT$ in the equation of state, Eq. 1. This equation can now be written:

$$\frac{P}{RT} = \frac{1}{v-b} - \alpha\left(\frac{1}{v} - \frac{1}{v+b}\right) \tag{A1}$$

from which the fugacity coefficient can be derived as:

$$\ln\phi_i = \ln\left[\frac{RT}{P(v-b)}\right] + \left[\frac{1}{v-b} - \frac{\alpha}{v+b}\right]b_{ii} - \ln\left[\left(\frac{v+b}{v}\right)\left(\frac{\partial(n\alpha)}{\partial n_i}\right)\right]_{T,n_j} \tag{A2}$$

The composition derivative of $(n\alpha)$ can be calculated from the MHV2 mixing rule, using:

$$(q_1 + 2\alpha q_2)\frac{\partial(n\alpha)}{\partial n_i} = q_1\alpha_{ii} + q_2(\alpha^2 + \alpha_{ii}^2) + \ln\gamma_i + \ln\frac{b}{b_{ii}} + \frac{b_{ii}}{b} - 1 \tag{A3}$$

where γ_i is the activity coefficient of component i, as calculated from g^{E*} at the current temperature and composition, i.e.,

$$\ln\gamma_i = \frac{1}{RT}\left[\frac{\partial(ng^{E*})}{\partial n_i}\right]_{T,n_j} \tag{A4}$$

The calculation of fugacity coefficients, given temperature, pressure, and phase composition z, thus proceeds as follows:

- Calculate pure-component parameters α_{ii} and b_{ii} and the mixture b parameter.
- Calculate the excess Gibbs energy and the activity coefficients from the g^E model.

- Determine the mixture α from Eq. 13, selecting the larger root of the quadratic equation. Calculate the composition derivatives from Eq. A3.
- Solve the equation of state, Eq. A1, for v, selecting, in the case of multiple roots, the larger for vapor-phase properties and the smaller for liquid-phase properties. Calculate fugacity coefficients from Eq. A2.

Notation

α = equation of state mixture parameter
a_{ij} = interaction energy parameter of UNIFAC and UNIQUAC, K
b = equation of state mixture parameter
$C1, C2, C3$ = pure component temperature dependence parameters
g^E = excess Gibbs energy
K_1, K_2 = constants used in the extrapolation rule, Eq. 14
n = number of moles
P = pressure, bar
q = function defined by Eqs. 9 and 10
q_1, q_2 = mixing rule constants, Eq. 7
Q = structural group- or molecular-surface area fraction
R = structural group- or molecular-volume
R = gas constant
T = temperature, K
u = reduced volume $= v/b$
v = molar volume
x = liquid mole fraction
y = vapor mole fraction
z = phase composition

Greek letters

α = equation of state mixture parameter, $\alpha = a/bRT$
α_{cut} = limiting value of α, Eq. 14
φ = fugacity coefficient

Superscripts

E = excess property
l = liquid-phase property
v = vapor-phase property

Subscripts

c = critical values
ii = parameter for pure component i
mix = mixture
r = reduced property

Literature Cited

Abrams, D. S., and J. M., Prausnitz, "Statistical Thermodynamics of Liquid Mixtures: a New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems," *AIChE J.*, **21**, 116 (1975).

Barr, D., and F. D. Barnett, "Vapor-Liquid Equilibrium at High Pressures," *J. Chem. Eng. Data*, **4**, 107 (1959).

Butcher, K. L., and M. S. Medani, "Thermodynamic Properties of Methanol-Benzene Mixtures at Elevated Temperatures," *J. Appl. Chem.*, **18**, 100 (1968).

Fredenslund, Aa., J. Gmehling, and P. Rasmussen, *Vapor-Liquid Equilibria Using UNIFAC*, Elsevier, New York (1977).

Gani, R., N. Tzouvaras, P. Rasmussen, and Aa. Fredenslund, "Prediction of Gas Solubility and Vapor-Liquid Equilibria by Group Contribution," *Fluid Phase Equilib.*, **47**, 133 (1989).

Gmehling, J., and U. Onken, "Vapor-Liquid Equilbrium Data Collection," *DECHEMA, Chemistry Data Ser.* **I/1**, Frankfurt/Main (1977).

Griswold, J., and S. Y. Wong, "Phase-Equilibria of the Acetone-Methanol-Water System from 100°C: into the Critical Region." *AIChE Symp. Ser.*, **48**, 18 (1952).

Gupte, P. A., P. Rasmussen, and Aa. Fredenslund, "A New Group-Contribution Equation of State for Vapor-Liquid Equilibria," *Ind. Eng. Chem. Fund.*, **25**, 636 (1986).

Heidemann, R. A., and S. L. Kokal, "Combined Excess Free Energy Models and Equations of State," *Fluid Phase Equilib.*, **56**, 17 (1990).

Huron, M. J., and J. Vidal, "New Mixing Rules in Simple Equations of State for Representing Vapor-Liquid Equilibria of Strongly Nonideal Mixtures," *Fluid Phase Equilib.*, **3**, 255 (1979).

Larsen, B. L., P. Rasmussen, and Aa. Fredenslund, "A Modified UNIFAC Group-Contribution Model for Prediction of Phase Equilibria and Heats of Mixing," *Ind. Eng. Chem. Res.*, **26**, 2274 (1987).

Mathias, P. M., and T. W. Copeman, "Extension of the Peng-Robinson Equation of State to Complex Mixtures: Evaluation of the Various Forms of the Local Composition Concept," *Fluid Phase Equilib.*, **13**, 91 (1983).

Michelsen, M. L., "A Modified Huron-Vidal Mixing Rule for Cubic Equations of State," *Fluid Phase Equilib.* **60**, 213 (1990a).

Michelsen, M. L., "A Method for Incorporating Excess Gibbs Energy Models in Equations of State," *Fluid Phase Equilib.* **60**, 42 (1990b).

Mollerup, J., "A Note on the Derivation of Mixing Rules from Excess Gibbs Energy Models," *Fluid Phase Equilib.*, **25**, 323 (1986).

Manuscript received July 6, 1990, and revision received Oct. 16, 1990.