THE SIMULATION OF VAPOR-LIQUID EQUILIBRIA IN IONIC SYSTEMS

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PREFACE

A method for predicting the degree of dissociation and pH of an electrolytic solution was developed. The procedure was expanded into an algorithm for predicting the vapor-liquid equilibria of ionic systems. By applying the algorithm to sour gas and carboxylic acid systems, the flexibility of the algorithm was demonstrated. Predictions were made using two equations of state and an activity coefficient model. Interaction coefficients for the aqueous binaries of H_2S and CO_2 were found to not be affected by inclusion or exclusion of the dissociation algorithm during fitting. By comparing predictions with the results from other algorithms, the approach was demonstrated to be capable of consistent accuracy.

This thesis is in multiple article format. The result of using this format is that the thesis does not contain a literature review. Likewise, equations or approaches not utilized but referred to are not listed explicitly.

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CHAPTER I

A GENERAL METHOD FOR THE PREDICTION OF ELECTROLYTE DISSOCIATION

Introduction

The behavior of aqueous electrolytes is important to all fields of endeavor, ranging from agriculture to zymology. Typically, most of these aqueous systems are nonvolatile, but many dissolved gaseous electrolytes are encountered in fields such as petroleum. When preparing oils and gases for transport, storage, and processing, the oil industry often separates common acid gas components from entrained water. The electric power industry utilizes acid-base reactions to remove sulfur from stack gases. In fact, enhanced water solubility of ionizing components affects even the home, as the very usefulness of household ammonia and vinegar depends upon dissociation of ammonia and acetic acid.

Despite wide experience with such systems, the ability to predict their vapor-liquid behavior is very limited. Because of the ionization effects, the systems are very far from ideal. Many components of interest are also outside their two-phase regions and thus place the application of

Raoult's Law beyond consideration and also make the use of activity coefficient models very difficult.

Description

Considerable risk is involved when relying on temperature dependent interaction parameters to describe vapor-liquid equilibria in electrolytic systems. Researchers, such as Panagiotopoulos and Reid (1985), have modified this classic equation of state approach by using composition dependent interaction parameters. Skjold-Jørgensen, et al. (1982) proposed a new UNIFAC/UNIQUAC parameter which may also be applied for the same purpose. A comparison with the experimental data by Wilson, et al. (1985) illustrates this unreliability. As can be seen in Table I, a typical equation of state based flash calculation does not accurately predict the two phase compositions. While the inert component compositions are well predicted, the distribution of the acid-gas components is not. In fact, the liquid compositions may not be correct to an order of magnitude. These errors occur because reality is completely ignored when relying on interaction parameters. Some components dissociate and even react.

The ability of an equation of state to solve this problem can be improved by including a provision for aqueous phase dissociation. Such an approach was used to generate the results listed in Table II using the methods described

TABLE I

NAIVE FLASH CALCULATION RESULTS

Temperature= 300 F   Pressure= 500 psia

Component	Vapor Mol Percent		Liquid Mol Percent	
	Exptl	Calc	Exptl	Calc
NH3	1.57	2.07	2.02	1.56
CO2	29.20	28.98	0.60	0.15
H2S	4.68	5.00	0.52	0.08
H2O	13.93	14.52	96.83	98.18
N2	6.40	6.26	0.0024	0.00
CH4	10.09	9.86	0.0065	0.01
H2	34.13	33.35	0.0227	0.03

TABLE II

CORRECTED FLASH CALCULATION RESULTS

Temperature= 300 F   Pressure= 500 psia

Component	Vapor Mol Percent		Liquid Mol Percent	
	Exptl	Calc	Exptl	Calc
NH3	1.57	1.75	2.02	1.84
CO2	29.20	29.10	0.60	0.36
H2S	4.68	4.79	0.52	0.36
H2O	13.93	14.40	96.83	97.14
N2	6.40	6.32	0.0024	0.00
CH4	10.09	9.97	0.0065	0.01
H2	34.13	33.70	0.0227	0.03

Experimental Data Reference: Wilson, et al. (1985)

herein. The acid gas component concentrations are of the correct order of magnitude even with respect to each other.

Ionization

Because the dissociation expression describes a relationship between an ion and its undissociated, molecular solute, it can be used to calculate the true aqueous phase composition. The distinction between the true and observed compositions is important to know because only molecules exert vapor pressures. Additionally, the typical equation of state describes only molecular behavior like volatility. The method for converting the apparent liquid composition to the true value is similar to that employed by Cruz and Renon (1979).

To describe ionization, the general ion dissociation equilibrium can be expressed as:

$$AB \longleftrightarrow A^+ + B^-$$

The concentrations are then evaluated using the equilibrium expression in terms of ionic activities:

$$K_{eq} = \frac{[a_{A+}][a_{B-}]}{[a_{AB}]}. \tag{1}$$

Using ionic activity coefficients, the equilibrium relation is

$$K_{eq} = \frac{(\gamma_{+-})^2 \; [A+] \; [B-]}{(\;_{AB} \; [AB])} \; . \qquad (2)$$

Typically, the concentrations are expressed as molar or molal concentrations. Because of the convenient relationship between mol fraction and molality,

$$m_{AB} = 55.51 \; x_{AB} \; / \; x_{H2O} \qquad (3)$$

molality is used in these calculations.

Ionic activity coefficient models are utilized to describe the dependence of ionic activity coefficients on the ionic strength I,

$$I = 1/2 \; \Sigma \; (\; [i] \; Z_i^{\;2} \;), \qquad (4)$$

where [i] is the molality of ion i and Z its charge.

The parameters required to describe ionic strength effects, as well as ion--ion interactions are obtained by regression. Wilson (1978), for example, regresses VLE data to obtain his modified dissociation equilibrium constants. Others, such as Cruz and Renon (1979) and Daumn, et al. (1986), include such effects in their models and again obtain the coefficients by regressing VLE data. Because the methods for obtaining ionic activity coefficients can be used to correct inappropriate phase models, these coefficients were not implemented in this and subsequent work.

In performing a general, if naive, calculation of the dissociation of ions, there are various important constraints:

1) Atom balances,
2) Charge balances, and
3) Mass balances.

For the typical acid with two dissociations, such as CO_2,

$$CO_2 + H_2O \longleftrightarrow H^+ + HCO_3^- \qquad K_1$$
$$HCO_3^- \longleftrightarrow H^+ + CO_3^= \qquad K_2$$

and the typical base,

$$NH_3 + H_2O \longleftrightarrow OH^- + NH_4^+ \qquad K_3$$

the following relationships for the remaining molecular solutes arise from Equation 1:

$$K_1\ [CO_2] - [H^+]\ [HCO_3^-] = 0 \qquad (5a)$$
$$K_2\ [HCO_3^-] - [H^+]\ [CO_3^=] = 0 \qquad (5b)$$
$$K_3\ [NH_3] - [OH^-]\ [NH_4^+] = 0 \qquad (5c)$$
$$K_w - [H^+]\ [OH^-] = 0 \qquad (6)$$

Manipulation gives the general acid dissociation relationships:

$$[CO_2] = [CO_2]^o\ [H^+]^2\ ([H^+]^2 + K_1\ ([H^+] + K_2))^{-1} \qquad (7)$$
$$[HCO_3^-] = K_1\ [CO_2]\ /\ [H^+] \qquad (8)$$
$$[CO_3^=] = [CO2]^o - [CO_2] - [HCO_3^-] \qquad (9)$$

and a similar equation for bases:

$$[NH_3] = [NH_3]^o [OH^-] ([OH^-] + K_3)^{-1} \tag{10}$$

$$[NH_4^+] = K_3 [NH_3] / [OH^-] \tag{11}$$

$$[OH^-] = K_w / [H^+] . \tag{12}$$

with the overall charge balance:

$$0 = [H^+] - [OH^-] + [NH_4^+] - [HCO_3^-] - 2[CO_3^=] \tag{13}$$

Note that additional acids or the omission of NH_3 affects only the charge balance. Because all of the equations can be expressed in terms of $[H^+]$, the problem can be solved by iterating about pH.

Because ammonia and carbon dioxide react to form carbamates, a provision for reactions must be included. The carbamate reaction is especially important because the product has limited solubility. An additional relationship must be introduced:

$$NH_3 + HCO_3^- \text{ <--> } H_2O + NH_2COO^- \qquad K_c$$

This reaction can affect the molecular concentrations by orders of magnitude. The equilibrium ammonia concentration becomes an implicit function of the H^+ and CO_2 concentrations, but first, a mass balance is performed on ammonia, accounting for molecular ammonia, the ammonium ion, and the carbamate ion.

$$[NH_3^o] = [NH_3] (1 + K_3/[OH^-] + K_1 K_c [CO_2]/[H^+]) \tag{14}$$

A mass balance is performed on the reacting acid, taking into account the first and second dissociation, as well as the carbamate reaction.

$$[CO_2] = [CO_2^o] / (1 + K_1 / [H^+] (1 + K_2 / [H^+] + K_c [NH_3])). \tag{15}$$

Additional acid terms are added to the ammonia mass balance (Equation 14) in the same manner as the carbon dioxide term. The fact that the ammonia mass balance is a nearly linear function of the ammonia concentration facilitates the approach to solving these additional equations. For a given pH value, only one ammonia concentration solves the ammonia mass balance. As can be seen in Figure 1, two nested loops are required to calculate the solute concentrations. The outer loop checks the charge balance (Equation 13) and dissociates nonreacting components. The inner loop checks the ammonia mass balance (Equation 14) and is invoked only if a reaction occurs. After exiting the inner loop, the charge balance (Equation 13) must be corrected for the formation of NH_2COO^-. This formulation allows the convenient and direct calculation of undissociated, molecular solute concentrations needed for the calculation of aqueous phase activity or fugacity coefficients. The extent of ionization must be defined utilizing pH calculation results:

$$d_{AB} = [AB]/[AB]^o, \tag{16}$$

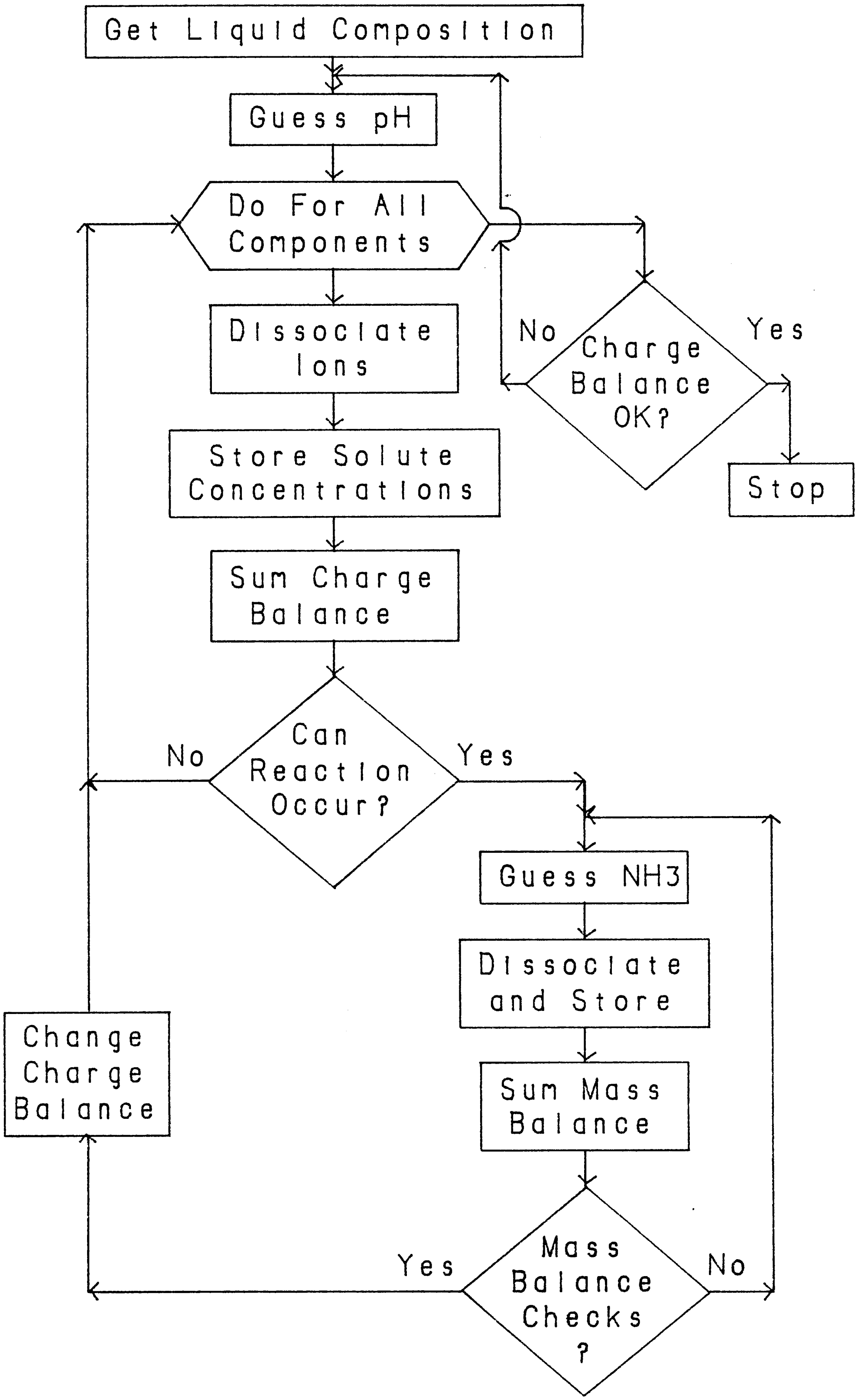

Figure 1. Dissociation Calculation Flow Diagram

where $[AB]^o$ represents the apparent or observed liquid molality of AB and [AB] represents the molality of molecular AB. A modified form of the vapor-liquid equilibrium expression is used,

$$y_{AB} = d_{AB} K_{AB} x_{AB}^o. \tag{17}$$

The K-values are calculated by replacing the apparent liquid composition with the true liquid composition, using:

$$x_{AB} = d_{AB} [AB]^o / (\Sigma d_j [j]) \tag{18}$$

For simplicity of programming, the extent of dissociation is included in the K-value so that

$$y_{AB} = K_{AB}^* x_{AB}^o, \tag{19}$$

with K_{AB}^* defined by

$$K_{AB}^* = K_{AB} d_{AB}. \tag{20}$$

The general approach for calculating vapor-liquid equilibria can be described by the flow chart in Figure 2. First, the true phase compositions are estimated. Vapor-liquid equilibrium K-values are calculated from these estimates and then the dissociation constants are calculated. An iterative calculation is performed to find the pH and the true composition. After converting the K-values to effective K-values, a check is made to determine if vapor-liquid equilibrium has been established.

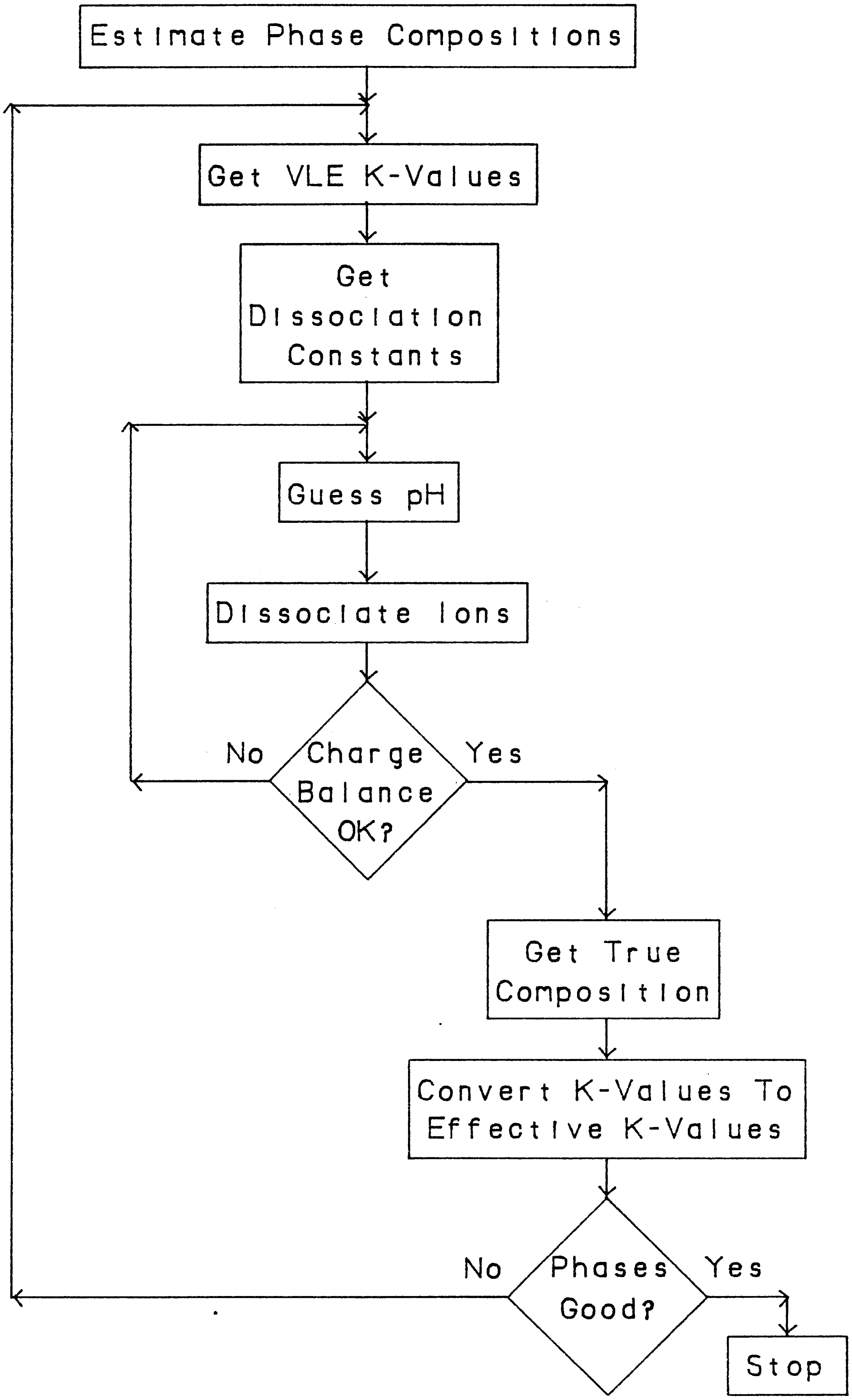

Figure 2. Equilibrium Calculation Flow Diagram

For these examples, the dissociation equilibrium constants were calculated using the equations reported by Edwards, et al. (1978), Robinson and Stokes (1959), and Cruz and Renon (1979) (See Table III). A comparison of Tables I and II demonstrates that the approach does indeed improve the accuracy of predictions using the Soave-Redlich-Kwong (Soave, 1972). The order of magnitude improvement in the H_2S solubility is quite dramatic.

pH Verification

To check the validity of the pH algorithm and at the same time eliminate errors which might be caused by the vapor-liquid equilibrium predictions, the approach was tested on a nonvolatile system. Predictions of the SO_2--NH_3--H_2O data taken by Scott and McCarthy (1967) are summarized in Table IV. This system was found to be subcooled at 25^o C. As can be seen in the table, the pH values for this system are well predicted by the dissociation algorithm despite the decision to ignore ionic activities. As a worst case approximation the calculations are valid to within 1 pH unit.

The ability to predict dissociation equilibria in volatile systems was tested using the pH values reported by Wilhelm and Kane (1986) for the system CO_2--H_2S--H_2O. The authors presented data in the form of a graph of pH as a function of CO_2 and H_2S partial pressures. Kane (1987) indicated that the labeled points were experimental values

TABLE III

COEFFICIENTS FOR DISSOCIATION EQUILIBRIUM CONSTANT EQUATIONS

$$\ln(K) = C_1 + C_2 / T + C_3 \ln(T) + C_4 T$$

Component		Ref	C_1	C_2 K	C_3	C_4 K^{-1}
CO_2	(a)	2	2292.0	-71298.0	-390.0	0.51706
	(b)	2	220.1	-12432.0	-35.5	0
	(c)	2	-5.6	1998.0	0.0	0
H_2S	(a)	1	218.6	-12995.0	-33.5	0
	(b)	1	-114.5	-2049.0	15.7	0
SO_2	(a)	1	122.5	-3768.0	-20.0	0
	(b)	1	-21.3	1333.4	0.0	0
H_2O		1	14.0	-10294.8	0.0	-0.03928
HCOOH	(a)	3	7.3	-2695.1	0.0	-0.03085
CH_3COOH	(a)	3	12.1	-3092.0	0.0	-0.03493
C_2H_5COOH	(a)	3	7.8	-2793.6	0.0	-0.03236
NH_3		2	2.7	-3335.7	1.5	-0.03706

References:
1- Beutier and Renon (1979)
2- Edwards, et al. (1978)
3- Robinson and Stokes (1959)

TABLE IV

SO_2--NH_3--H_2O Solution pH at 25° C

Molar Concentrations mmol / l		pH	
Ammonia	Sulfur Dioxide	Experimental	Calculated
0.0	1097.0	0.98	0.88
0.0	2.036	2.72	0.87
185.0	960.0	1.27	1.28
0.185	0.988	3.22	3.12
214.8	1117.0	1.27	1.26
0.466	2.506	2.77	2.74
65.7	167.1	1.79	1.76
0.577	1.481	3.08	3.04
636.0	1148.0	1.78	1.88
0.805	1.467	3.28	3.22
919.0	1110.0	2.32	2.45
1.067	1.295	3.69	3.67
1140.0	1204.0	2.78	3.01
3.242	3.423	3.83	3.82
1418.0	1413.0	4.16	4.92
4.124	4.11	5.14	4.92
1086.0	1054.0	4.78	5.79
1.069	1.037	5.57	5.82
1814.0	1241.0	6.33	7.21
1.699	1.162	7.00	7.21
1745.0	928.0	6.96	7.90
0.799	0.403	7.57	8.06
2323.0	1013.0	9.41	8.50
1.891	0.826	8.53	8.48
6300.0	1113.0	10.93	8.50
5.960	1.053	9.33	9.48
5970.0	120.0	11.20	10.60
5.810	0.1169	10.12	10.32
5950.0	0.0	12.48	12.00
		Average Deviation	0.82

Reference: Scott and McCarthy (1967)

with undetermined uncertainties. The data points read from that graph are reproduced in Figure 3, together with the results predicted by the Parameters From Group Contribution (Cunningham, 1974) and Soave-Redlich-Kwong equations (Soave, 1972). Both equations of state were implemented using the approach described above. As can be seen from the graph, the computed results are also within one pH unit of the "experimental" data points. The results were generated by performing two-phase flash calculations at 25^{o} C and adjusting the compositions to get the desired partial pressures. In this case, the PFGC equation of state provided the best estimate of the solution pH at all conditions.

Conclusions

An efficient algorithm for calculating a value for the pH of an aqueous solution was developed and tested. The results from the prediction of two systems, one subcooled, and one volatile, were quite satisfactory. Likewise, the general approach was shown to dramatically improve the ability of a cubic equation of state to predict the phase distribution of multicomponent systems. The ability to predict pH will be applicable to fields such as corrosion prevention.

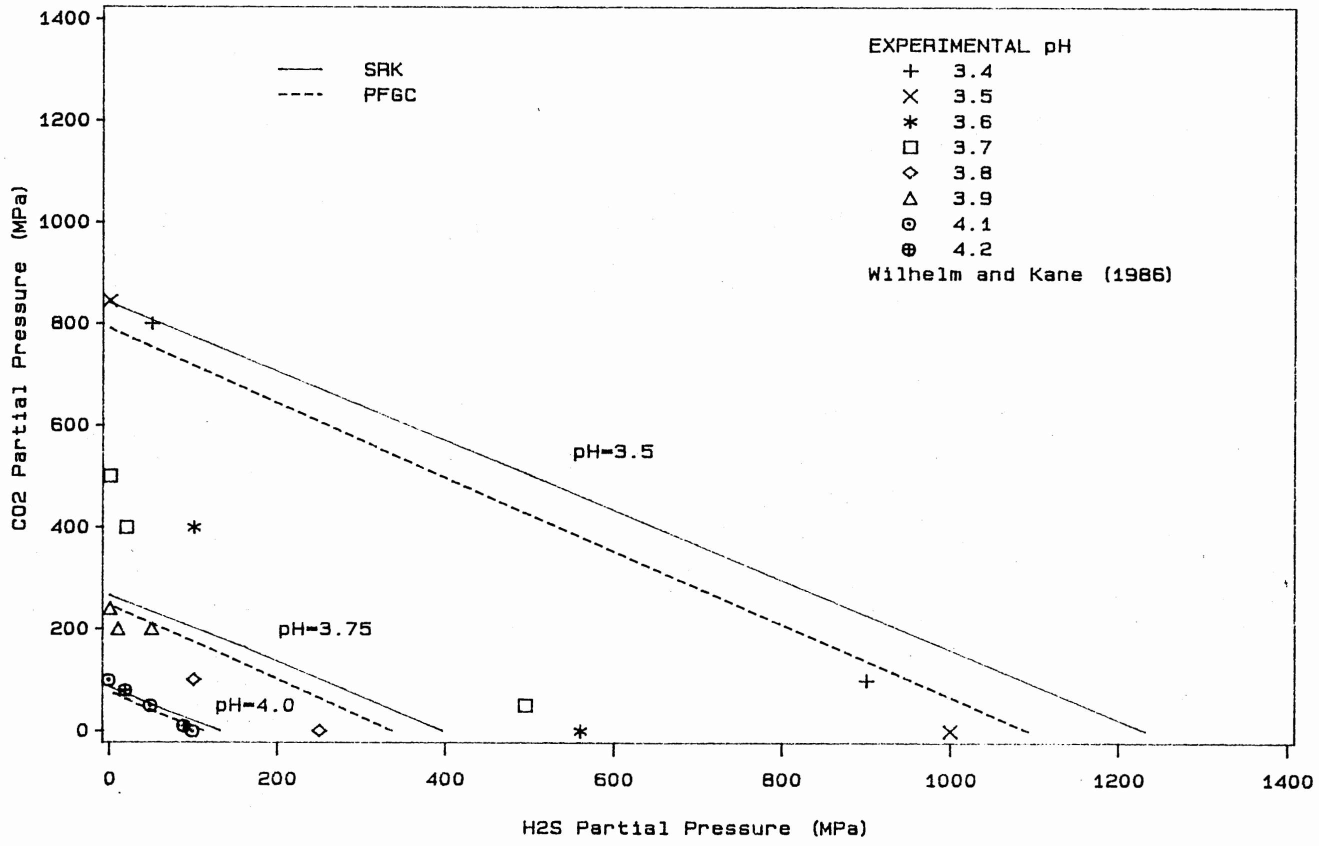

Figure 3. pH as a Function of the H_2S and CO_2 Partial Pressures

CHAPTER REFERENCES

Beutier, D. and Renon, H., "Representation of NH3--H2S--H2O, NH3--CO2--H2O, and NH3--SO2--H2O Vapor-Liquid Equilibrium", Ind. Eng. Chem. Process Des. Dev., 17(3), 220-230, 1978.

Cruz, J. L. and Renon, H., "Nonideality in Weak Binary Electrolytic Solutions. Vapor-Liquid Equilibrium Data and Discussion of the System Water--Acetic Acid", Ind. Eng. Chem. Fundam., 18(2), 168-180, 1979.

Cunningham, J. R., "Calculation of Parameters from Group Contributions for the PFGC Equation of State", M. S. Thesis, Brigham Young University, 1974.

Daumn, K. J., Harrison, B. K., Manley, D. B., and Poling, B. E., "An Equation of State Description of Weak Electrolyte VLE Behavior", Presented at the Fourth International Conference on Fluid Properties and Phase Equilibria for Chemical Process Design, Helsingør, DK, 11-16 May, 1986.

Edwards, T. J., Maurer, G., Newman, J., and Prausnitz, J. M., "Vapor-Liquid Equilibria in Multicomponent Aqueous Solutions of Volatile Weak Electrolytes", AIChE J., 24(6), 966-976, 1978.

Kane, R. D., Telephone Conversation, 20 July, 1987.

Panagiotopoulous, A. C. and R. C. Reid, "A New Mixing Rule for Cubic Equations of State Highly Polar, Asymmetric Systems", Presented at the ACS Spring National Meeting, Miama, FL, 1 May, 1985.

Pawlikowski, E. M., Newman, J., and Prausnitz, J. M., "Phase Equilibria for Aqueous Solutions of Ammonia and Carbon Dioxide", Ind. Eng. Chem. Process Des. Dev., 21(4), 764-770, 1982.

Robinson, R. A. and Stokes, R. H., Electrolyte Solutions, Academic Press, New York, and Butterworths Scientific Publications, London, 1959.

Scott, W. D. and McCarthy, J. L., "The System Sulfur Dioxide--Ammonia--Water at 25 C.", *Ind. Eng. Chem. Fundam.*, 6(1), 41-48, 1967.

Skjold-Jørgensen, S., Rasmussen, P., and Fredenslund, Aa., "On the Concentration Dependence of the UNIQUAC/UNIFAC Models", *Chem. Eng. Sci.*, 37(1), 99-111, 1982.

Wilhelm, S. M. and Kane, R. D., "Selection of Materials for Sour Service in Petroleum Production", *J. Pet. Tech.*, Oct., 1051-1061, 1986.

Wilson, G. M., *A New Correlation of NH3, CO2, and H2S Volatility Data from Aqueous Sour Water Systems: API Publication 955*, Refining Department, American Petroleum Institute, Washington, March, 1978.

CHAPTER II

THE USE OF EQUATIONS OF STATE TO PREDICT VOLATILE ELECTROLYTE BEHAVIOR

Introduction

Many fields of process engineering need to predict the phase distributions of volatile weak electrolytes. Such knowledge is important in factors ranging from corrosion to environmental protection. The typical equation of state cannot predict phase distributions of weak electrolytes with great accuracy, but the simple inclusion of an allowance for aqueous dissociation can improve the results. In Chapter I of this work, an algorithm for the prediction of ionic dissociation equilibria and its effect on phase behavior was developed. The present paper describes the application of this approach to multicomponent phase behavior predictions.

Ionization

Before attempting to use an equation of state to describe electrolyte phase behavior, a method of calculating the ionization of the liquid phase is needed. Equations of state describe only molecular components because ions are not volatile. The approach used here is summarized in Figure 1. Phase compositions are first estimated. From these estimates, an equation of state is used to generate vapor-liquid K-values. The apparent composition is converted to the true composition by performing an iterative dissociation calculation. The molecular solute concentrations are then obtained from the true composition and used to define an effective K-value. This effective K-value is applied in the usual manner to check for vapor-liquid equilibrium using apparent mol fractions.

Activities and Fugacities

Two equations of state were studied to determine their applicability to electrolyte phase behavior. The Soave-Redlich-Kwong (SRK) (Soave, 1972) and Parameters From Group Contribution (PFGC) (Cunningham, 1974) equations were implemented using the aforementioned dissociation equilibria approach. The basic equations for the two equations of state are listed in Figures 2 and 3. Explanation and derivation of the terms in these equations can be found in the works by Soave (1972) (for the SRK equation) and Cunningham (1974) (for the PFGC equation). Briefly, the SRK is an improvement of the Redlich Kwong equation of state, using a temperature dependent coefficient on the attractive term. According to Majeed (1983), the PFGC equation of state represents an attempt to produce a chemical potential form based on an activity coefficient model. Majeed

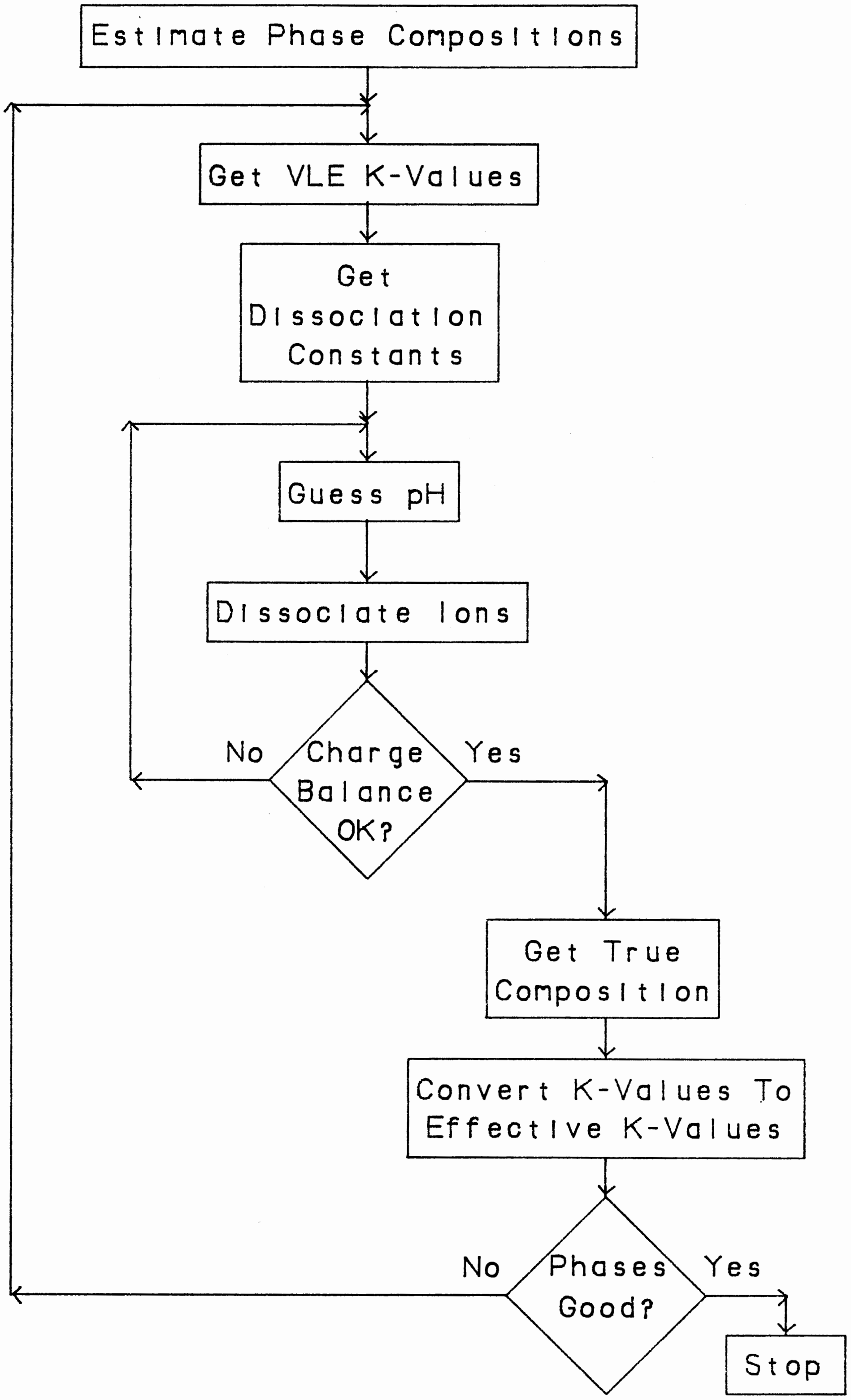

Figure 1. Equilibrium Calculation Flow Diagram

General Equation for Volume

$$P = \frac{R\ T}{v - b} - \frac{a(\ T\ )}{v\ (\ v + b\ )}$$

Definition of Coefficients

$$a = 0.42747\ (R\ T_c\ (1 + m\ (\ 1 - T_R{}^{1/2})))^2\ /\ P_c$$

$$m = 0.480 + \omega\ (1.574 - 0.176\quad)$$

$$b = 0.08664\ R\ T_c\ /\ P_c \qquad \text{Covolume}$$

$$\omega \qquad \text{Acentric Factor}$$

Alternate Compressibility Form

$$Z\ (A - B\ (B + 1) + Z\ (Z - 1)) - A\ B = 0$$

Definition of Coefficients

$$A = 0.42747\ P_R\ ((1 + m\ (1 - T_R{}^{1/2}))/T_R)^2$$

$$B = 0.08664\ P_R\ /\ T_R$$

Fugacity Formula

$$\ln\ (\ \phi_i\ ) = b_i\ (Z - 1)\ /\ b - \ln\ (Z - B) - A\ (2\ (a_i/a)^{1/2} - b_i/b)\ \ln\ (1 + B/Z)$$

Mixing Rules

$$a = \Sigma\ \Sigma\ x_i\ x_j\ (1 - k_{ij})\ (a_i\ a_j)^{1/2}$$

$$b = \Sigma\ x_i\ b_i$$

Reference: Soave (1972)

Figure 2: Equations for the Soave-Redlich-Kwong (SRK) Equation of State.

General Equation for Compressibility

$$Z = 1 - \frac{s\,v}{b} \ln (1 - v/b) - s + b\,(c/b_H)\sum_i \phi_i\, b \left(\frac{1 - \sum_j \phi_j\, l_{ij}}{v - b + b \sum_j \phi_j\, l_{ij}} \right)$$

Definition of Coefficients

$b = \sum_I x_I\, b_I$	Mixture covolume
$b_I = \sum_i m_I^i\, b_i$	Component covolume
c/b_H	Universal Constant
$E_{ij} = a_{ij}\,(E_{ii} + E_{jj})/2$	Group Interaction
$E_{ii} = E_{ii}^o + \left(\frac{283.2}{T,\ K} - 1\right)(E_{ii}^1 + E_{ii}^2 + \left(\frac{283.2}{T,\ K} - 1\right))$	
$l_{ij} = \exp\,(-E_{ij}/kT)$	Group Interaction
m_I^i	Number of Groups i in Component I
$s = \sum_I x_I\, s_I$	Mixture Degrees of Freedom
$s_I = \sum_i m_I^i\, s_i$	Component Degrees of Freedom
$\phi_i = \sum_i x_I \frac{m_I^i}{b} b_i$	Mixture Group Fraction
v	Molar Volume

Reference: Majeed (1983)

Figure 3: Equations for the Parameters From Group Contribution (PFGC) Equation of State.

converted the PFGC to the fugacity form which was utilized in this work. The equation is based on accounting for molecular and atomic contributions to the Helmholtz free energy. The groups listed in Table I provide the basis for the various parameters used in these calculations.

Regression Results

In order to study this application of the SRK and PFGC equations, binary data for aqueous ionizing components were fitted using dissociation coefficients from Beutier and Renon (1978) and Edwards, et al. (1978). (See the data sets listed in the regression data references). This optimization was performed to obtain binary interaction parameters which reflected the implementation of the dissociation algorithm. A Fibonacci search algorithm was used to optimize isothermal SRK binary interaction parameters. The results from three k_{ij} fitting methods were compared for all systems but SO_2--water:

1) Matching fugacities based on experimental vapor and liquid phase compositions.
2) Minimizing the sum of the relative errors in K-values at the calculated dew point.
3) Minimizing the sum of the relative errors in K-values at the calculated bubble point.

The three different approaches yielded very similar results. The results for individual isotherms were plotted as a

TABLE I

PFGC Groups

ID	Group		ID	Group	
1	H_2		16	H_2O	
2	CH_4		17	=C	
3	CH_3		18	SO_2	
4	CH_2		19	CH_3OH	
5	CH		20	=C	(ortho)
6	C		21	=C	(para)
7	$=CH_2$		22	=C	(meta)
8	CH_2	(cyclo)	23	=C=	
9	CH	(aro)	24	CH	(cyclo)
10	=C	(aro)	25	O_2	
11	=CH		26	CH_2OH	
12	N_2		27	CH_2OCH_2	
13	CO_2		28	NH_3*	
14	CO		29	HCOOH*	
15	H_2S		30	COOH*	

Reference: unlabelled Majeed (1983)
* This work.

function of temperature. Figures 4 and 5 illustrate the results for aqueous binaries of carbon dioxide and sulfur dioxide, respectively. In both cases, including or excluding the dissociation effects did not change the optimized k_{ij} function. The rest of the parameters were obtained from GPA*SIM, (Erbar, 1980).

The pure group PFGC parameters for NH_3 were obtained from the work of Moshfeghian (Wagner, 1987) and verified (using the program of Erbar, 1980) against the vapor pressure data of Vargaftik (1975). Noting that the liquid phase model did not affect the SRK parameters for H_2S and CO_2, binary aqueous solution data for ammonia and sulfur dioxide were regressed. In each case, optimizations were performed both with and without dissociation. Again, the use of the dissociation algorithm did not affect the results. The ammonia--water group and binary interaction parameters for the PFGC and SRK equations were found to be temperature independent over the temperature range extending from 0^o C to 340^o C. To further test the assumption that the implementation of the dissociation model does not affect the interaction parameters, the rest of the parameters were taken from the work by Majeed (1983).

The fitted interaction parameters for the system sulfur dioxide--water are presented in Figures 5 and 6. Much of the data were either in the form of solubilities or were nonisothermal, so individual values for the interaction coefficients are presented. Comparing the results for the

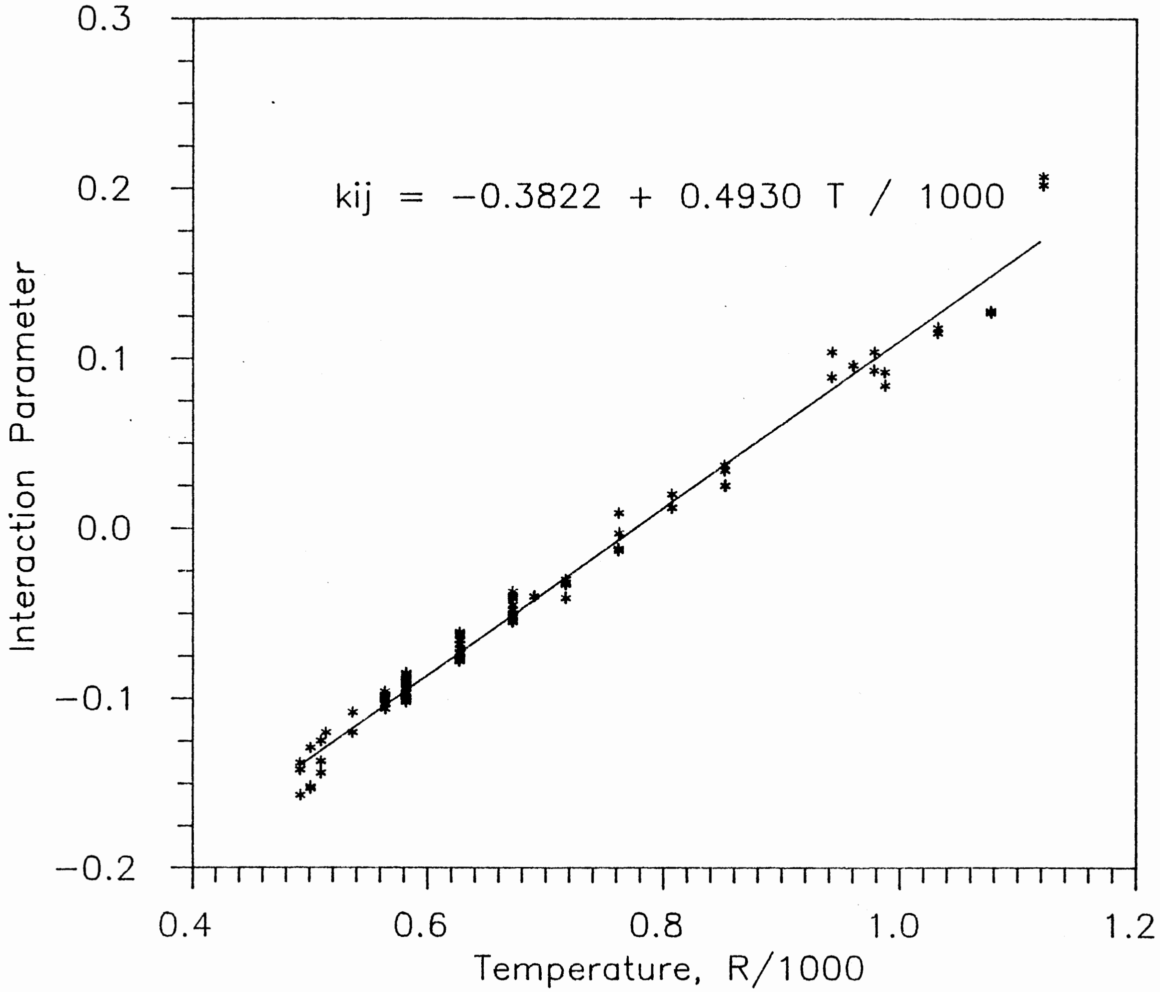

Figure 4. Temperature Dependence of SRK Binary Interaction Parameters for CO_2--H_2O

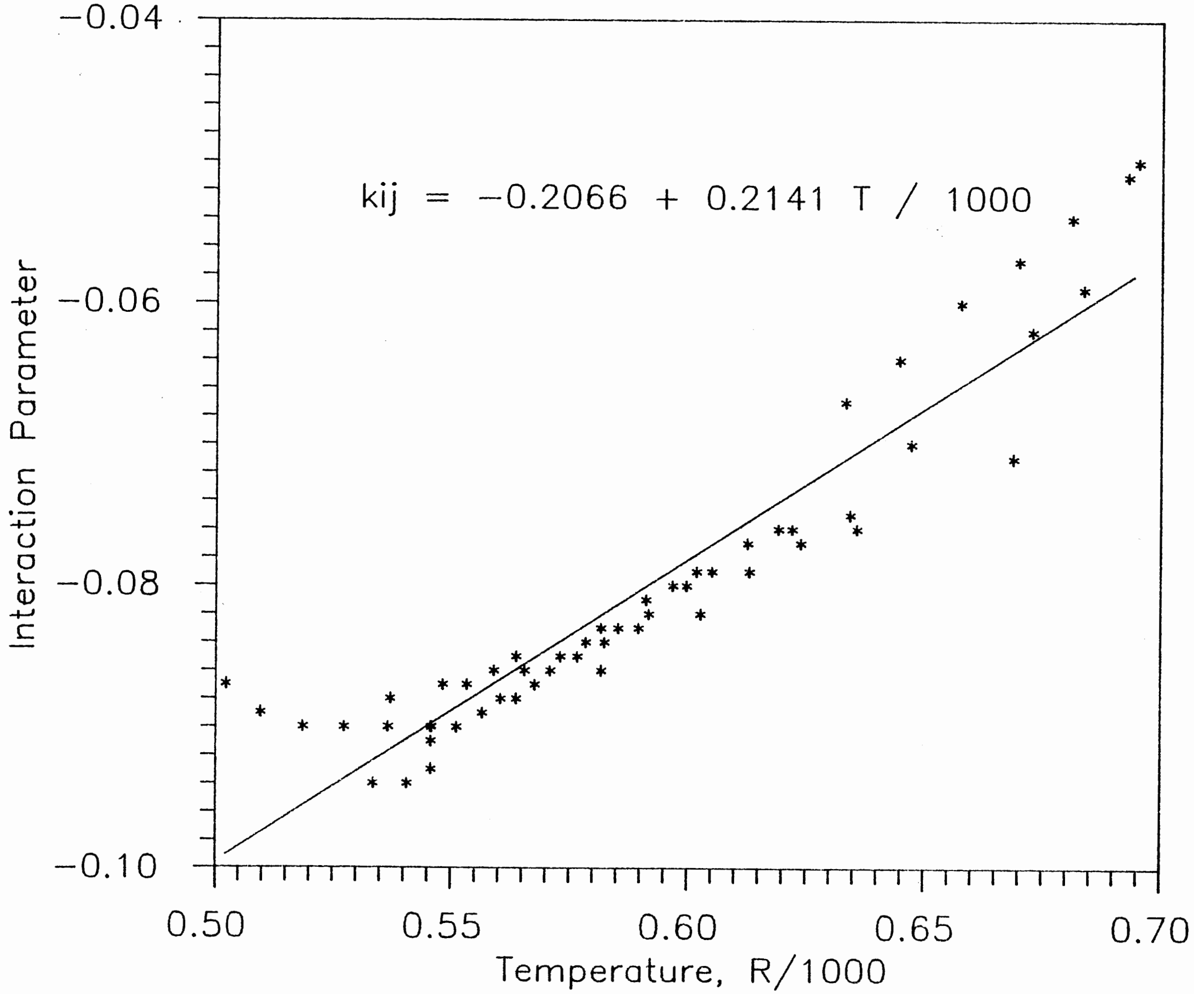

Figure 5. Temperature Dependence of SRK Binary Interaction Parameters for SO_2--H_2O

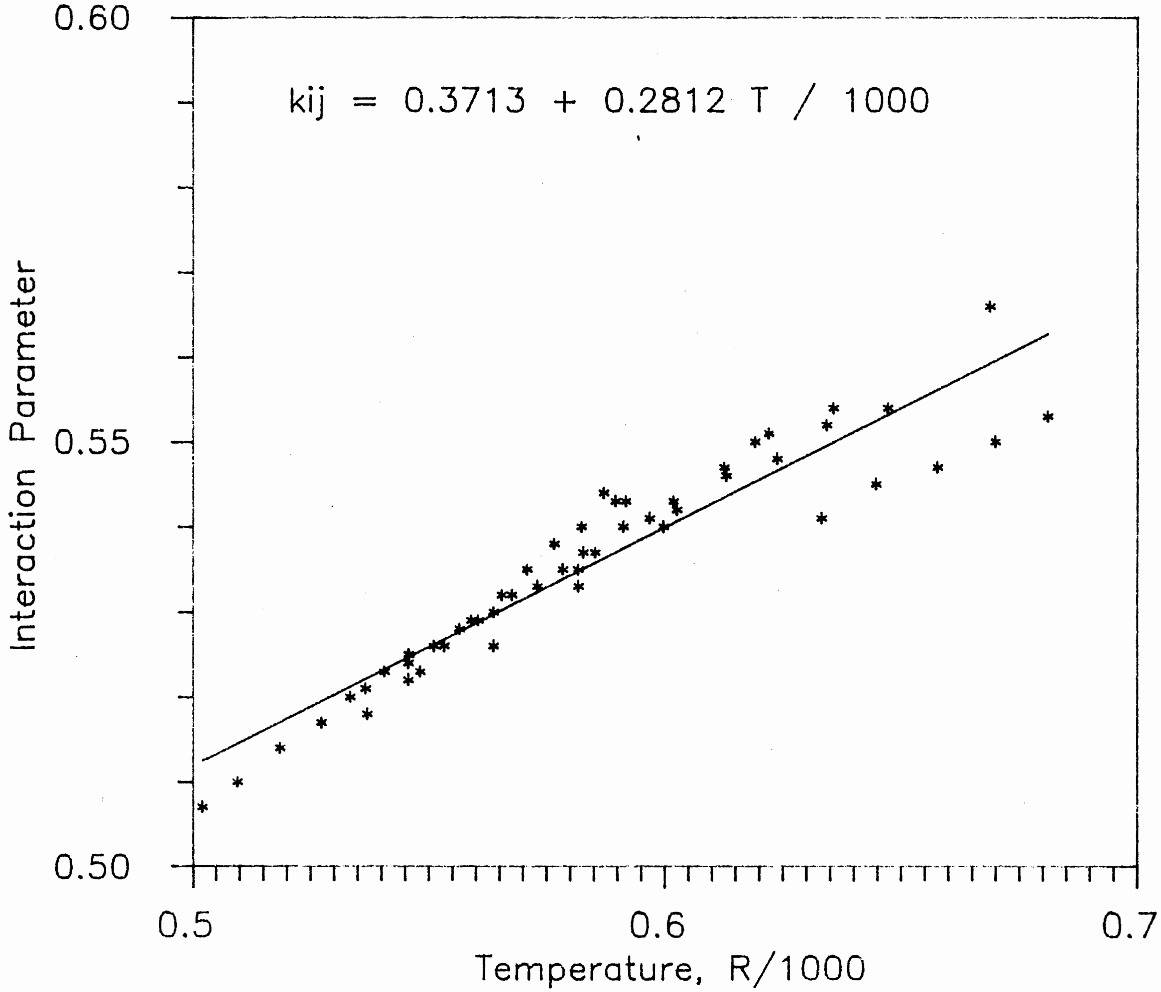

Figure 6. Temperature Dependence of PFGC Group Interaction Parameters for SO_2--H_2O

two figures, an obvious nonlinearity is evident in the SRK parameters. The results for the PFGC are, on the other hand, much more linear. The five "outliers" represent dilute composition data. Convergence problems in the PFGC program are responsible for the different number of data points seen between Figures 5 and 6. A summary of all of the results can be found in Tables II and III.

Predictions of Ternary Data

Daumn, et al (1986), in discussing their model, summarized the ability of several approaches to predict ternary acid--base systems. The results they reported as well as the results generated in this work are presented in Tables IV and V. The reported average relative errors (ARE) from the Beutier and Renon (BR) (1978), Sour Water EQuilibrium (SWEQ) (Wilson, 1978), Edwards, Maurer, Newman, and Prausnitz (EMNP) (1978) and Extended Gmehling (EG) (Daumn, et al., 1986), equations are those reported by Daumn, et al. (1986). The reported results for the SRK and PFGC equations were obtained by bubble point calculations. All of the various models had considerable trouble with at least one of the data sets. As the relative amounts of NH_3 and CO_2 became dissimilar, the effect of the carbamate reaction resulted in overestimation of pressures by the two equations of state. Extremely low pressure CO_2--NH_3--H_2O systems were poorly represented by the SRK and PFGC equations. (The asterisks indicate that the maximum

TABLE II

FITTED COEFFICIENTS FOR SRK

Binary	k_{ij} =	a a	+	b T/1000 b, R^{-1}	Avg K-Value Error %	Data Points
CO_2--H_2O		-0.3822		0.4930	6	116
SO_2--H_2O		-0.2066		0.2141	4^*	60
NH_3--H_2O		-0.2751		0.0	14	317

TABLE III

NEW PFGC PARAMETERS

Binary	k_{ij} =	a	+	b T/1000	Avg K-Value Error %	Data Points
SO_2--H_2O		0.3713		0.2812	5^*	60
NH_3--H_2O		1.0000		0.0	16	317

Group	B	S	E_0	E_1	E_2
NH_3	0.3832	4.8593	-1444.9	-838.00	210.0

* Estimated from errors in partial pressures.

TABLE IV

PARTIAL PRESSURES FOR NH_3--CO_2--H_2O

				Partial Pressure, Bar					
				Experimental		Calculated			
	T,	Molalities				SRK		PFGC	
	C	NH_3	CO_2	NH_3	CO_2	NH_3	CO_2	NH_3	CO_2
P	150	8.36	2.20	4.73	24.1	6.35	45.6	6.42	41.5
		7.38	1.49	4.12	19.4	5.60	29.2	5.69	24.9
		2.62	1.24	0.82	30.5	1.66	53.0	1.86	48.5
		5.10	1.38	1.76	28.2	3.65	36.6	3.86	32.5
		4.82	0.56	3.03	8.4	3.63	9.0	3.79	7.7
		4.29	0.32	3.91	2.1	3.29	4.5	3.44	3.6
		2.78	1.10	1.13	29.8	1.80	42.5	2.00	38.6
		2.79	0.71	1.02	18.5	1.88	21.6	2.06	18.9
		2.74	0.41	1.35	9.1	1.93	9.1	2.13	7.7
			Avg. Rel. Error (%)			53	49	60	32
				ARE (%) EMNP		30	25		
				ARE (%) EG		25	25		
G	149	1.16	0.99	0.41	43.8	0.60	60.5	0.71	56.7
		2.31	0.27	1.73	1.6	1.61	4.8	1.74	4.1
	204	1.41	1.00	2.84	79.4	2.13	70.4	2.73	76.5
		2.35	0.27	4.68	11.8	3.89	9.9	4.45	9.7
	260	1.36	1.22	5.84	78.8	3.06	59.9	4.47	75.4
		2.40	0.29	9.35	16.2	6.36	7.4	7.92	7.9
			Avg. Rel. Error (%)			24	59	20	46
				ARE (%) SWEQ		36	79		
				ARE (%) EG		21	245		
vK	60	0.50	0.32	0.01	0.12	0.01	0.43	0.01	0.34
		1.00	0.20	0.06	0.01	0.05	0.04	0.06	0.03
		1.00	0.67	0.02	0.29	0.02	0.95	0.02	0.72
		2.00	0.37	0.13	0.01	0.11	0.07	0.12	0.05
		2.00	1.34	0.02	0.53	0.05	1.66	0.05	1.24
	40	0.50	0.26	0.01	0.01	0.01	0.04	0.01	0.03
		1.00	0.51	0.01	0.02	0.01	0.08	0.02	0.07
			Avg. Rel. Error (%)*			30	380	38	264
				ARE (%) SWEQ		8	8		
				ARE (%) EMNP		28	102		
				ARE (%) EG		8	41		

References:
P- Pawlikowski, et al. (1982)
G- Gillespie, et al. (1984) from Daumn, et al. (1986)
vK- van Krevelen (1949) from Daumn

allowable dissociation was changed to allow complete ionization.) Much of this error occurred because of the occurrence of the carbamate reaction and its resultant precipitate:

$$NH_3 + HCO_3^- \longleftrightarrow NH_2COO^- + H_2O.$$

According to Pawlikowski, et al. (1982) this reaction occurs at temperatures below 60^o C. Without allowing for dissociation, both equations predicted that the first 60^o C data point had a CO_2 partial pressure greater than 10 bar. These results represent a vast improvement over an approach which ignores dissociation. The SRK and PFGC equations gave the best predictions of the Gillespie data. The ammonia solubility in the Pawlikowski data was much higher than either equation of state predicted.

Similar results for the system NH_3--H_2S--H_2O were also obtained from Daumn, et al. (1986). As is illustrated in Table V, the results calculated in this study were better than those of the SWEQ, and EMNP models. The SRK and PFGC predictions were the best at predicting the data collected by Gillespie. In fact, the PFGC was the most consistent for this system, being very nearly the best at predicting the Lekyo data as well.

Wilson, et al. (1985) presented some data for systems with inerts. Table VI presents a sample composition of such a stream and various examples of predicted phase distributions. Each different prediction represents a value

TABLE V

PARTIAL PRESSURES FOR NH_3--H_2S--H_2O

				Partial Pressure, Bar					
				Experimental		Calculated			
	T,	Molalities				SRK		PFGC	
	C	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S	NH_3	H_2S
G	149	2.38	0.59	1.64	1.8	1.42	3.1	1.55	2.9
		1.15	1.11	0.39	13.6	0.41	15.9	0.47	16.2
	204	2.39	0.63	4.37	8.1	3.63	10.1	4.18	9.7
		1.20	0.86	1.93	25.8	1.54	24.8	1.88	25.2
	260	2.62	0.88	10.40	20.5	6.92	18.5	8.97	17.6
		1.29	1.70	5.13	47.7	3.10	40.8	4.35	40.9
			Avg. Rel. Error (%)			21	28	10	23
				ARE (%) SWEQ		34	81		
				ARE (%) EG		8	36		
L	50	15.65	7.45	0.34	0.4	0.60	0.5	0.44	0.5
		9.35	4.45	0.25	0.3	0.31	0.4	0.14	0.4
		4.91	2.34	0.12	0.2	0.14	0.4	0.13	0.3
			Avg. Rel. Error (%)*			39	53	24	20
				ARE (%) BR		26	12		
				ARE (%) EMNP		7	134		
				ARE (%) EG		18	15		

References: G- Gillespie, et al. (1984) from Daumn, et al. (1986)
L- Lekyo (1959) from Daumn, et al. (1986)

* These results were obtained by changing the maximum amount of allowable dissociation.

TABLE VI

EFFECT OF DISSOCIATION ON SRK FLASH COMPOSITIONS

Temperature= 100^{O}F Pressure= 1000 psia

Maximum Dissociation	Component	Mol Fraction	
		Vapor	Liquid
Exptl	H2	0.4913	0.0005
	CH4	0.1346	0.0001
	N2	0.1033	0.0001
	CO	0.2693	0.0000
	CO2	0.0000	0.0027
	H2S	0.0002	0.0053
	H2O	0.0009	0.9709
	NH3	0.0004	0.0211
0.92	H2	0.4888	0.0002
	CH4	0.1337	0.0002
	N2	0.1028	0.0000
	CO	0.2678	0.0000
	CO2	0.0022	0.0005
	H2S	0.0032	0.0023
	H2O	0.0011	0.9757
	NH3	0.0005	0.0211
0.63	H2	0.4878	0.0002
	CH4	0.1334	0.0002
	N2	0.1026	0.0000
	CO	0.2672	0.0000
	CO2	0.0025	0.0001
	H2S	0.0047	0.0008
	H2O	0.0011	0.9776
	NH3	0.0006	0.0211
0.0	H2	0.4876	0.0002
	CH4	0.1333	0.0002
	N2	0.1026	0.0000
	CO	0.2671	0.0000
	CO2	0.0026	0.0001
	H2S	0.0052	0.0003
	H2O	0.0011	0.9779
	NH3	0.0006	0.0211

References: Wilson, Gillespie, and Owens (1985) of the maximum dissociation. The 92 percent dissociation value represents the highest value for which convergence was still possible. Higher levels of allowable dissociation generated composition estimates very much like the experimental results, but the convergence algorithm had difficulty with the "disappearance" of CO_2 from the vapor phase and with oscillations in K-values. Wilson commented that he had trouble with data analysis because of precipitation in the sample lines.

The data in Tables VII and VIII represent comparisons of the SRK and PFGC predictions against a portion of the experimental data presented by Wilson, et al. (1985). The deviations were calculated by subtracting the experimental value from the calculated value. The equations of state generated very similar results. Like the 100^{o} F data in Table VI, the 200^{o} F predictions indicate that carbon dioxide is much more volatile than the experimental results. The predictions at 400^{o} F are much better than the 200^{o} F results. The similarity between the two liquid compositions at 200^{o} F is reflected in all of the 100^{o} F data points. Again, these results represent an improvement over the naive results.

Table IX presents an analysis of the ability of the modified SRK and PFGC equations to predict consistent saturation pressures from experimental phase compositions. Specifically, bubble and dew point calculations were performed on the experimental liquid and vapor compositions.

TABLE VII

SRK FLASH COMPOSITIONS

Conditions			Mol Fractions			
T	P		Experimental		Calculated	Deviations
F	psia		Vapor	Liquid	Vapor	Liquid
200	500	H2	0.4976	0.0002	-0.0042	0.0000
		CH4	0.1258	0.0001	-0.0010	0.0000
		N2	0.0953	0.0000	-0.0008	0.0000
		CO	0.2460	*	-0.0021	0.0000
		CO2	0.0032	0.0025	0.0021	-0.0021
		H2S	0.0047	0.0051	0.0033	-0.0033
		H2O	0.0224	0.9715	0.0016	0.0067
		NH3	0.0048	0.0205	0.0013	-0.0012
200	1000	H2	0.5106	0.0004	-0.0042	0.0001
		CH4	0.1268	0.0001	-0.0010	0.0000
		N2	0.0984	0.0000	-0.0008	0.0000
		CO	0.2458	0.0002	-0.0018	-0.0002
		CO2	0.0018	0.0026	0.0023	-0.0023
		H2S	0.0026	0.0052	0.0036	-0.0036
		H2O	0.0112	0.9713	0.0014	0.0064
		NH3	0.0028	0.0202	0.0006	-0.0005
400	1000	H2	0.1987	0.0006	-0.0112	0.0001
		CH4	0.1002	0.0001	-0.0057	0.0001
		N2	0.0813	*	-0.0046	0.0000
		CO	0.0000	0.0000	0.0000	0.0000
		CO2	0.2228	0.0045	-0.0117	-0.0007
		H2S	0.1244	0.0084	-0.0049	-0.0018
		H2O	0.2399	0.9651	0.0405	0.0003
		NH3	0.0327	0.0213	-0.0024	0.0020
400	1000	H2	0.2576	0.0006	-0.0158	0.0003
		CH4	0.0727	0.0002	-0.0043	-0.0001
		N2	0.0462	0.0001	-0.0027	0.0001
		CO	0.0000	0.0000	0.0000	0.0000
		CO2	0.2715	0.0077	-0.0133	-0.0030
		H2S	0.0818	0.0061	-0.0031	-0.0017
		H2O	0.2387	0.9652	0.0415	0.0024
		NH3	0.0315	0.0202	-0.0024	0.0020
		Average Absolute Deviation			0.0066	0.0013

References: Wilson, Gillespie, and Owens (1985)

* Indicates estimated values.

TABLE VIII

PFGC FLASH COMPOSITIONS

Conditions			Mol Fractions			
T	P		Experimental		Calculated Deviations	
F	psia		Vapor	Liquid	Vapor	Liquid
200	500	H2	0.4976	0.0002	-0.0050	0.0001
		CH4	0.1258	0.0001	-0.0012	0.0000
		N2	0.0953	0.0000	-0.0010	0.0000
		CO	0.2460	*	-0.0025	0.0000
		CO2	0.0032	0.0025	0.0022	-0.0023
		H2S	0.0047	0.0051	0.0039	-0.0040
		H2O	0.0224	0.9715	0.0012	0.0086
		NH3	0.0048	0.0205	0.0025	-0.0024
200	1000	H2	0.5106	0.0004	-0.0045	0.0002
		CH4	0.1268	0.0001	-0.0011	0.0001
		N2	0.0984	0.0000	-0.0009	0.0001
		CO	0.2458	0.0002	-0.0020	-0.0001
		CO2	0.0018	0.0026	0.0022	-0.0023
		H2S	0.0026	0.0052	0.0037	-0.0037
		H2O	0.0112	0.9713	0.0010	0.0073
		NH3	0.0028	0.0202	0.0016	-0.0016
400	1000	H2	0.1987	0.0006	-0.0144	-0.0002
		CH4	0.1002	0.0001	-0.0074	0.0001
		N2	0.0813	*	-0.0060	0.0001
		CO	0.0000	0.0000	0.0000	0.0000
		CO2	0.2228	0.0045	-0.0152	-0.0010
		H2S	0.1244	0.0084	-0.0067	-0.0021
		H2O	0.2399	0.9651	0.0497	0.0041
		NH3	0.0327	0.0213	-0.0001	-0.0009
400	1000	H2	0.2576	0.0006	-0.0197	-0.0001
		CH4	0.0727	0.0002	-0.0055	-0.0001
		N2	0.0462	0.0001	-0.0035	-0.0001
		CO	0.0000	0.0000	0.0000	0.0000
		CO2	0.2715	0.0077	-0.0174	-0.0034
		H2S	0.0818	0.0061	-0.0042	-0.0019
		H2O	0.2387	0.9652	0.0505	0.0062
		NH3	0.0315	0.0202	-0.0002	-0.0008
		Average Absolute Deviation			0.0074	0.0017

References: Wilson, Gillespie, and Owens (1985)

* Indicates estimated values.

TABLE IX

WILSON SATURATION PRESSURES

			Pressure, Psia			
Measured		SWEQ	SRK		PFGC	
T, F	P, psia	Total	Dew	Bubble	Dew	Bubble
100	33.4	33	40.3	-	40.0	-
	500.0	500	535.4	-	518.4	-
	1000.0	1000	1211.0	-	1134.0	-
200	500.0	500	540.3	590.0	529.5	*
	1000.0	1000	1146.0	*	1105.0	*
300	500.0	490	541.0	-	553.0	-
	500.0	508	519.2	633.4	525.0	510.0
	1000.0	1012	1200.0	1159.0	1186.0	1100.0
	1000.0	1032	1133.0	-	*	-
400	1000.0	1312	1198.0	-	1245.0	-
	1000.0	1554	1204.0	1198.0	1248.0	1325.0
Avg. Rel. Error (%)		9	14	20	14	15

- Incomplete liquid analysis given.
* Program would not converge completely.

References: Wilson, Gillespie, and Owens (1985)

As would be expected from the aforementioned lack of unique saturation pressures, converged bubble point calculations were difficult to obtain. The two equations of state performed equally well at predicting consistent saturation pressures. The SWEQ error estimate was obtained by summing Wilson's values for the SWEQ-predicted vapor pressures along with the experimental inert pressures. All of the errors in the SWEQ predictions occurred at 400° F. Unlike SWEQ, the two equations of state were consistent in their errors and performed quite well. The dashes indicate data points with incomplete phase analyses, and the asterisks indicate equation of state nonconvergence.

Conclusions and Recommendations

The proposed electrolyte equilibrium model was found to perform as well as the methods of other researchers. None of the methods predicted all of the data. High pressures are important for the petroleum industry. The method described here provided the best predictions for wide temperature and pressure ranges. The approach had the considerable advantages of being quite easy to install and needing minimal additional data regression. Partially because of the reduced number of fitted coefficients, the proposed prediction algorithm was consistent in its errors, failing only at extremely low pressures.

CHAPTER REFERENCES

Beutier, D. and Renon, H., "Representation of NH3--H2S--H2O, NH3--CO2--H2O, and NH3--SO2--H2O Vapor-Liquid Equilibrium", Ind. Eng. Chem. Process Des. Dev., 17(3), 220-230, 1978.

Cunningham, J. R., "Calculation of Parameters from Group Contributions for the PFGC Equation of State", M. S. Thesis, Brigham Young University, 1974.

Daumn, K. J., Harrison, B. K., Manley, D. B., and Poling, B. E., "An Equation of State Description of Weak Electrolyte VLE Behavior", Presented at the Fourth International Conference on Fluid Properties and Phase Equilibria for Chemical Process Design, Helsingør, DK, 11-16 May, 1986.

Edwards, T. J., Maurer, G., Newman, J., and Prausnitz, J. M., "Vapor-Liquid Equilibria in Multicomponent Aqueous Solutions of Volatile Weak Electrolytes", AIChE J., 24(6), 966-976, 1978.

Erbar, J. H., "Comments on the Multiproperty and Multicomponent fit Program 'MPMCGC' for the PFGC Equation of State", Internal Communication, Linde A/G, Munich, 1980.

Erbar, J. H. and Gas Processors Association, "The GPA*SIM Program", Tulsa, 1980.

Majeed, A. I., "Prediction of Inhibition of Hydrate Formation Using the PFGC Equation of State", PhD. Thesis, School of Chemical Engineering, Oklahoma State University, Stillwater, Oklahoma, 1983.

Pawlikowski, E. M., Newman, J., and Prausnitz, J. M., "Phase Equilibria for Aqueous Solutions of Ammonia and Carbon Dioxide", Ind. Eng. Chem. Process Des. Dev., 21(4), 764-770, 1982.

Soave, G., "Equilibrium Constants From a Modified Redlich-Kwong Equation of State", Chem. Eng. Sci., 27, 1197-1203, 1972.

Vargaftik, N.B., Handbook of Physical Properties of Liquids and Gases: Pure Substances and Mixtures, 2nd ed., Hemisphere Publishing, Washington and New York, 1975.

Wagner, J., Personal Communication, Oklahoma State University, Stillwater, Oklahoma, 1987.

Wilson, G. M., A New Correlation of NH3, CO2, and H2S Volatility Data from Aqueous Sour Water Systems: API Publication 955, Refining Department, American Petroleum Institute, Washington, March, 1978.

Wilson, G. M., Gillespie, P. C., and Owens, J. L., "Sour Water Equilibria Extended to High-Temperatures and with Inerts Present", in Acid and Sour Gas Treating Processes, S. A. Newman, Ed., Gulf Publishing, Houston, 1985, pp. 753-785.

REGRESSION DATA REFERENCES

Beuschlein, W. L. and Simenson, L. O., "Solubility of Sulfur Dioxide in Water", _Chem. Rev._, 62(Mar.), 610-612, 1940.

Douabul, A. and Riley, J., "Solubility of Sulfur Dioxide in Distilled Water and Decarbonated Sea Water", _J. Chem. Eng. Data_, 24(4), 274-276, 1979.

Guillevic, J. L., Richon, D., and Renon, H., "Vapor-Liquid Equilibrium Data for the Binary System Water--Ammonia at 403.1, 453.1, and 503.1 K up to 7.0 MPa", _J. Chem. Eng. Data_, 30(3), 332-335, 1985.

Hirata, M., Ohe, S., and Nagahama, K., _Computer Aided Data Book of Vapor-Liquid-Equilibria_, Kodansha Limited, and Elsevier Scientific Publishing Co., Tokyo, 1975, pp. 435-437, 579, 758-767, 799.

Pawlikowski, E. M., Newman, J., and Prausnitz, J. M., "Phase Equilibria for Aqueous Solutions of Ammonia and Carbon Dioxide", _Ind. Eng. Chem. Process Des. Dev._, 21(4), 764-770, 1982.

Rabe, A. E. and Harris, J. F., "Vapor Liquid Equilibrium Data for the Binary System, Sulfur Dioxide and Water", _J. Chem. Eng. Data_, 8(3), 333-336, 1963.

Rizvi, S. S. H., and Heidemann, R. A., "Vapor-Liquid Equilibria in the Ammonia--Water System", _J. Chem. Eng. Data_, 32(2), 183-191, 1987.

Selleck, F. T., Carmichael, L. T., and Sage, B. H., "Phase Behavior in the Hydrogen Sulfide--Water System", _Ind. Eng. Chem._, 44(9), 2219-2226, 1952.

Stewart, P. B. and Munjal, P., "Solubility of Carbon Dioxide in Pure Water, Synthetic Sea Water, and Synthetic Sea Water Concentrates at -5 to 25 C. and 10- to 45-Atm. Pressure", _J. Chem. Eng. Data_, 15(1), 67-71, 1970.

Takenouchi, S., and Kennedy, G. C., "The Binary System H2O--CO2 at High Temperatures and Pressures", _Am. Jour. Sci._, 262, Nov., 1053-1074, 1962.

Vargaftik, N.B., Handbook of Physical Properties of Liquids and Gases: Pure Substances and Mixtures, 2nd ed., Hemisphere Publishing, Washington and New York, 1975.

Wiebe, R. and Gaddy, V. L., "The Solubility in Water of Carbon Dioxide at 50, 75 and 100 [C], at Pressures to 700 Atmospheres", Chem. Rev., 61(Feb.), 315-318, 1939.

Wiebe, R. and Gaddy, V. L., "The Solubility of Carbon Dioxide in Water at Various Temperatures from 12 to 40 [C] and at Pressures to 500 Atmospheres, Critical Phenomena", Chem. Rev., 62(Apr.), 815-817, 1941.

Zawisza, A. and Malesinska, B., "Solubility of Carbon Dioxide in Liquid Water and of Water in Gaseous Carbon Dioxide in the Range 0.2-5 MPa and at Temperatures up to 473 K", J. Chem. Eng. Data, 26(4), 388-391, 1981.

CHAPTER III

SIMULATION WITH GROUP CONTRIBUTION FUGACITY AND ACTIVITY COEFFICIENTS

Introduction

The ability of equations of state to predict the phase distribution of wet sour gases has been well established. However, the typical equation of state does not adequately describe more nonideal systems. Components like the organic acids require the use of more aggressive approaches to predict their vapor-liquid behavior. One equation of state, the Parameters From Group Contribution (PFGC) (Cunningham, 1974), has been claimed to better describe nonidealities. Typically, an activity coefficient model such as UNIFAC (Fredenslund, et al., 1975) is applied to modeling such systems. Because organic acids ionize, any attempt to describe these components must take this dilute solution behavior into account. In Chapter II of this work, an equation of state based algorithm for describing volatile electrolyte behavior was developed. This paper describes the application of that approach to systems of organic acid systems using the UNIFAC and PFGC models.

Approaches

The UNIversal Functional-group Activity Coefficients (UNIFAC) model (Fredenslund, 1975) is one of the most popular activity coefficient models. The equations for this model and its groups are listed in Figure 1 and Table I. The chief advantage of this model is that the group parameters, excluding interaction energies, can be directly calculated. If temperature dependence is ignored, a typical system such as formic acid-water has only two adjustable parameters for the interactions:

$HCOOH <--> H_2O$
$H_2O <--> HCOOH$

The UNIFAC interaction energies can be inferred from data for the system of acetic acid--water which has six interactions:

$CH_3- <--> -COOH$
$-COOH <--> CH_3-$
$CH_3- <--> H_2O$
$H_2O <--> CH_3-$
$-COOH <--> H_2O$
$H_2O <--> -COOH$

By assumption, the groups HCOOH and -COOH are considered to have no mutual interaction and share the same data for hetero-interactions (Fredenslund, 1977). The UNIFAC

Governing Equation

$$\ln(\gamma_i) = \ln(\Gamma_i^{C}) + \ln(\Gamma_i^{R})$$

Combinatorial Term

$$\ln(\Gamma_i^{C}) = \ln\left(\frac{\Phi_i}{x_i}\right) + \frac{1}{2} z\, q_i \ln\left(\frac{\Theta_i}{\Phi_i}\right) + l_i - \Phi_i \sum_j x_j\, l_j$$

$$l_i = 0.5\, z\, (r_i - q_i) - (r_i - 1) \qquad z = 10$$

$$\Theta_i = q_i\, x_i \,/ \sum_j q_j\, x_j \qquad \text{Area Fraction}$$

$$\Phi_i = r_i\, x_i \,/ \sum_j r_j\, x_j \qquad \text{Segment Fraction}$$

$$q_i = \sum_k m_k^{i}\, Q_k \qquad \text{Molecular Surface Area}$$

$$r_i = \sum_k m_k^{i}\, R_k \qquad \text{Molecular van der Waals Volume}$$

Residual Term

$$\ln(\Gamma_i^{R}) = \sum_k m_k^{i}\,(\ln(\gamma_k) - \ln(\gamma_k^{i})) \qquad \text{Sum Over all Groups}$$

γ_k refers to group k in overall solution

$$\ln(\gamma_k) = Q_k\left(1 - \ln\left(\sum_m \Theta_m \quad mk\right) - \sum_m \frac{\Theta_m\, \psi_{km}}{\sum_n \Theta_n\, \psi_{nm}}\right)$$

γ_k^{i} refers to group k in solution of pure component i

$$\Theta_m = Q_m\, X_m \,/ \sum_n Q_n\, X_n$$

X_m Mol Fraction of Group m in Mixture

$$\psi_{mn} = \exp(-a_{mn} / T) \qquad \text{Group Interaction}$$

Reference: Reid, et al. (1977)

Figure 1. Equations for the Universal Functional-Group Activity Coefficients (UNIFAC) Model.

TABLE I

UNIFAC GROUPS

ID	Group	ID	Group
1	H_2O	18	$CH_2{=}C$
2	CH_3	19	OH
3	CH_2	20	CH_3OH
4	CH	21	CH (aro)
5	C	22	=C (aro)
6	H_2	23	CCH_3 (aro)
7	CH_4	24	CCH_2 (aro)
8	N_2	25	$CH_2{=}C{=}CH_2$
9	O_2	26	$CH_2{=}C{=}CH{-}CH_3$
10	CO	27	EG
11	CO_2	28	DEG
12	H_2S	29	TEG
13	SO_2	30	COOH
14	$CH_2{=}CH_2$	31	CH_3CO
15	$CH_2{=}CH$	32	CH_2CO
16	CH=CH	33	CHO
17	CH=C	34	HCOOH

Reference: Rearranged from Skjold-Jørgensen (1979).

model needs values for the six interaction energies to describe such a system by extension from acetic acid.

The parameter sets by Skjold-Jørgensen, et al. (1979) and others unfortunately do not include any components which are also groups such as, H_2S, CO_2, etc. Data for ionizing systems like acetic acid and water were, however, available at low pressures, allowing the activity coefficient model to be analyzed for applicability to ionizing components. The equations describing the UNIFAC model are those from Reid, et al. (1977), and are well explained in any of the many articles by Fredenslund and his co-workers. (Fredenslund, et al., 1975, 1977, Gmehling, et al., 1982, Skjold-Jørgensen, et al., 1979, etc.)

A Powell-Botm (Kuester and Mize, 1973) optimization algorithm was used to calculate the optimal interaction energies for the UNIFAC parameters based on:

1) Matching K-values, calculated using the SRK vapor fugacities, UNIFAC liquid activities and using liquid reference fugacities predicted by the liquid vapor pressure correlation. The SRK k_{ij}'s were obtained by regression using the algorithm described by Friedemann (1987).
2) Using Fredenslund's quick method (Fredenslund, 1977) which assumes that the experimental compositions produce accurate vapor fugacities from which activity coefficients can be derived

using. The results from this algorithm provided initial values for the first option.

The Parameters From Group Contribution equation of state (PFGC) is claimed to have a better liquid phase approach than other equations of state. The equation has the severe drawback that all of its parameters must be obtained by regression. As can be seen in Figure 2 and Table II, the approach and groups are considerably different from the UNIFAC implementation of group contribution. Each group has five parameters (three for isothermal data). At best, an initial fit to describe the formic acid--water system, which has two groups and one group interaction, requires at least seven data points. At worst, there are eleven parameters to find. A broad range of data is available for water but not for formic acid. Using a typical cubic equation of state implementation, the same system has only three adjustable parameters (the applicability of which is another question).

Unfortunately, the UNIFAC equation also requires some pure component experimental data. Activity coefficient models need a vapor fugacity model and a liquid-phase reference fugacity. The reference fugacity coefficients were calculated at the system temperature and pure component vapor pressures using the Soave-Redlich-Kwong (SRK) equation of state (Soave, 1972). The reference state vapor pressures used with UNIFAC were calculated using the Riedel-Plank-

General Equation for Compressibility

$$Z = 1 - \frac{s\ v}{b} \ln (1 - v/b) - s + b\ (c/b_H) \sum_i \phi_i\ b \left(\frac{1 - \sum_j \phi_j l_{ij}}{v - b + b \sum_j \phi_j l_{ij}} \right)$$

Definition of Coefficients

$b = \sum_I x_I b_I$	Mixture covolume
$b_I = \sum_i m_I^i b_i$	Component covolume
c/b_H	Universal Constant
$E_{ij} = a_{ij} (E_{ii} + E_{jj})/2$	Group Interaction
$E_{ii} = E_{ii}^o + (\frac{283.2}{T,\ K} - 1)(E_{ii}^1 + E_{ii}^2 + (\frac{283.2}{T,\ K} - 1))$	
$l_{ij} = \exp (-E_{ij}/kT)$	Group Interaction
m_I^i	Number of Groups i in Component I
$s = \sum_I x_I s_I$	Mixture Degrees of Freedom
$s_I = \sum_i m_I^i s_i$	Component Degrees of Freedom
$\phi_i = \sum_i x_I \frac{m_I^i}{b} b_i$	Mixture Group Fraction
v	Molar Volume

Reference: Majeed (1983)

Figure 2: Equations for the Parameters From Group Contribution (PFGC) Equation of State.

TABLE II

PFGC Groups

ID	Group		ID	Group	
1	H_2		16	H_2O	
2	CH_4		17	=C	
3	CH_3		18	SO_2	
4	CH_2		19	CH_3OH	
5	CH		20	=C	(ortho)
6	C		21	=C	(para)
7	$=CH_2$		22	=C	(meta)
8	CH_2	(cyclo)	23	=C=	
9	CH	(aro)	24	CH	(cyclo)
10	=C	(aro)	25	O_2	
11	=CH		26	CH_2OH	
12	N_2		27	CH_2OCH_2	
13	CO_2		28	NH_3*	
14	CO		29	HCOOH*	
15	H_2S		30	COOH*	

References: unlabelled Majeed (1983)
* This work.

Miller vapor pressure correlation as described by Reid, et al. (1977).

Highly polar components such as acetic acid associate in both phases, implying a significant self-interaction. Since all of the available data for this system was found to be at low pressure, such dimerization was expected to have little effect. Ito, et al. (1963) state, "There is no evidence that with a recirculation-type apparatus the retention time for vapor is long enough to attain the association equilibria."

Regression and Prediction

The UNIFAC and PFGC models were studied for their applicability to electrolytic systems. The acetic acid--water system was utilized as the base (or regressed) data set. The ternary system formic acid--acetic acid--water was predicted by the UNIFAC equation using the extrapolation from acetic acid. The results were compared to predictions made using the Soave-Redlich-Kwong equation of state. The system acetic acid--propionic acid--water was studied to compare the PFGC and UNIFAC results.

Most of the pure component parameters for these acids were obtained from Reid, et al. (1977). Originally, the critical pressure for formic acid was estimated using Lydersen's method, but Ambrose and Ghiassee (1987) provided some better estimates. The propionic acid critical pressure reported by Ambrose differed significantly from the value listed by Reid. The difference was found to not significantly affect the results.

The -COOH--H_2O group interaction energies were refit against data for acetic acid because of the inclusion of the dissociation algorithm. (See the regression data references.) The ionization constants used in predicting the dissociation were those published by Robinson and Stokes (1959). Initially, the two optimization programs had the same primal function, but because of a preference for least fractional errors, the Powell-Botm optimizer was changed. Fredenslund's program was intentionally left unmodified. After allowing for the difference in optimization functions, both optimizations yielded similar parameters. These were, however, quite different from those of Gmehling. To provide a comparison with simple equation of state behavior, an SRK interaction parameter was also found by regression, using a Fibonacci search. The acetic acid--water k_{ij} value of -0.172 was found to be temperature independent.

The PFGC parameters for the COOH group were regressed against the same acetic acid data using the program developed by Erbar (1980). Because the number of regression variables required thoughtful initial values, a surface map was generated by fixing the B and S parameters and allowing the interaction contribution polynomial to be fitted by the optimization. Using the vapor pressure data of Vargaftik (1975), the fitted parameters resulted in a 0.9 percent error in predicted vapor pressure. Regression to find the optimum COOH--H_2O interaction coefficient yielded an average K-value error of 13 percent (as compared to the UNIFAC result of 16 percent).

A comparison between the experimental results of Brown and Ewald (1950) and the various predictions of an atmospheric acetic acid system can be made by studying Figure 3. As expected, the UNIFAC equation predicts the x-y plot better than does the SRK equation, especially for higher water concentrations. The UNIFAC approach also performs better than the PFGC method because the PFGC equation predicted an azeotrope at high aqueous mol fractions.

Cruz and Renon (1979) studied the behavior of dilute aqueous acetic acid solutions by taking dilute solution experimental data and developing a model to describe their results. The x-y diagram in Figure 4 demonstrates that the modified UNIFAC liquid model predicts the experimental data as well as the model by Cruz and Renon. This data set reflects the most ionized conditions, where deviation from ideality is most pronounced.

The extrapolation from one component to another is an important feature of group contribution methods. The system of acetic acid and water exhibited negative deviations from ideality. Formic acid has much more deviation from ideality and is also the first component in the alkanoic acid series. The graph in Figure 5 illustrates that the use of the extrapolation from acetic acid predicts the binary data with

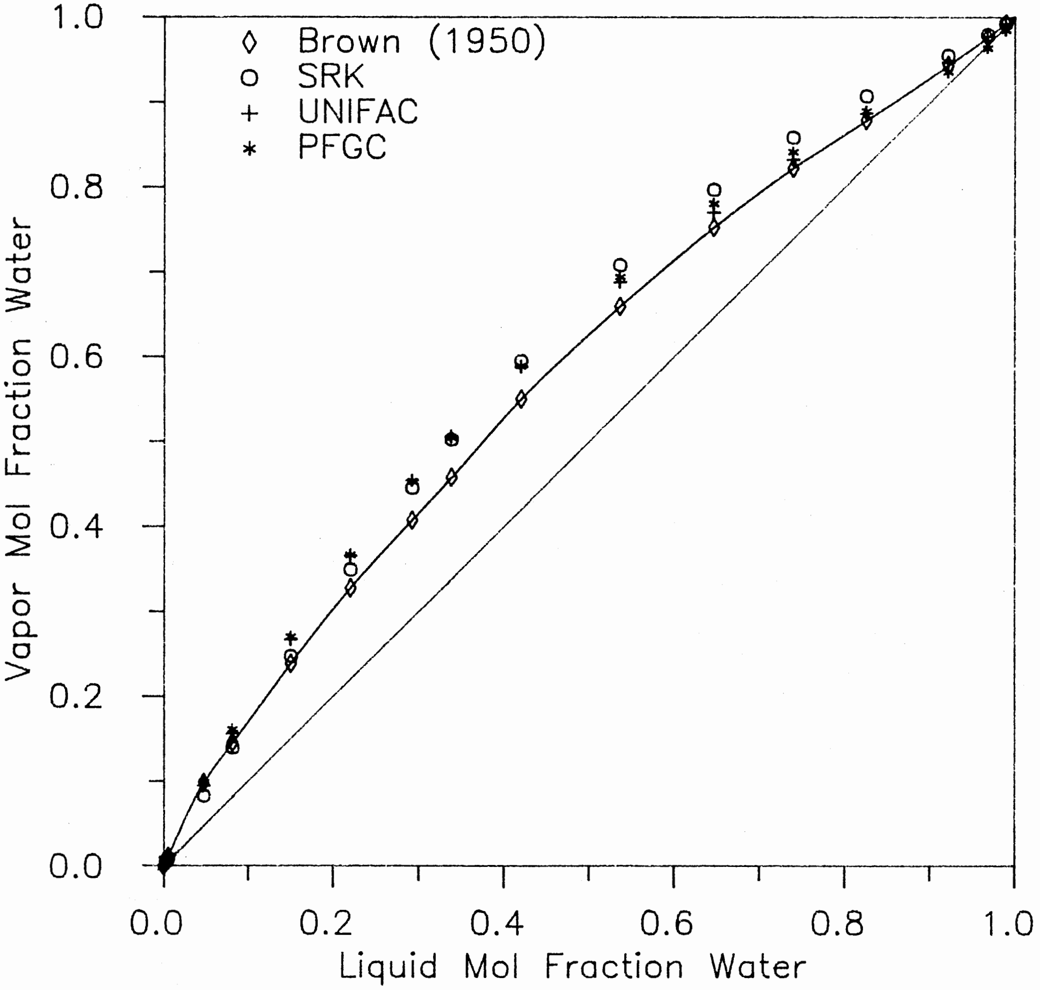

Figure 3. Acetic Acid--Water X-Y Diagram

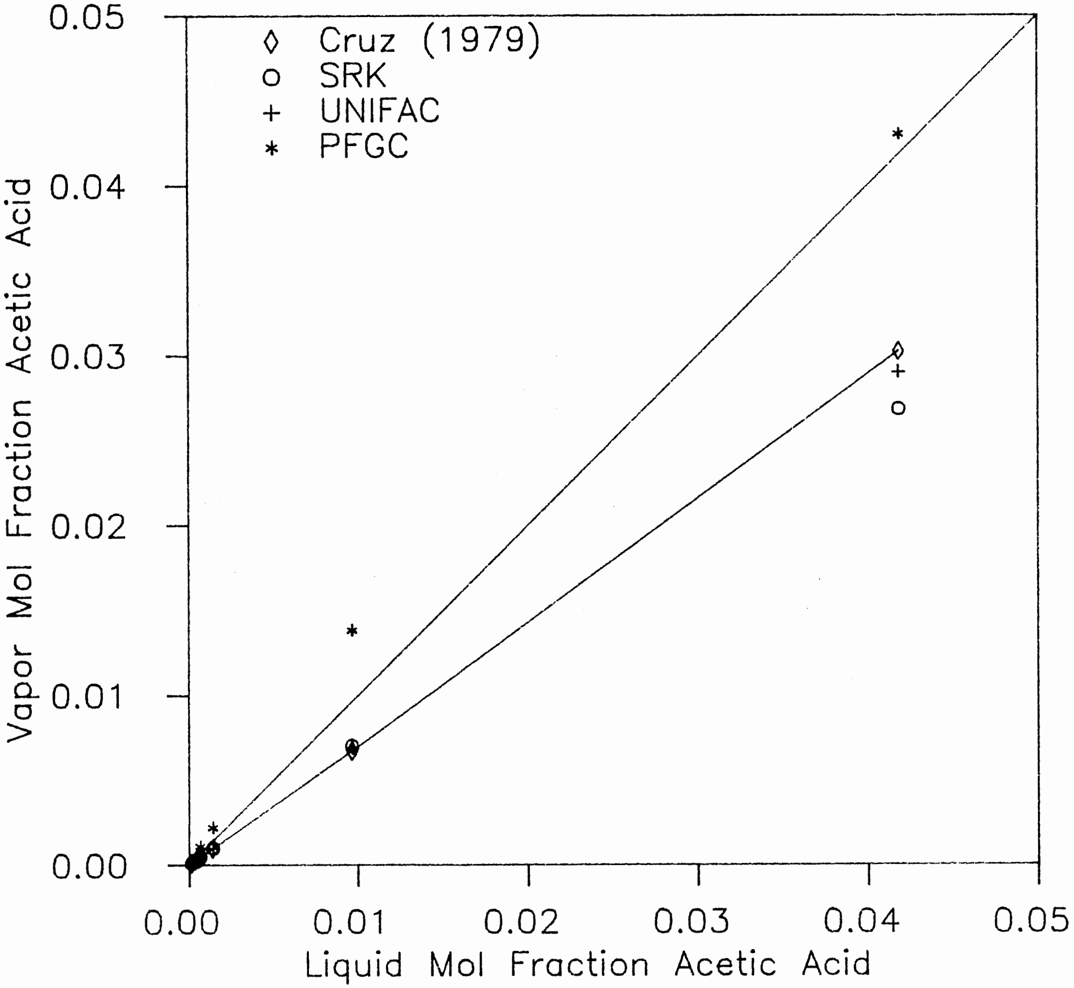

Figure 4. Dilute Acetic Acid--Water X-Y Diagram

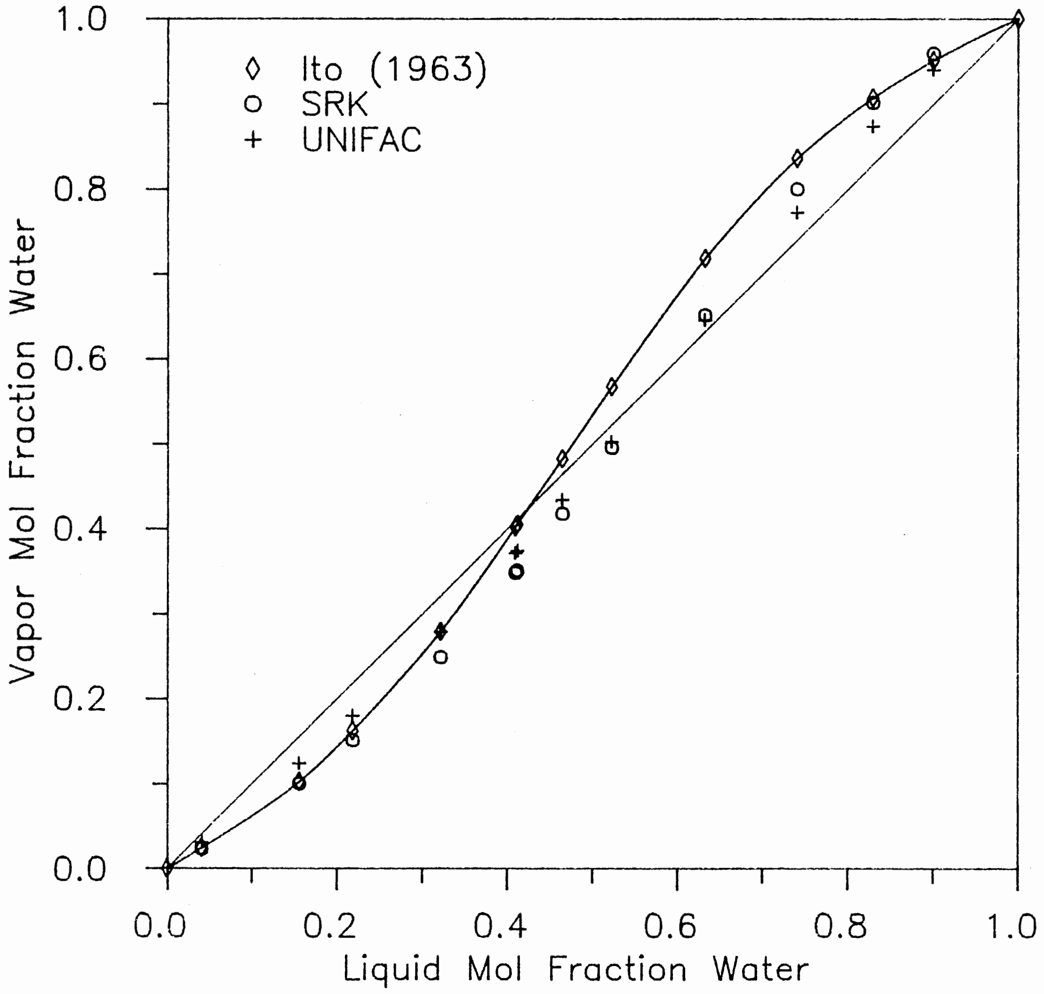

Figure 5. Formic Acid--Water X-Y Diagram

a typical K-value error of 12 percent. This error compares to the fitted SRK average error of 10 percent. The high polarity of this system and the reduced degrees of freedom available in a binary consisting of single group components is expected to be the cause of these poor results. Both of the liquid phase approaches predict the azeotropic behavior. Using the available pure component formic acid data, the PFGC equation yielded an average K-Value error of 38 percent. A simultaneous binary fit improved the results significantly, but neither parameter set was applicable to multicomponent aqueous systems.

Wisniak and Tamir (1977) presented data for the ternary system formic acid--acetic acid--water at 1 atm. The system exhibited an azeotrope at 107° C with a composition of 36.3 mol percent water and 46.9 mol percent formic acid. To test the extension of the UNIFAC model to this system, dew point and bubble point calculations were made on the respective phases. Figure 6 presents the experimental liquid phase composition and the calculated liquid phases in equilibrium with the experimental vapor phases from Figure 7. The UNIFAC correlation predicts the ionized dilute solution at 103° C. Both algorithms accurately predict the system at 105° C. Comparing Figure 6 and Figure 7, the UNIFAC equation does an especially good job of predicting the azeotropic trajectory at 107° C. Neither of the two approaches predicts the 109° C trajectory where phase

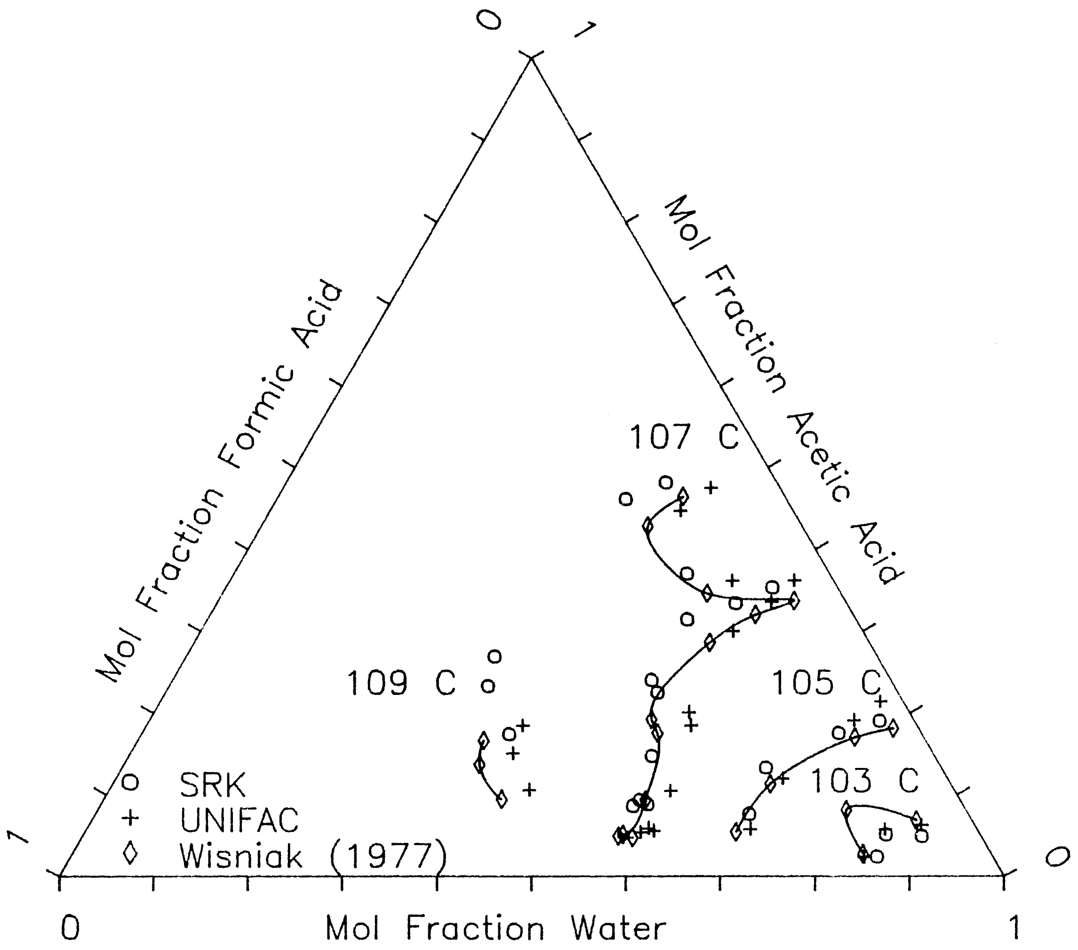

Figure 6. Bubble Point Compositions for the System Water--Formic Acid--Acetic Acid

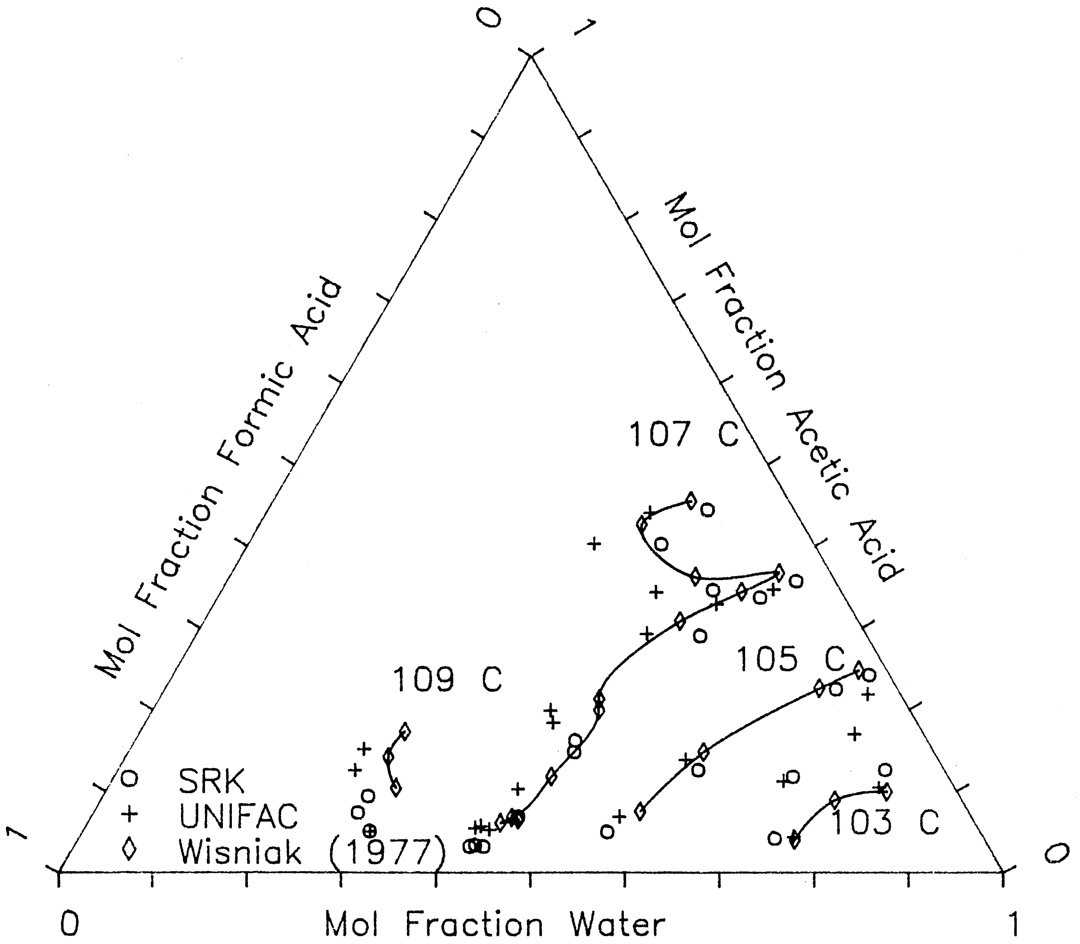

Figure 7. Dew Point Compositions for the System Water--Formic Acid--Acetic Acid

dimerization effects are considerably greater than the degree of ionization.

Some data were located which were ideal for simultaneously testing the flexibility of the PFGC equation and comparing the results with UNIFAC. First, the binary propionic acid--water system was studied. As can be seen in Figure 8, the two methods did not predict the atmospheric x-y diagram with any accuracy at all. Both methods predicted the azeotrope with some accuracy but failed to predict the rest of the equilibrium curve.

Wisniak and Tamir (1977) presented some ternary vapor-liquid equilibrium data for the system consisting of water--acetic acid--propionic acid. Calculated results were generated by performing bubble point calculations on the liquid compositions described by Figure 9. A perusal of Figure 10 yields the conclusion that despite the poor binary results for propionic acid--water, the UNIFAC equation reflects the experimental vapor compositions quite well. The PFGC equation over predicts the water volatility in the same manner as the propionic acid results. This error may have been caused by the assumption that the CH_3- and CH_2-group interactions with COOH were identical and not position dependent.

Conclusions

The electrolyte equilibria approach can be utilized with an activity coefficient model to describe the behavior

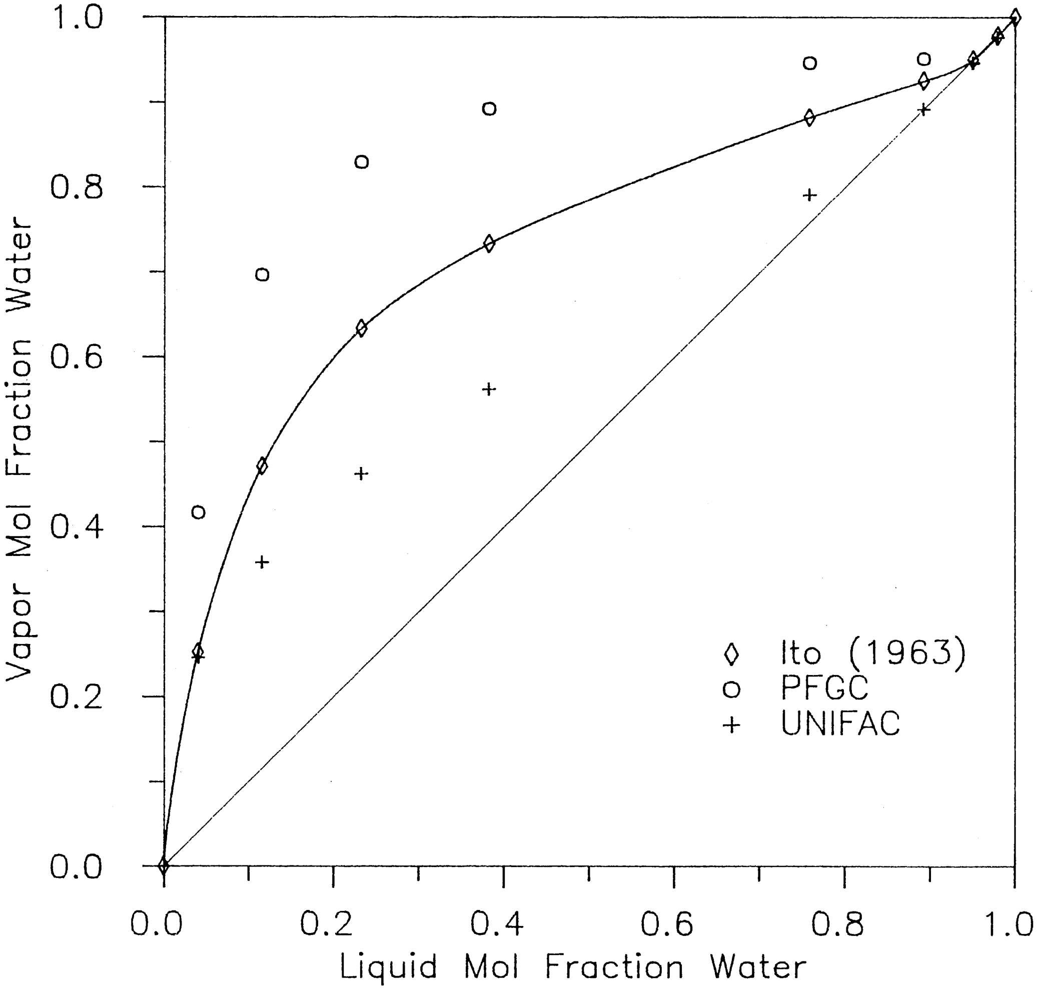

Figure 8. Propionic Acid--Water X-Y Diagram

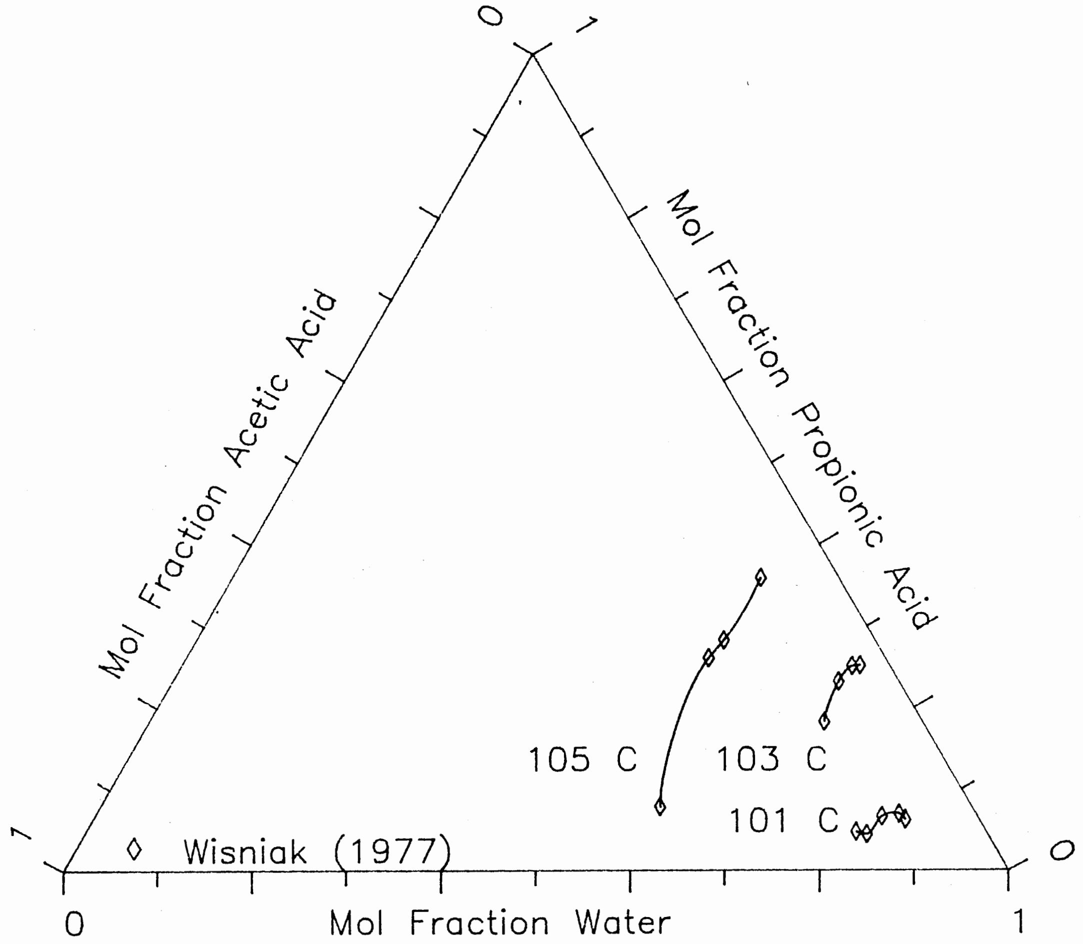

Figure 9. Bubble Point Compositions for the System Water--Acetic Acid--Propionic Acid

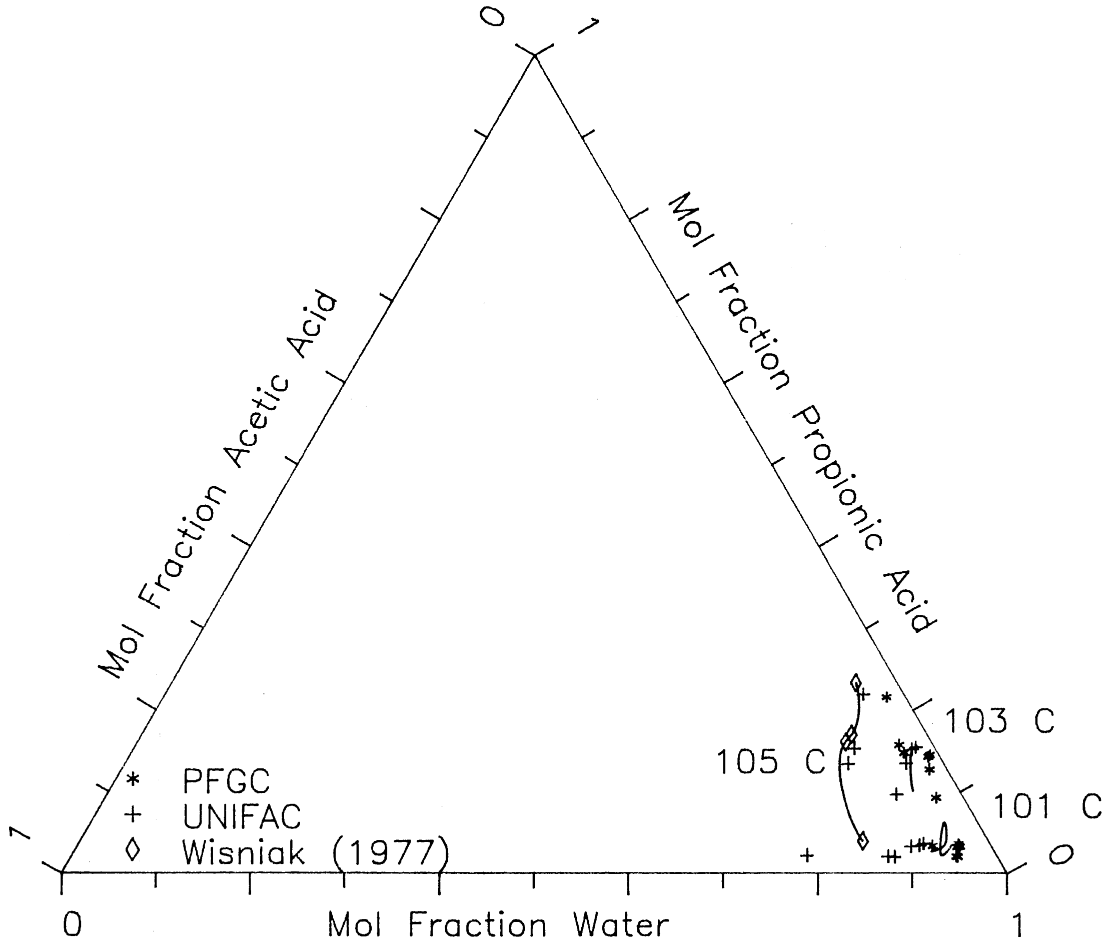

Figure 10. Dew Point Compositions for the System Water--Acetic Acid--Propionic Acid

of solutions of organic acids. The two group contribution approaches which were tested in this study gave markedly different results, with the UNIFAC method yielding the best predictions. Neither of the two methods extended well to binaries, but both gave better predictions when more than two components were present.

CHAPTER REFERENCES

Ambrose, D. and Ghiassee, N. B., "Vapour Pressures and Critical Temperatures and Critical Pressures of Some Alkanoic Acids: C1 to C10", J. Chem. Thermodynamics, 19(5), 505-519, 1987.

Brown, I. and Ewald, A. H., "Liquid-Vapour Equilibria: 1. The Systems Carbon Tetrachloride--Cyclohexane and Water--Acetic Acid", Austr. J. Sci. Res. Phys. Ser., 3, 306-323, 50.

Cruz, J. L. and Renon, H., "Nonideality in Weak Binary Electrolytic Solutions. Vapor-Liquid Equilibrium Data and Discussion of the System Water--Acetic Acid", Ind. Eng. Chem. Fundam., 18(2), 168-180, 1979.

Cunningham, J. R., "Calculation of Parameters from Group Contributions for the PFGC Equation of State", M. S. Thesis, Brigham Young University, 1974.

Erbar, J. H., "Comments on the Multiproperty and Multicomponent fit Program 'MPMCGC' for the PFGC Equation of State", Internal Communication, Linde A/G, Munich, 1980.

Fredenslund, Aa., Jones, R. L., Prausnitz, J. M., "Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures", AIChE J., 21(4), 1086-1099, 1975.

Fredenslund, Aa., Gmehling, J., and Rasmussen, P., Vapor-Liquid Equilibria Using UNIFAC: A Group-Contribution Method, Elsevier Scientific Publishing, New York, 1977.

Gmehling, J., Rasmussen, P., and Fredenslund, Aa., "Vapor-Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension 2", Ind. Eng. Chem. Process Des. Dev., 21(1), 118-127, 1982.

Ito, T. and Yoshida, F., "Vapor-Liquid Equilibria of Water--Lower Fatty Acid Systems: Water--Formic Acid, Water--Acetic Acid, and Water--Propionic Acid", J. Chem. Eng. Data, 8(3), 315-320, 1963.

Kuester, J. L. and Mize, J. H., *Optimization Techniques with Fortran*, McGraw-Hill, 1973.

Majeed, A. I., "Prediction of Inhibition of Hydrate Formation Using the PFGC Equation of State", PhD. Thesis, School of Chemical Engineering, Oklahoma State University, Stillwater, Oklahoma, 1983.

Reid, R. C., Prausnitz, J. M., and Sherwood, T. K., *The Properties of Gases and Liquids*, 3rd ed., McGraw-Hill, New York, 1977.

Robinson, R. A. and Stokes, R. H., *Electrolyte Solutions*, Academic Press, New York, and Butterworths Scientific Publications, London, 1959.

Skjold-Jørgensen, S., Kolbe, B., Gmehling, J., and Rasmussen, P., "Vapor-Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension", *Ind. Eng. Chem. Process Des. Dev.*, 18(4), 714-722, 1979.

Soave, G., "Equilibrium Constants From a Modified Redlich-Kwong Equation of State", *Chem. Eng. Sci.*, 27, 1197-1203, 1972.

Wisniak, J. and Tamir, A., "Vapor Equilibrium in Ternary Systems: Water--Formic Acid--Acetic Acid and Water--Acetic Acid--Propionic Acid", *J. Chem. Eng. Data*, 22(3), 253-260, 1977.

REGRESSION DATA REFERENCES

Alpert, N. and Elving, P. J., "Vapor-Liquid Equilibria in Binary Systems: Ethylene Dichloride-Toluene and Formic Acid-Acetic Acid", Ind. Eng. Chem., 41(12), 2864-2867, 1949.

Brown, I. and Ewald, A. H., "Liquid-Vapour Equilibria: 1. The Systems Carbon Tetrachloride-Cyclohexane and Water-Acetic Acid", Austr. J. Sci. Res. Phys. Ser., 3, 306-323, 50.

Conti, J. J., Othmer, J. J., and Gilmont, R., "Composition of Vapors from Boiling Binary Solutions: Systems Containing Formic Acid, Acetic Acid, Water, and Chloroform", J. Chem. Eng. Data, 5(3), 301-307, 1960.

Cruz, J. L. and Renon, H., "Nonideality in Weak Binary Electrolytic Solutions. Vapor-Liquid Equilibrium Data and Discussion of the System Water-Acetic Acid", Ind. Eng. Chem. Fundam., 18(2), 168-180, 1979.

Hirata, M., Ohe, S., and Nagahama, K., Computer Aided Data Book of Vapor-Liquid-Equilibria, Kodansha Limited, and Elsevier Scientific Publishing Co., Tokyo, 1975, pp. 435-437, 579, 758-767, 799.

Ito, T. and Yoshida, F., "Vapor-Liquid Equilibria of Water-Lower Fatty Acid Systems: Water-Formic Acid, Water-Acetic Acid, and Water-Propionic Acid", J. Chem. Eng. Data, 8(3), 315-320, 1963.

Sebastiani, E. and Lacquanti, L., "Acetic Acid-Water System Thermodynamical Correlation of Vapor-Liquid Equilibrium Data", Chem. Eng. Sci., 22, 1155-1162, 1967.

Vargaftik, N.B., Handbook of Physical Properties of Liquids and Gases: Pure Substances and Mixtures, 2nd ed., Hemisphere Publishing, Washington and New York, 1975.

Wisniak, J. and Tamir, A., "Vapor Equilibrium in Ternary Systems: Water-Formic Acid-Acetic Acid and Water-Acetic Acid-Propionic Acid", J. Chem. Eng. Data, 22(3), 253-260, 1977.

APPENDIX A

FITTED PARAMETERS

TABLE A-I

FITTED COEFFICIENTS FOR SRK

Binary	k_{ij} = a	+ b T/1000	Avg K-Value Error %	Data Points
CO_2--H_2O	-0.3822	0.4930	6	116
SO_2--H_2O	-0.2066	0.2141	4*	60
NH_3--H_2O	-0.2751	0.0	14	317
HCOOH--H_2O	-0.2700	0.0	10	54
CH_3COOH--H_2O	-0.1720	0.0	24	131
C_2H_5COOH--H_2O	-0.1190	0.0	30	24

* Estimated from partial pressure errors.

TABLE A-II

FITTED COEFFICIENTS FOR UNIFAC

Binary	a_{mn}	a_{nm}	Avg K-Value Error %	Data Points
COOH--H_2O	197.0	-349.0	16	54

TABLE A-III

FITTED COEFFICIENTS FOR PFGC

Binary	k_{ij} = a	+ b T/1000	Avg K-Value Error %	Data Points
SO_2--H_2O	0.3713	0.2812	5*	60
NH_3--H_2O	1.0000	0.0	16	317
COOH--H_2O	1.0445	0.0	13	54
CH_3--COOH	1.3710	0.0	13	54

* Estimated from partial pressure errors.

TABLE A-IV

PFGC GROUP PARAMETERS

Group	B	S	E_0	E_1	E_2
COOH	0.4614	4.7675	-941.8	-671.23	300.0
NH_3	0.3832	4.8593	-1444.9	-838.00	210.0

BIBLIOGRAPHY

Alpert, N. and Elving, P. J., "Vapor-Liquid Equilibria in Binary Systems: Ethylene Dichloride--Toluene and Formic Acid--Acetic Acid", Ind. Eng. Chem., 41(12), 2864-2867, 1949.

Ambrose, D. and Ghiassee, N. B., "Vapour Pressures and Critical Temperatures and Critical Pressures of Some Alkanoic Acids: C1 to C10", J. Chem. Thermodynamics, 19(5), 505-519, 1987.

Beuschlein, W. L. and Simenson, L. O., "Solubility of Sulfur Dioxide in Water", Chem. Rev., 62(Mar.), 610-612, 1940.

Beutier, D. and Renon, H., "Representation of NH3--H2S--H2O, NH3--CO2--H2O, and NH3--SO2--H2O Vapor-Liquid Equilibrium", Ind. Eng. Chem. Process Des. Dev., 17(3), 220-230, 1978.

Brown, I. and Ewald, A. H., "Liquid-Vapour Equilibria: 1. The Systems Carbon Tetrachloride--Cyclohexane and Water--Acetic Acid", Austr. J. Sci. Res. Phys. Ser., 3, 306-323, 50.

Conti, J. J., Othmer, J. J., and Gilmont, R., "Composition of Vapors from Boiling Binary Solutions: Systems Containing Formic Acid, Acetic Acid, Water, and Chloroform", J. Chem. Eng. Data, 5(3), 301-307, 1960.

Cruz, J. L. and Renon, H., "Nonideality in Weak Binary Electrolytic Solutions. Vapor-Liquid Equilibrium Data and Discussion of the System Water--Acetic Acid", Ind. Eng. Chem. Fundam., 18(2), 168-180, 1979.

Cunningham, J. R., "Calculation of Parameters from Group Contributions for the PFGC Equation of State", M. S. Thesis, Brigham Young University, 1974.

Daumn, K. J., Harrison, B. K., Manley, D. B., and Poling, B. E., "An Equation of State Description of Weak Electrolyte VLE Behavior", Presented at the Fourth International Conference on Fluid Properties and Phase Equilibria for Chemical Process Design, Helsingør, DK, 11-16 May, 1986.

Douabul, A. and Riley, J., "Solubility of Sulfur Dioxide in Distilled Water and Decarbonated Sea Water", J. Chem. Eng. Data, 24(4), 274-276, 1979.

Edwards, T. J., Maurer, G., Newman, J., and Prausnitz, J. M., "Vapor-Liquid Equilibria in Multicomponent Aqueous Solutions of Volatile Weak Electrolytes", AIChE J., 24(6), 966-976, 1978.

Erbar, J. H., "Comments on the Multiproperty and Multicomponent fit Program 'MPMCGC' for the PFGC Equation of State", Internal Communication, Linde A/G, Munich, 1980.

Erbar, J. H. and Gas Processors Association, "The GPA*SIM Program", Tulsa, 1980.

Fredenslund, Aa., Jones, R. L., Prausnitz, J. M., "Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures", AIChE J., 21(4), 1086-1099, 1975.

Fredenslund, Aa., Gmehling, J., and Rasmussen, P., Vapor-Liquid Equilibria Using UNIFAC: A Group-Contribution Method, Elsevier Scientific Publishing, New York, 1977.

Gmehling, J., Rasmussen, P., and Fredenslund, Aa., "Vapor-Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension 2", Ind. Eng. Chem. Process Des. Dev., 21(1), 118-127, 1982.

Guillevic, J. L., Richon, D., and Renon, H., "Vapor-Liquid Equilibrium Data for the Binary System Water--Ammonia at 403.1, 453.1, and 503.1 K up to 7.0 MPa", J. Chem. Eng. Data, 30(3), 332-335, 1985.

Hirata, M., Ohe, S., and Nagahama, K., Computer Aided Data Book of Vapor-Liquid-Equilibria, Kodansha Limited, and Elsevier Scientific Publishing Co., Tokyo, 1975, pp. 435-437, 579, 758-767, 799.

Ito, T. and Yoshida, F., "Vapor-Liquid Equilibria of Water--Lower Fatty Acid Systems: Water--Formic Acid, Water--Acetic Acid, and Water--Propionic Acid", J. Chem. Eng. Data, 8(3), 315-320, 1963.

Kane, R. D., Telephone Conversation, 20 July, 1987.

Kuester, J. L. and Mize, J. H., Optimization Techniques with Fortran, McGraw-Hill, 1973.

Majeed, A. I., "Prediction of Inhibition of Hydrate Formation Using the PFGC Equation of State", PhD. Thesis, School of Chemical Engineering, Oklahoma State University, Stillwater, Oklahoma, 1983.

Panagiotopoulous, A. C. and R. C. Reid, "A New Mixing Rule for Cubic Equations of State Highly Polar, Asymmetric Systems", Presented at the ACS Spring National Meeting, Miama, FL, 1 May, 1985.

Pawlikowski, E. M., Newman, J., and Prausnitz, J. M., "Phase Equilibria for Aqueous Solutions of Ammonia and Carbon Dioxide", *Ind. Eng. Chem. Process Des. Dev.*, 21(4), 764-770, 1982.

Rabe, A. E. and Harris, J. F., "Vapor Liquid Equilibrium Data for the Binary System, Sulfur Dioxide and Water", *J. Chem. Eng. Data*, 8(3), 333-336, 1963.

Reid, R. C., Prausnitz, J. M., and Sherwood, T. K., *The Properties of Gases and Liquids*, 3rd ed., McGraw-Hill, New York, 1977.

Rizvi, S. S. H., and Heidemann, R. A., "Vapor-Liquid Equilibria in the Ammonia--Water System", *J. Chem. Eng. Data*, 32(2), 183-191, 1987.

Robinson, R. A. and Stokes, R. H., *Electrolyte Solutions*, Academic Press, New York, and Butterworths Scientific Publications, London, 1959.

Scott, W. D. and McCarthy, J. L., "The System Sulfur Dioxide--Ammonia--Water at 25 C.", *Ind. Eng. Chem. Fundam.*, 6(1), 41-48, 1967.

Sebastiani, E. and Lacquanti, L., "Acetic Acid--Water System Thermodynamical Correlation of Vapor-Liquid Equilibrium Data", *Chem. Eng. Sci.*, 22, 1155-1162, 1967.

Selleck, F. T., Carmichael, L. T., and Sage, B. H., "Phase Behavior in the Hydrogen Sulfide--Water System", *Ind. Eng. Chem.*, 44(9), 2219-2226, 1952.

Skjold-Jørgensen, S., Kolbe, B., Gmehling, J., and Rasmussen, P., "Vapor-Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension", *Ind. Eng. Chem. Process Des. Dev.*, 18(4), 714-722, 1979.

Skjold-Jørgensen, S., Rasmussen, P., and Fredenslund, Aa., "On the Concentration Dependence of the UNIQUAC/UNIFAC Models", *Chem. Eng. Sci.*, 37(1), 99-111, 1982.

Soave, G., "Equilibrium Constants From a Modified Redlich-Kwong Equation of State", Chem. Eng. Sci., 27, 1197-1203, 1972.

Stewart, P. B. and Munjal, P., "Solubility of Carbon Dioxide in Pure Water, Synthetic Sea Water, and Synthetic Sea Water Concentrates at -5 to 25 C. and 10- to 45-Atm. Pressure", J. Chem. Eng. Data, 15(1), 67-71, 1970.

Takenouchi, S., and Kennedy, G. C., "The Binary System H2O--CO2 at High Temperatures and Pressures", Am. Jour. Sci., 262, Nov., 1053-1074, 1962.

Vargaftik, N.B., Handbook of Physical Properties of Liquids and Gases: Pure Substances and Mixtures, 2nd ed., Hemisphere Publishing, Washington and New York, 1975.

Wagner, J., Personal Communication, Oklahoma State University, Stillwater, Oklahoma, 1987.

Wiebe, R. and Gaddy, V. L., "The Solubility in Water of Carbon Dioxide at 50, 75 and 100 [C], at Pressures to 700 Atmospheres", Chem. Rev., 61(Feb.), 315-318, 1939.

Wiebe, R. and Gaddy, V. L., "The Solubility of Carbon Dioxide in Water at Various Temperatures from 12 to 40 [C] and at Pressures to 500 Atmospheres, Critical Phenomena", Chem. Rev., 62(Apr.), 815-817, 1941.

Wilhelm, S. M. and Kane, R. D., "Selection of Materials for Sour Service in Petroleum Production", J. Pet. Tech., Oct., 1051-1061, 1986.

Wilson, G. M., A New Correlation of NH3, CO2, and H2S Volatility Data from Aqueous Sour Water Systems: API Publication 955, Refining Department, American Petroleum Institute, Washington, March, 1978.

Wilson, G. M., Gillespie, P. C., and Owens, J. L., "Sour Water Equilibria Extended to High-Temperatures and with Inerts Present", in Acid and Sour Gas Treating Processes, S. A. Newman, Ed., Gulf Publishing, Houston, 1985, pp. 753-785.

Wisniak, J. and Tamir, A., "Vapor Equilibrium in Ternary Systems: Water--Formic Acid--Acetic Acid and Water--Acetic Acid--Propionic Acid", J. Chem. Eng. Data, 22(3), 253-260, 1977.

Zawisza, A. and Malesinska, B., "Solubility of Carbon Dioxide in Liquid Water and of Water in Gaseous Carbon Dioxide in the Range 0.2-5 MPa and at Temperatures up to 473 K", J. Chem. Eng. Data, 26(4), 388-391, 1981.

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