

CORRELATION OF VAPOR-LIQUID EQUILIBRIUM DATA FOR BINARY MIXTURES CONTAINING ONE POLAR COMPONENT BY THE PARAMETERS FROM GROUP CONTRIBUTIONS EQUATION OF STATE

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ABSTRACT

Use of a quadratic mixing rule in the Parameters from Group Contributions Equation of State increases the range of compounds for which vapor-liquid equilibrium behavior can be satisfactorily correlated. This is demonstrated by correlation of vapor-liquid equilibrium for several binary mixtures containing at least one polar component.

NOMENCLATURE

- a_{jn} Binary interaction coefficient of energy term between molecules j and n
- b Molecular volume of system, m^3/kg mole
- b_i Molecular volume of component i , m^3/kg mole
- b_j Molecular volume of group j , m^3/kg mole
- B_i Term in the quadratic mixing rule defined by equation (12)
- c Total number of components in the system
- E_j Energy term of group j
- E_{jn} Interaction energy term between groups j and n
- E_j^0 Energy parameter in equation (9.A)
- E_j^1 Energy parameter in equation (9.A)
- E_j^2 Energy parameter in equation (9.A)

g	Total number of groups in system
k_{ij}	Binary interaction parameter between groups i and j for molecular volume b
l_{ij}	Binary interaction parameter between groups i and j for degrees of freedom s
m_{ij}	Number of group j in molecule i
p_{jn}	Binary parameter between groups j and n
P	Pressure of system, atm.
P_c	Critical pressure, atm.
P_r	Reduced pressure, (P/P_c)
q_{jn}	Binary parameter between groups j and n
R	Universal gas constant
s	Degrees of freedom
s_i	Degrees of freedom for component i
s_j	Degrees of freedom for group j
S_i	Term in the quadratic mixing rule defined by equation (12).
T	Temperature of the system, K
T_c	Critical temperature, K
T_r	Reduced temperature, (T/T_c)
v	Volume of system, m^3/kg mole
x	Defined as (b/v)
y_i	Mole fraction of component i
Z	Compressibility factor
Γ_j	Fraction of volume for group j
Θ_{jn}	Energy parameter between groups j and n
μ_i	Chemical potential for component i

INTRODUCTION

Equations of state (EOS) are widely used for correlating and predicting thermodynamic properties of light hydrocarbon and gaseous component mixtures. They are an integral part of all contemporary process simulators. The reliability and accuracy of a process simulation are largely dependent on the accuracy of the equation of state used for calculating vapor-liquid equilibrium and other thermodynamic properties.

Because EOS are so important to calculations of equilibrium and thermodynamic properties in chemical engineering, extensive work has been done by many authors to develop new EOS and also to improve existing EOS.

done by many authors to develop new EOS and also to improve existing EOS. The literature on this is so extensive only a few examples are cited, such as Soave (1972), Cunningham and Wilson (1974), Peng and Robinson (1976), Trebble (1986) and Pults, et al. (1989). In spite of this large volume of research, there is still a wide range of components and mixtures that existing EOS cannot predict satisfactorily. Also, most EOS contain parameters that must be obtained from experimental VLE data in order to satisfactorily predict VLE and thermodynamic properties accurately. Polar components and mixtures containing polar constituents are difficult for all EOS to handle well.

Two procedures for improving the predictive capability of EOS are through proper mixing rules and use of binary interaction parameters as suggested by Huron and Vidal (1979), Adachi and Sugie (1986), Mansoori (1986), Panagiotopoulos and Reid (1986) and Schwartzentruber et al. (1990).

The work reported here utilizes a quadratic mixing rule instead of a linear one in the Parameters from Group Contribution (PFGC) equation of state. The strength of this technique is illustrated by correlating VLE data for several binaries containing at least one polar component.

PARAMETERS FROM GROUP CONTRIBUTION EQUATION OF STATE

Cunningham and Wilson (1974) first presented the PFGC equation of state. Moshfeghian et al. (1979, 1980) developed an improved and extended set of parameters for groups found in components of typical natural gas mixtures. Several group parameters for the PFGC equation of state have been published and the predicted VLE based on them compared with experimental measurements, Moshfeghian (1989), Moshfeghian et al. (1989). The dimensionless form of the compressibility factor for the PFGC equation of state is:

$$Z = 1 - \left(\frac{s}{x} \right) \ln(1-x) - s + 12bx \sum_s \Gamma_n \left[\frac{1 - \sum_j \Gamma_j \Theta_{nj}}{1 - x + x \sum_j \Gamma_j \Theta_{nj}} \right] \quad (1)$$

Where $x = b/v$.

The following mixing rules were proposed by Cunningham and Wilson (1974). The molecular volume of the system, b , is defined as

$$b = \sum_i^c y_i b_i \quad (2)$$

where b_i , the component molecular volume, is

$$b_i = \sum_j^g m_{ij} b_j \quad (3)$$

Similarly the parameter proportional to the degrees of freedom, s , is

$$s = \sum_i^c y_i s_i \quad (4)$$

where s_i , the component degrees of freedom, is

$$s_i = \sum_j^g m_{ij} s_j \quad (5)$$

In equations (2) and (4) y_i is the mole fraction of component i in molecule i . The fraction of molecular volume, Γ_j , for group j is

$$\Gamma_j = \frac{\sum_i^c y_i m_{ij} b_j}{b} \quad (6)$$

The interaction parameter between groups j and n is

$$\Theta_{jn} = \exp(-E_{jn} / RT) \quad (7)$$

where E_{jn} , the interaction energy between groups j and n is given by

$$E_{jn} = a_{jn} (E_j + E_n) / 2 \quad (8)$$

In equation (8) a_{jn} is constant and defined as the binary interaction coefficient between groups j and n . The energy term, E_j , for group j is calculated from

$$E_j = E_j^0 + E_j^1 (283.2 / T - 1) \quad (9)$$

$$E_j = E_j^0 + E_j^1[(283.2/T) - 1] + E_j^2[(283.2/T)^2 - 1] \quad (9.A)$$

In the above equations b_j , s_j , E_j^0 , E_j^1 , and E_j^2 are parameters of group j that must be determined from PVT data for the pure compounds making up the binary mixture. The third term in equation 9.A allows for greater variation with temperature for the interaction energies.

PROPOSED MODIFICATIONS

In order to extend the capabilities and improve the accuracy of the PFGC equation of state in predicting the thermodynamic properties and VLE behavior of mixtures containing polar components, the authors propose the following modifications to the PFGC equations:

1. Replace the linear mixing rules in equations (2) and (4) by a quadratic mixing rule

$$b = \sum_j^c \sum_i^c y_i y_j (b_i b_j)^{0.5} k_{ij} \quad (2.A)$$

$$s = \sum_j^c \sum_i^c y_i y_j (s_i s_j)^{0.5} l_{ij} \quad (4.A)$$

In equations (2.A) and (4.A) k_{ij} and l_{ij} are binary interaction coefficients between groups i and j and must be determined from experimental VLE data.

2. Expressing a_{jn} , the binary interaction coefficient in equation (8) as a linear function of temperature allows for additional flexibility

$$a_{jn} = p_{jn} + q_{jn} T/1000 \quad (10)$$

p_{in} and q_{in} are binary parameters between groups j and n .

3. Treating each compound as a group. This forces m_{ij} in equation (5) above to the value of 1.0. This is necessary because the mixtures being considered contain only limited numbers of components from the same

3. Treating each compound as a group. This forces m_{ij} in equation (5) above to the value of 1.0. This is necessary because the mixtures being considered contain only limited numbers of components from the same homologous series. To adequately describe the behavior of groups, a number of members from the same homologous series must be considered. Also, first members of an homologous series (methanol, methane) frequently must be considered as a separate "group." This is also often true for the second member (ethanol) of a series.

Based on the quadratic mixing rule the expression for the chemical potential, μ_i , is derived to be

$$\left(\frac{\mu_i}{RT}\right) = S_i \left[1 - \left(\frac{1}{x}\right) \right] \ell n(1-x) - B_i \left[1 - s - \left(\frac{s}{x}\right) \ell n(1-x) \right] - \ell n(Z) -$$

$$12 \left[\sum_n^s m_{in} b_n \ell n \left(\frac{1-x+x \sum_j \Gamma_j \Theta_{nj}}{\Theta_{ni}} \right) + x \sum_n^s \Gamma_n \left(\frac{b_i - \sum_j m_{ij} b_j \Theta_{nj}}{1-x+x \sum_j \Gamma_j \Theta_{nj}} \right) \right] \quad (11)$$

where B_i and S_i are defined by

$$B_i = \left[b - \sum_j y_j (b_i b_j)^{0.5} k_{ij} \right] / b \quad (12)$$

$$S_i = s - \sum_j y_j (s_i s_j)^{0.5} \ell_{ij} \quad (13)$$

Equations (1) to (13) were used to predict the VLE behavior of four binary mixtures containing one polar component.

RESULTS AND DISCUSSION

The necessary first step in using the PFGC equation of state is to evaluate the five parameters, b_j , s_j , E_j^0 , E_j^1 , and E_j^2 , for each compound. These parameters are determined from pure component vapor pressure, vapor and liquid density, and latent heat of vaporization data. The optimized parameters for the six compounds are shown in Table 1. These parameters provide good representation of the pure component properties for all six compounds. Table 2 shows overall deviations in each pure component property for the six compounds.

Figure 1 shows deviations for the four individual pure component properties for methanol. Except for the region near the critical ($T_r > 0.95$), deviations for calculated values are less than 5%. From the overall errors shown in Table 2 this is true for all components and all properties. Of particular interest is the low error in calculated liquid density for all six materials. The error shown in Table 2 is 30-40% less than is found for similar equations of state for liquid density.

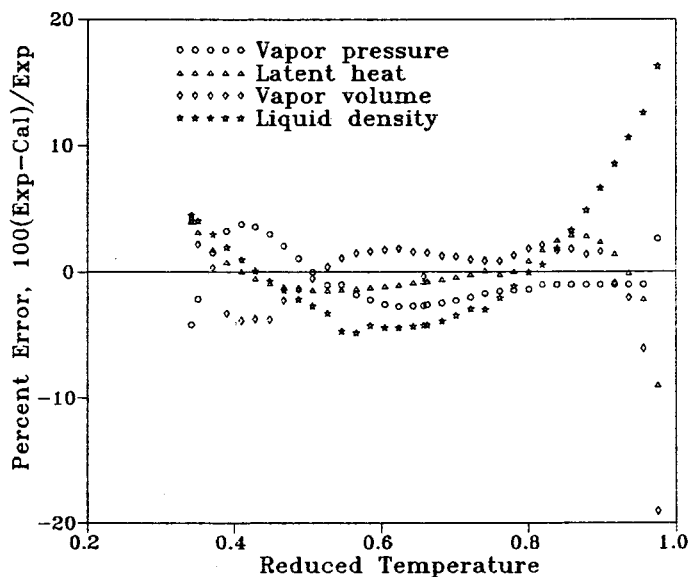


Figure 1: Error in calculated properties of methanol

Using the pure component parameters from Table 1 the binary interaction coefficients for several binary mixtures were determined by non-linear

Table 1. PFMC Parameters for Individual Compounds

Compound	b m ³ /kg mole	s	E ⁰ /R	E ¹ /R	E ² /R
CH ₄	0.03638	1.87100	-71.6667	-31.7778	3.8889
CO ₂	0.02060	3.69850	-341.5000	-111.7778	11.1111
NH ₃	0.01743	3.04420	-556.1611	-312.8117	55.3644
H ₂ O	0.01249	2.20000	-1472.9445	-1544.0556	476.9445
CH ₃ OH	0.01456	6.66045	-1227.0443	-708.3664	166.8566
C ₂ H ₅ OH	0.02689	8.02048	-779.7945	-504.0206	137.7889

Table 2. Error in PFMC Calculated PVT Data for Pure Compounds

Compound	No. of Points	Reduced Temperature Range	Aver. Absolute % Deviation				Reference
			Vapor Pressure	Vapor Volume	Liquid Density	Latent Heat	
CH ₄	32	0.524-0.976	1.61	2.55	5.02	2.88	ASHRAE, 1987
CO ₂	31	0.712-0.986	1.00	4.47	3.99	4.71	ASHRAE, 1987
NH ₃	33	0.482-0.958	1.00	1.34	5.04	0.61	ASHRAE, 1987
H ₂ O	29	0.423-0.824	1.91	2.01	4.53	1.79	ASHRAE, 1987
CH ₃ OH	35	0.342-0.975	1.93	2.36	4.07	1.50	PERRY, 1973
C ₂ H ₅ OH	26	0.680-0.988	1.25	--	--	--	ESDU, 1988

regression. The procedure and computer program discussed by Fathi, Moshfeghian and Maddox (1990) were used to obtain the interaction coefficients based on experimentally determined data for each binary mixture. The four optimized interaction parameters for each binary mixture are shown in Table 3.

The parameters shown in Tables 1 and 3 were used to calculate the dew point water content of methane over a range of pressures at four different temperatures. Calculated and experimental results are compared graphically in Figure 2, and are shown to be in excellent agreement. This illustrates the power of the fitting of the PFGC parameters to pure component data, because there is no region of temperature in which the pure component VLE data of methane ($T_c = 190.6 \text{ K}$) and water ($T_{\text{Freezing}} = 273.15 \text{ K}$) overlap.

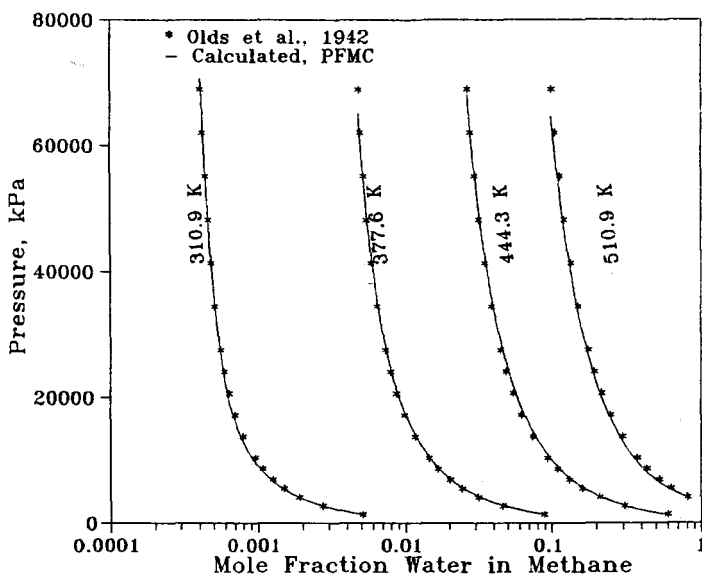


Figure 2: Calculated and reported dew point water content of methane

Calculated and reported phase compositions for the ammonia – water system are shown in Figure 3 for a temperature of 273.2 K and in Figure 4 for 349.9 K. Both cases cover the full composition range and both give good agreement between the calculated and reported values. There is some variance in the liquid compositions in the mid range for both temperatures. Considering the small composition change in the vapor phase that would be caused by

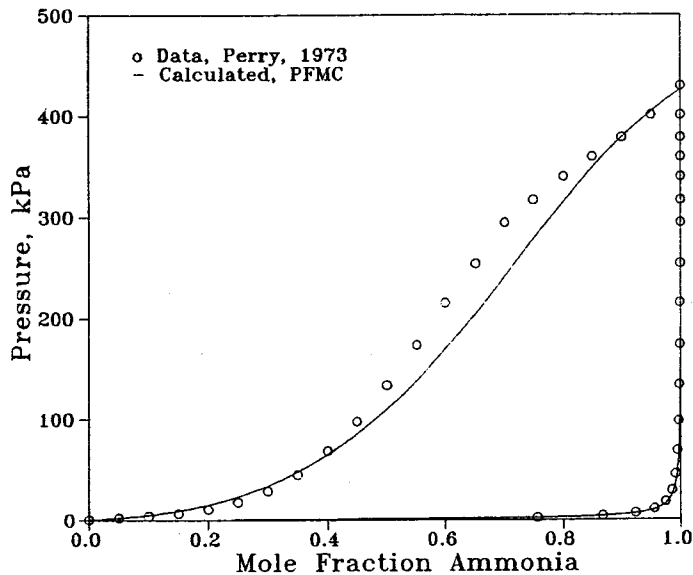


Figure 3: Calculated and reported phase behavior of ammonia-water system at 273.2 K.

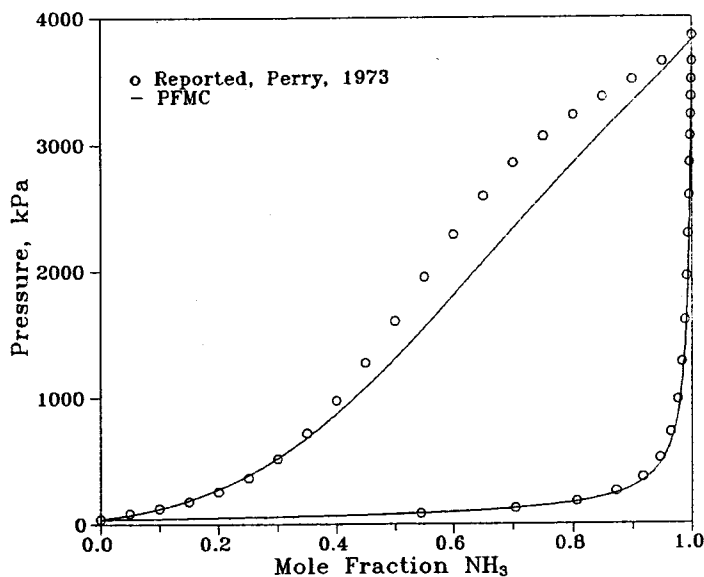


Figure 4: Reported and calculated phase behavior of ammonia-water system at 349.9K.

correcting the liquid composition, the variance is not large enough to be really significant.

Two sets of reported data for the carbon dioxide – methyl alcohol system at a nominal 313 K are shown in Figure 5. In general the PFGC calculated values fall within the range of composition that covers the difference in the two different sets of reported values. As could be expected, deviations are greater at higher pressures.

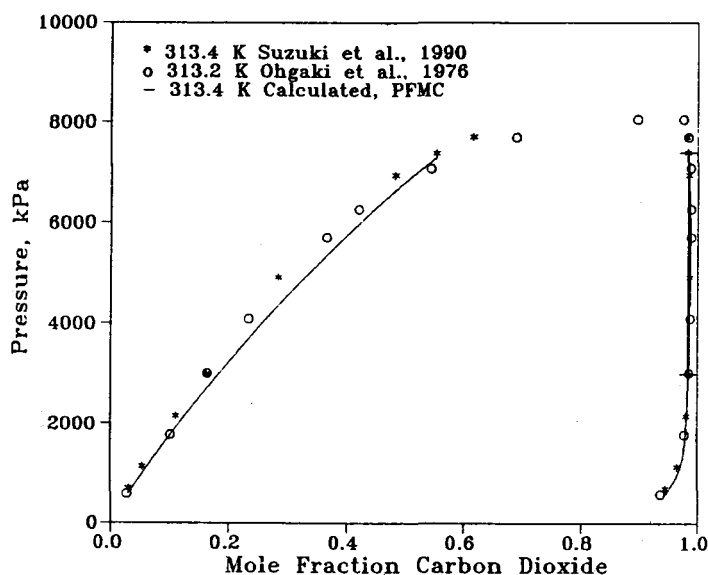


Figure 5: Reported and calculated phase behavior of the carbon dioxide-methanol system

Phase behavior of the carbon dioxide – ethyl alcohol system is shown in Figure 6 for temperatures of 313.4 K and 333.4 K. The PFGC calculated values are in good agreement over the entire composition range.

A summary of the percentage deviation in calculated equilibrium constants and calculated bubble point pressure is shown in Table 4 for the CO_2 – methanol, CO_2 – ethanol and NH_3 – H_2O binary systems. Considering the shape of the P – T envelope and the small change in vapor composition over a wide range of liquid compositions and bubble point pressures, the calculated and experimentally measured values are in excellent agreement for all three of the binary systems.

Table 3. Optimized Binary Interaction Coefficients

System		Temp. Range, K	Pressure Range, kPa	p_{ij}	q_{ij}	k_{ij}	l_{ij}
1	2						
CO ₂	+ CH ₃ OH	313-333	680-7100	0.73073	0.18504	1.09754	1.03786
CO ₂	+ C ₂ H ₅ OH	313-333	510-9025	0.85963	-0.00574	1.04941	1.07902
NH ₃	+ H ₂ O	273-395	2.3-3465	0.85795	0.09779	0.67704	0.8784
CH ₄	+ H ₂ O	311-511	1380-68950	0.19809	0.20653	1.13081	1.11453

Table 4. Comparison of Calculated and Experimental Equilibrium Constants and Pressure at Boiling Point

System		No. of Points	Temp. Range, K	Pressure Range, kPa	Average Absolute Percent Deviation			Reference
1	2				K1	K2	Pressure	
CO ₂	- CH ₃ OH	23	313-333	680-7100	0.12	6.1	6.28	Ohgaki et al., 1976 Suzuki et al., 1990
CO ₂	- C ₂ H ₅ OH	19	313-333	510-9025	0.18	7.97	8.07	Suzuki et al., 1990
NH ₃	- H ₂ O	100	273-395	2.3-3465	1.91	19.39	9.53	Perry, 1973

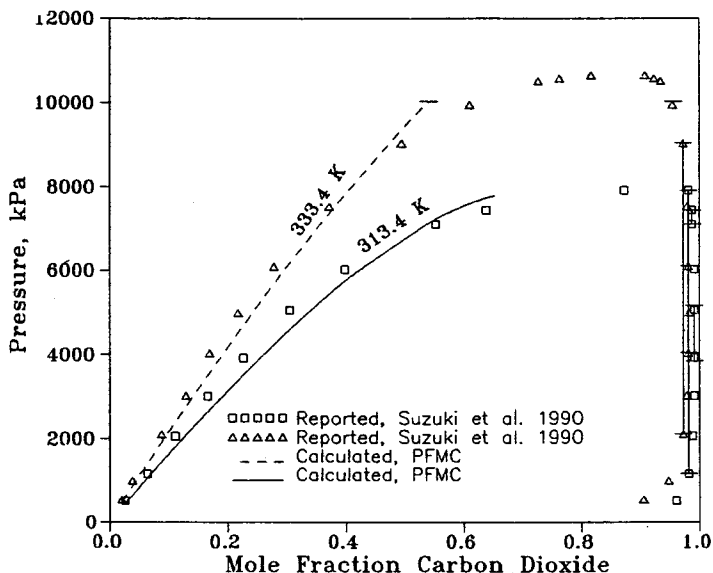


Figure 6: Reported and calculated phase behavior for the carbon dioxide-ethyl alcohol system

CONCLUSIONS

Use of a quadratic mixing rule in the PFGC equation of state and using first and second members of an homologous series as molecules rather than groups extend the capabilities of the PFGC to correlation of VLE data for polar compounds and mixtures. For the binary mixtures studied very good agreement was obtained between calculated and reported values. At the highest pressures studied ($P_r > 0.9$) errors increased, but were still within acceptable ranges.

The pure component parameters for six compounds were determined and reported. Binary interaction parameters k_{ij} and l_{ij} were considered constant, but a_{ij} was considered a linear function of temperature.

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