Extension and Application of the Pitzer Equation for Vapor-Liquid Equilibrium of Aqueous Electrolyte Systems with Molecular Solutes

The semi-empirical Pitzer equation for modeling equilibrium in aqueous electrolyte systems has been extended in a thermodynamically consistent manner to allow for molecular as well as ionic solutes. Under limiting conditions, the extended model reduces to the well-known Setschenow equation for the salting out effect of molecular solutes. To test the validity of the model, correlations of vapor-liquid equilibrium data were carried out for three systems: the hydrochloric acid aqueous solution at 298.15°K and concentrations up to 18 molal; the NH_3-CO_2 aqueous solution studied by Van Krevelen et al. (1949) at 293.15°K; and the K_2CO_3-CO_2 aqueous solution of the Hot Carbonate Process with temperatures from 343.15°K to 413.15°K and concentrations up to 40 weight percent equivalent potassium carbonate. The success of the correlations suggests the validity of the model for aqueous electrolyte systems of industrial interest.

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SCOPE

The use of modern process simulators for analysis and design of processes involving electrolytes has been greatly limited by the lack of adequate correlations for electrolyte thermodynamics. For most systems of industrial importance, empirical correlations are applicable only to one particular system, over a limited range of conditions. The empirical correlations do not provide a framework for treating new systems or for extending the range of existing data, because the nonidealities have not been accounted for in a general and consistent manner.

Aqueous electrolyte systems are common in the chemical industry. One example of interest is the potassium carbonate aqueous solution used in the Hot Carbonate Process as the acid gas removal agent in coal conversion plants. The Hot Carbonate Process was developed by the U.S. Bureau of Mines as part of a program on the synthesis of liquid fuel from coal. It provides an economical chemical absorption process for removing large quantities of CO_2 from synthesis gases (Riesenfeld and Kohl 1974).

Knowledge of the equilibrium solubility of carbon dioxide in the potassium carbonate aqueous solution is essential to the design of the Hot Carbonate Process. A large amount of comprehensive physical data on the K_2CO_3-CO_2 aqueous solution system is available in the literature. However, due to inability to properly correlate electrolyte thermodynamics, empirical equations or nomographs of the vapor-liquid equilibrium data have been used as basic design tools (Bocard and Mayland 1962, Maddox and Burns 1967, Mapstone 1966, Wen 1971).

Recently, there have been a number of significant developments in the modeling of electrolyte behavior. Bromley (1973), Meissner and Tester (1972), Meissner and Kusik (1972), Pitzer and co-workers (1973a, 1973b, 1974, 1976), and Cruz and Renon (1978), presented models for calculating the mean ionic activity coefficients of many types of aqueous electrolytes. In addition, Edwards et al. (1975) proposed a thermodynamic framework to calculate equilibrium vapor-liquid compositions for aqueous solutions of one or more volatile weak electrolytes which involved activity coefficients of ionic species. Most recently, Beutier and Renon (1978) and Edwards et al. (1978) used simplified forms of the Pitzer equation to represent ionic activity coefficients.

The purposes of this study are to 1) reformulate the Pitzer equation in a more rigorous way, to obtain a thermodynamic model for aqueous electrolyte systems containing both ionic and molecular solutes, and 2) apply the model to various aqueous electrolyte systems encountered in industry to demonstrate its validity.

CONCLUSIONS AND SIGNIFICANCE

Extending Pitzer equation, a thermodynamic model for both ionic and molecular solutes in aqueous electrolyte systems is obtained. Model parameters include binary ion-ion interaction and difference parameters, ternary ion-ion interaction and difference parameters, salt-molecule interaction parameters or Setschenow constants, salt-salt difference parameters for molecular solute salting, and unsymmetric Margules parameters for molecule-molecule interactions. Like the Pitzer equation, the model is designed for convenient and accurate representation and to predict aqueous electrolyte systems, including mixtures with any number of molecular and ionic solutes.

With this model, vapor-liquid equilibrium data for three systems are correlated. Significant parameters in the model for each system of interest are identified by a preliminary order of magnitude analysis and adjusted in the vapor-liquid equilibrium data correlation. The results show satisfactory agreement between experimental equilibrium vapor pressure data and the correlations, and, therefore, suggest the validity of the model for aqueous electrolyte systems of industrial interest.

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Table 1. Expressions for Debye-Hückel Coefficient, Henry's Constants and Equilibrium Constants

$$A_\phi^{a} = -1.306568 + 0.1328238\mathrm{D}\text{-}1\,(T) - 0.3550803\mathrm{D}\text{-}4\,(T^2) + 0.3381968\mathrm{D}\text{-}7\,(T^3)$$

$$\ln H_{CO_2}^{a} = -8477.711\,(1/T) - 21.95743\ln(T) + 0.005780748\,(T) + 155.1699$$

$$\ln H_{NH_3}^{b} = -157.552\,(1/T) + 28.1001\ln(T) - 0.049227\,(T) - 149.006$$

$$PK_{HCl}^{c} = -3.8 \text{ (at } 298.15°\mathrm{K})$$

$$\ln K_{NH_3}^{b} = -3335.7\,(1/T) + 1.4971\ln(T) - 0.0370566\,(T) + 2.76$$

$$\ln K_{NH_2COO^-}^{b} = -8.6 + 2900\,(1/T)$$

$$\ln K_{CO_2}^{b} = -12092.1\,(1/T) - 36.7816\ln(T) + 235.482$$

$$\ln K_{HCO_3^-}^{b} = -12431.7\,(1/T) - 35.4819\ln(T) + 220.067$$

$$\ln K_{H_2O}^{b} = -13445.9\,(1/T) - 22.4773\ln(T) + 140.932$$

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[a] Correlated in this study.

[b] Obtained from Edwards et al. (1978).

[c] Obtained from Cruz and Renon (1978).

A molecular thermodynamic framework for vapor-liquid equilibrium of aqueous electrolyte systems containing both ionic and molecular solutes has been proposed by Edwards et al. (1975). Vapor pressures of ionic solutes are taken as negligible. The vapor-liquid equilibrium relationship for molecular solutes is

$$y_m\Phi_m P = m_m\gamma_m{}^* H_m{}^{(p_w{}^s)}\exp\frac{\overline{V}_m(P - p_w{}^s)}{RT} \qquad (1)$$

Similarly, the vapor-liquid equilibrium expression for the solvent, water, is

$$y_w\Phi_w P = a_w p_w{}^s \Phi_w{}^s \exp\frac{\overline{V}_w(P - p_w{}^s)}{RT} \qquad (2)$$

To correlate vapor-liquid equilibrium data using these expressions requires models for water activity and solute activity coefficients. From an expression for the excess Gibbs free energy of a system and its partial derivatives, all of the activities and activity coefficients of interest can be computed. The next several sections of this article are concerned with the excess Gibbs free energy of aqueous electrolyte systems.

THE PITZER EQUATION

In a continuing series of papers, Pitzer and his coworkers (1973*a*, 1973*b*, 1974) proposed a very useful semiempirical equation for the unsymmetric excess Gibbs free energy of aqueous electrolyte systems. The basic equation is

$$\frac{G^{ex}}{n_w RT} = f(I) + \sum_i\sum_j \lambda_{ij}(I)m_i m_j + \sum_i\sum_j\sum_k \mu_{ijk}m_i m_j m_k \qquad (3)$$

where i, j and k can be any solutes.

The function $f(I)$ expresses the effect of long-range electrostatic forces between ions. It takes into account the hard-core effects in Debye-Hückel theory, and is a function of ionic strength, temperature and solvent properties. The empirical form chosen by Pitzer for $f(I)$ is

$$f(I) = -A_\phi \frac{4I}{1.2}\ln(1 + 1.2\sqrt{I}) \qquad (4)$$

where A_ϕ is the usual Debye-Hückel constant for the osmotic coefficient. Values of the Debye-Hückel constant were tabulated as a function of temperature in Silvester and Pitzer's paper (1976) and these values have been correlated in this study as a cubic function of temperature. The correlation result is given in Table 1.

The parameters λ_{ij} are second virial coefficients giving the effect of short-range forces between solutes i and j; the parameters μ_{ijk} are corresponding third virial coefficients for the interaction of three solutes i, j, and k. The second virial coefficients for ion-ion interactions are a function of ionic strength. However, dependence of the third virial coefficients on ionic strength is neglected. The λ and μ matrices are taken to be symmetric, i.e., $\lambda_{ij} = \lambda_{ji}$, etc.

To make the basic Pitzer equation more useful for data correlation of aqueous strong electrolyte systems, Pitzer modified it by defining a new set of more directly observable parameters to represent certain combinations of the second and third virial coefficients. The modified Pitzer equation is

$$\frac{G^{ex}}{n_w RT} = f(I) + \sum_c\sum_{c'} m_c m_{c'}\left(\theta_{cc'} + \sum_a m_a\psi_{cc'a}\right) + \sum_a\sum_{a'} m_a m_{a'}\left(\theta_{aa'} + \sum_c m_c\psi_{aa'c}\right) + 2\sum_c\sum_a m_c m_a\left[B_{ca}(I) + \frac{\sum_c m_c Z_c}{\sqrt{Z_c Z_a}}C_{ca}\right] \qquad (5)$$

where c and c', a and a', and Z stand for cations, anions and absolute value of ionic changes respectively.

Essentially, the new parameters B and θ are binary ion-ion parameters and C and ψ ternary ion-ion parameters. The ion-ion interaction parameters, B and C, are characteristic of each aqueous single-electrolyte system and are determined by the properties of pure electrolytes. The ion-ion difference parameters, θ and ψ, are characteristic of each aqueous mixed-electrolyte system. They represent differences between the virial coefficients for interaction of unlike ions of the same sign from the average of interactions of like ions of the same sign. In Pitzer's derivation, the third virial coefficients for ternary interactions with all ions of the same sign were eliminated, as they were certain to be exceedingly small. The defining relations for B, C, θ, and ψ are

$$B_{ca}(I) = \lambda_{ca}(I) + \left(\frac{\nu_c}{2\nu_a}\right)\lambda_{cc}(I) + \left(\frac{\nu_a}{2\nu_c}\right)\lambda_{aa}(I) \qquad (6)$$

$$C_{ca} = \frac{3}{2\sqrt{\nu_c\nu_a}}(\nu_c\mu_{cca} + \nu_a\mu_{caa}) \qquad (7)$$

$$\theta_{cc'} = \lambda_{cc'}(I) - \left(\frac{Z_{c'}}{2Z_c}\right)\lambda_{cc}(I) - \left(\frac{Z_c}{2Z_{c'}}\right)\lambda_{c'c'}(I) \qquad (8)$$

$$\psi_{cc'a} = 6\mu_{cc'a} - \left(\frac{3Z_{c'}}{Z_c}\right)\mu_{cca} - \left(\frac{3Z_c}{Z_{c'}}\right)\mu_{c'c'a} \qquad (9)$$

The defining relations for $\theta_{aa'}$ and $\psi_{aa'c}$ are obtained from Equations (8) and (9) by replacing c with a and a with c.

Recognizing the ionic strength dependence of the effect of short range forces in binary interactions, Pitzer was able to develop an empirical relation for $B_{ca}(I)$. The expression for systems containing strong electrolytes with one or both ions univalent is

$$B_{ca}(I) = \beta_{ca}^{(0)} + \frac{\beta_{ca}^{(1)}}{2I}\left[1 - (1 + 2\sqrt{I}) \exp(-2\sqrt{I})\right] \tag{10}$$

Therefore, the adjustable parameters in the modified Pitzer equation are $\beta^{(0)}$, $\beta^{(1)}$, C, θ, and ψ. The modified Pitzer equation has been successfully applied to the available data for many pure aqueous electrolytes (Pitzer and Mayorga 1973) and mixed aqueous electrolytes (Pitzer and Kim 1974). The fit to the experimental data is within the probable experimental error up to molalities of 6.

Thus, the modified Pitzer equation appears to be a useful tool for the representation of aqueous electrolytes including mixed electrolytes. However, it can not be used in the form just presented to represent systems containing molecular solutes.

Hereafter, Equation (3) is referred to as the basic Pitzer equation and Equation (5) is called the Pitzer equation.

EXTENSION OF THE PITZER EQUATION

In most aqueous electrolyte systems of industrial interest, not only strong electrolytes but also weak ones and molecular nonelectrolytes are present. For example, in the Hot Carbonate Process, potassium carbonate and potassium bicarbonate are strong electrolytes, carbon dioxide is a weak electrolyte, and methane, carbon monoxide and hydrogen are molecular nonelectrolytes. Strong electrolytes dissociate completely to ionic solutes, and weak electrolytes dissociate partially to ionic solutes. A unified thermodynamic model for both ionic solutes and molecular solutes is required to model these kinds of systems. In the previous section, we discussed how Pitzer modified his basic equation for strong electrolyte solutes by introducing a set of new, observable parameters. In this study the same approach is adopted to include appropriate terms for molecular solutes.

To obtain an extended form of the Pitzer equation that applies to electrolyte systems with molecular solutes, the virial coefficients in the basic Pitzer equation for molecule-ion and molecule-molecule interaction must be considered. The contribution to the excess Gibbs free energy resulting from the presence of molecular solutes is

$$\begin{aligned}\left(\frac{G^{ex}}{n_w RT}\right)_{\text{molecule}} &= \sum_m \sum_{i \neq m} m_m m_i \left(2\lambda_{mi} + 6 \sum_j m_j \mu_{mij}\right) \\ &+ \sum_m \sum_{m'} m_m m_{m'} \left(\lambda_{mm'} + \sum_{m''} m_{m''} \mu_{mm'm''}\right)\end{aligned} \tag{11}$$

where the subscripts m, m' and m'' represent molecular solutes and i, j represent all solutes.

The new observable parameters for binary molecule-ion interactions, D and ω, are defined as follows.

$$D_{ca,m} = 2\left(\frac{\lambda_{cm}}{\nu_a} + \frac{\lambda_{am}}{\nu_c}\right) \Big/ \nu_c = D_{ac,m}\left(\frac{\nu_a}{\nu_c}\right) \tag{12}$$

$$\omega_{cc',m} = 2\left(\frac{\lambda_{cm}}{Z_c} - \frac{\lambda_{c'm}}{Z_{c'}}\right) \Big/ Z_{c'} \tag{13}$$

$$\omega_{aa',m} = 2\left(\frac{\lambda_{am}}{Z_a} - \frac{\lambda_{a'm}}{Z_{a'}}\right) \Big/ Z_{a'} \tag{14}$$

The parameters $D_{ca,m}$ are binary parameters representing the interactions between salt ca and molecular solute m in an aqueous single salt, single molecular solute system. Binary parameters $\omega_{cc',m}$ and $\omega_{aa',m}$ represent the differences between the interactions of a specific molecular solute with two unlike salts sharing one common anion or cation. Ternary molecule-ion virial coefficients are neglected in this study to simplify the extension.

It is interesting to note that the molecule-ion interaction contribution in Equation (11) is consistent with the well-known Setschenow equation. The Setschenow equation is used to represent the salting out effect of salts on molecular nonelectrolyte solutes, when the solubilities of the latter are small (Gordon 1975). The Setschenow equation is

$$\ln \gamma_m^* = k_{s,m} m_s \tag{15}$$

where $k_{s,m}$ is the Setschenow constant (a salt-molecule interaction parameter) and m_s is the molality of the salt. The D's are equivalent to the Setschenow constants and the ω's are equivalent to differences between Setschenow constants.

Approximate additivity of ionic contributions to the Setschenow constants is observed for inorganic salts (Gordon 1975). This suggests that third virial coefficients in Equation (11) for molecule-ion interactions can be neglected for inorganic salts. Salt mixtures involving organic ions, however, are non-additive in their salting out contributions. Therefore, neglecting ternary molecule-ion interactions can result in discrepancies for organic salt systems.

The third virial coefficients for molecule-molecule interactions can be taken as zero for aqueous systems containing molecular solutes at low concentration. The expression for molecule-molecule interaction contribution reduces to an unsymmetric two-suffix Margules model.

Summarizing the results of this section, the extended form of the Pitzer equation proposed in this study is

$$\begin{aligned}\frac{G^{ex}}{n_w RT} &= f(I) + \sum_c \sum_{c'} m_c m_{c'} \left(\theta_{cc'} + \sum_a m_a \psi_{cc'a}\right) \\ &+ \sum_a \sum_{a'} m_a m_{a'} \left(\theta_{aa'} + \sum_c m_c \psi_{aa'c}\right) \\ &+ 2 \sum_c \sum_a m_c m_a \left[B_{ca}(I) + \frac{\sum_c m_c Z_c}{\sqrt{Z_c Z_a}} C_{ca}\right] \\ &+ \sum_m \sum_{m'} m_m m_{m'} \lambda_{mm'} \\ &+ \sum_m \left(\sum_a D_{ca,m} m_m m_a - \sum_{c'} \omega_{cc',m} m_m m_{c'}\right)\end{aligned} \tag{16}$$

PREVIOUS APPLICATIONS

Recently, the Pitzer equation has been applied to model vapor-liquid equilibrium behavior of weak electrolyte systems by Beutier and Renon (1978) and Edwards et al. (1978). Their works are briefly discussed here.

Beutier and Renon considered the excess Gibbs free energy G^{ex} of aqueous electrolyte systems as the sum of three terms, corresponding to ion-ion, ion-molecule, and molecule-molecule interactions.

$$G^{ex} = G^{ex}_{\text{ion-ion}} + G^{ex}_{\text{ion-molecule}} + G^{ex}_{\text{molecule-molecule}} \qquad (17)$$

The Pitzer equation was used only for the ion-ion interaction contribution. The second virial coefficients for binary interactions between ions of the same sign were neglected. This eliminates θ in Equation (5) and simplifies $B_{ca}(I)$ to $\lambda_{ca}(I)$. Beutier and Renon also neglected all third virial coefficients except $\mu_{caa'}$ and $\mu_{cc'a}$, and they further assumed that

$$\mu_{caa'} = \frac{1}{2}\left(\mu_{caa} + \mu_{ca'a'}\right) \qquad (18\text{-}a)$$

$$\mu_{cc'a} = \frac{1}{2}\left(\mu_{cca} + \mu_{c'c'a}\right) \qquad (18\text{-}b)$$

which eliminates the difference parameters ψ for ternary interactions among univalent ions. Other ternary difference parameters were also taken to be zero.

Ion-molecule interactions were estimated using Debye-McAulay's electrostatic theory (Harned and Owen 1958). For the molecule-molecule interactions, binary and ternary interactions between two different molecules were neglected, but both second and third virial terms were retained for each individual molecular solute. The form of the excess Gibbs free energy equation used by Beutier and Renon can be written as

$$\frac{G^{ex}}{n_w RT} = f(I) + 2\sum_c\sum_a m_c m_a \left[\lambda_{ca}(I) + \frac{\sum_c m_c Z_c}{\sqrt{Z_c Z_a}}\, C_{ca}\right] + W_{el} + \sum_m \lambda_{mm} m_m^2 + \sum_m \mu_{mmm} m_m^3 \qquad (19)$$

where

$$C_{ca} = \frac{3}{2\sqrt{\nu_c \nu_a}}\left(\nu_c \mu_{cca} + \nu_a \mu_{caa}\right) \qquad (20)$$

with an additional assumption that

$$\mu_{cca} = \mu_{caa} \qquad (21)$$

W_{el} in Equation (19) is the Debye-McAulay electrostatic work term used for the ion-molecule interaction contribution.

Beutier and Renon applied Bromley's idea (1973) on approximating interaction parameters as the sum of values for individual ions. A correlation with partial molar entropy of ions at infinite dilution was used to obtain $\lim_{I\to 0} \lambda_{ca}(I)$ $(= \beta^{(0)}_{ca} + \beta^{(1)}_{ca})$. Values of C^{ϕ}_{ca} (which are twice the values of C_{ca}) were used as the only adjustable parameters to fit the vapor-liquid equilibrium data of the three weak electrolyte systems considered by them.

Unlike Beutier and Renon, Edwards et al. (1978) adopted Equation (10) for all ion-ion, ion-molecule, and molecule-molecule binary virial coefficients of the basic Pitzer equation. Ternary interactions of all types were totally neglected. Model parameters were further eliminated by excluding the second virial coefficients for binary interactions between ions of the same sign and parameters $\beta^{(1)}$ for binary interactions with one or both solutes molecular. The parameters $\beta^{(0)}$ for binary interactions with both solutes molecular are the same as the unsymmetric Margules parameters used in this study for molecule-molecule interactions.

Edwards et al. also used the ideas of Bromley (1973) on additivity of interaction parameters of individual ions and correlation between individual ion and partial molar entropy of ions at infinite dilution. The idea of additivity of interaction parameters of specific ions was extended to molecule-ion interaction parameters. The form of the excess Gibbs free energy equation used by Edwards et al. is

$$\frac{G^{ex}}{n_w RT} = f(I) + 2\sum_c\sum_a m_c m_a \left\{\beta^{(0)}_{ca} + \frac{\beta^{(1)}_{ca}}{2I}\left[1 - (1 + 2\sqrt{I})\exp(-2\sqrt{I})\right]\right\} + \sum_m\sum_i \beta^{(0)}_{mi} m_m m_i \qquad (22)$$

Both Beutier and Renon and Edwards et al. assumed the temperature dependence of the ion-ion interaction parameters to be negligible. Molecule-ion and molecule-molecule interaction parameters were treated as temperature dependent.

DISCUSSION OF PREVIOUS APPLICATIONS

One new and two previous expressions for the excess Gibbs free energy of aqueous electrolyte systems have been presented. They all incorporate, in different ways, the Pitzer equation. In this section we point out some limitations of the previous approaches that do not apply to the new approach.

First, theoretical aspects of the physical chemistry of aqueous electrolyte solutions, including salting out effects on non-electrolytes, are still in a development stage. Although many theories have been proposed in the literature, none is quantitatively satisfactory. Adopting Debye-McAulay's electrostatic theory for molecular-ion interactions, Beutier and Renon (1978) note, for example, that their model does not seem reliable to represent solutions with high molalities of undissociated ammonia.

Second, the Pitzer equation is a virial-expansion type equation and semi-empirical in nature. The exact meaning and interrelationships between the adjustable parameters are not fully understood. As shown in the results of Beutier and Renon (1978) and Edwards et al. (1978), estimating interaction parameters from ionic partial molar entropy at infinite dilution can only give acceptable results for aqueous electrolyte systems at low ionic strength. A more precise way to estimate the parameters is required for the high ionic strength solutions often encountered in industrial processes.

Third, Brönsted's principle of specific ion interaction is the basis for assuming that interactions among ions of the same sign can be neglected. While both Beutier and Renon and Edwards et al. accept Brönsted's idea, the principle of specific ion interaction has been disproved, as stated in Pitzer's paper (1973). Thus, difference parameters should not be neglected for systems of high ionic strength.

Fourth, ternary ion-ion interaction and difference parameters in the Pitzer equation are significant for systems of high ionic strength. For example, the K_2CO_3-CO_2 aqueous solution system employed in the Hot Carbonate Process is a highly concentrated one. The ionic strength can be as high as 18 molal for solutions of 40% equivalent potassium carbonate at a conversion of 100%. Further, ternary parameters are kept as adjustable parameters in Pitzer's paper (1973*a*) for data fitting, unless ionic strength is less than 2 molality. Thus, ternary ion-ion interaction parameters should not be neglected without an analysis of the particular system of interest.

LIQUID PHASE EQUATIONS

For aqueous systems containing electrolytes with one or both ions univalent, expressions for activity of water, activity coefficients of ionic solutes and activity coefficients of molecular solutes can be derived from the extended Pitzer equation as follows with the assumption that θ, λ_{mm}, D and ψ are ionic strength independent.

$$\begin{aligned}
\ln a_w &= \ln x_w + \ln \gamma_w \\
&= \ln\left(\frac{55.55}{55.55 + \sum\limits_i m_i}\right) + \frac{(\partial G^{ex}/\partial n_w)}{55.55\,RT} \\
&= \ln\left(\frac{55.55}{55.55 + \sum\limits_i m_i}\right) - \frac{(\phi - 1)\sum\limits_i m_i}{55.55}
\end{aligned} \tag{23}$$

$$\begin{aligned}
(\phi - 1)\sum_i m_i = {} & - A_\phi\left(\frac{2I^{3/2}}{1 + 1.2\sqrt{I}}\right) \\
& + 2\sum_c\sum_a m_c m_a \left[\beta^{(0)}_{ca} + \beta^{(1)}_{ca}\exp(-2\sqrt{I}) + \frac{2\sum\limits_c m_c Z_c}{\sqrt{Z_c Z_a}} C_{ca}\right] \\
& + \sum_c\sum_{c'} m_c m_{c'}\left(\theta_{cc'} + \sum_a m_a \psi_{cc'a}\right) \\
& + \sum_a\sum_{a'} m_a m_{a'}\left(\theta_{aa'} + \sum_c m_c \psi_{aa'c}\right) \\
& + \sum_m\sum_{m'} m_m m_{m'} \lambda_{mm'} \\
& + \sum_m \left(\sum_a D_{ca,m} m_m m_a - \sum_{c'} \omega_{cc',m} m_m m_{c'}\right)
\end{aligned} \tag{24}$$

$$\begin{aligned}
\ln\gamma_a{}^{*} = {} & \frac{1}{n_w RT}\left(\frac{\partial G^{ex}}{\partial m_a}\right) \\
= {} & - A_\phi Z_a{}^2\left[\frac{\sqrt{I}}{1 + 1.2\sqrt{I}} + \frac{2}{1.2}\ln(1 + 1.2\sqrt{I})\right] \\
& + 2\sum_c m_c\left\{\beta^{(0)}_{ac} + \frac{\beta^{(1)}_{ac}}{2I}[1 - (1 + 2\sqrt{I})\exp(-2\sqrt{I})]\right\} \\
& + 2\sum_{a'} m_{a'}\theta_{aa'} \\
& - \frac{Z_a{}^2}{2I^2}\sum_c\sum_{a'} m_c m_{a'} \beta^{(1)}_{ca'}[1 - (1 + 2\sqrt{I} + 2I)\exp(-2\sqrt{I})] \\
& + \sum_c\sum_{a'} m_c m_{a'}(6C_{ca'} + 6\psi_{caa'}) \\
& + \sum_m m_m D_{ca,m}
\end{aligned} \tag{25}$$

$$\begin{aligned}
\ln\gamma_m{}^{*} &= \frac{1}{n_w RT}\left(\frac{\partial G^{ex}}{\partial m_m}\right) \\
&= 2\sum_{m'} m_{m'}\lambda_{mm'} + \sum_a D_{ca,m} m_a - \sum_{c'} \omega_{cc',m} m_{c'}
\end{aligned} \tag{26}$$

The equations for water activity and solute activity coefficients must be solved simultaneously with three other types of equations in order to calculate values for the activity and activity coefficients. They are: the equation of charge balance, equations of elemental mass balance and equations of chemical equilibrium. The equation of charge balance is

$$\sum_c m_c Z_c = \sum_a m_a Z_a \tag{27}$$

The equations of elemental mass balance and chemical equilibrium depend upon the system under consideration. In general, equations of elemental mass balance are

$$\sum_j A_{ej} m_j = b_e \tag{28}$$

For a reaction $m = i + j$, equations of chemical equilibrium are

$$K_m(T) = \frac{a_i \cdot a_j}{a_m} = \frac{m_i \cdot \gamma_i{}^{*} \cdot m_j \cdot \gamma_j{}^{*}}{m_m \cdot \gamma_m{}^{*}} \tag{29}$$

Expressions for the equilibrium constants $K(T)$ are required.

In this study, the equations for the liquid phase were solved with a general non-linear equation solver using a modified Gauss-Newton algorithm.

VAPOR-LIQUID EQUILIBRIUM DATA CORRELATION

Data correlations were carried out for three systems with quite different characteristics to illustrate the range of application of the extended Pitzer equation. Since the extended Pitzer equation reduces to the Pitzer equation for aqueous strong electrolyte systems and is consistent with the Setschenow equation for molecular non-electrolytes in aqueous electrolyte systems, the main interest here is aqueous systems with weak electrolytes or partially dissociated strong electrolytes. The three systems considered are 1) hydrochloric acid aqueous solution at 298.15°K, 2) NH_3-CO_2 aqueous solution at 293.15°K, and 3) the K_2CO_3-CO_2 aqueous solution used in the Hot Carbonate Process. Although dilute hydrochloric acid is normally assumed to be a strong electrolyte in water, it is actually a partially dissociated electrolyte and is so treated here.

The parameters in the proposed model are numerous if several solutes are present. In practice, the characteristics of each system may be studied to determine which parameters should be included and which can be assumed negligible. As shown in Pitzer and Mayorga's results (1973), $\beta^{(0)}$ and $\beta^{(1)}$ are of the order of 0.1; C is of the order of 0.001. Also, D (Gordon 1975) and λ_{mm} (Edwards et al. 1978) are of the order of 0.1. Although only a few data are available for θ and ψ (Pitzer and Kim 1974) and no data are available for ω, it should be reasonable to expect that θ, ψ, and ω are about of the same order of magnitude as $\beta^{(0)}$, C, and D, respectively. For systems of low concentrations, ternary parameters may be unnecessary. If concentrations of molecular solutes are exceedingly small,

TABLE 2. REPRESENTATION OF VAPOR-LIQUID EQUILIBRIUM OF HCl-H_2O SYSTEM (VEGA AND VERA, HCl-H_2O DATA AT 298.15°K)

(gmole/kg of solvent) m_{HCl}	y^{exp}_{HCl}	y^{calc}_{HCl}	$(N/m^2) \times 10^{-3}$ p_{exp}	p_{calc}
3.045	0.0003	0.0002	2.66_6	2.68_8
4.462	0.0018	0.0016	2.40_0	2.40_2
6.017	0.0095	0.0090	2.08_0	2.08_0
6.854	0.022	0.022	1.92_0	1.92_0
7.735	0.051	0.051	1.77_3	1.78_4
8.656	0.116	0.116	1.72_0	1.70_7
9.635	0.243	0.246	1.76_0	1.76_1
10.67	0.446	0.449	2.10_6	2.10_0
11.75	0.668	0.667	3.01_3	3.02_3
12.90	0.836	0.830	5.18_6	5.17_6
14.13	0.928	0.921	9.85_2	9.89_2
15.42	0.970	0.963	19.5_2	19.4_0
16.81	0.987	0.982	37.4_1	37.6_1
18.28	0.994	0.991	69.0_5	68.9_5

	$\overset{(0)}{\beta}_{HCl}$	$\overset{(1)}{\beta}_{HCl}$	C_{HCl}	$D_{HCl,HCl}$	$\lambda_{HCl,HCl}$	H_{HCl}	$\delta P/P$	δy_{HCl}
a)	0.2266	1.1635	−0.0011	0.2898	0.1146	0.651D-3	0.44	0.35
b)							0.99	0.34

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[a] This work.

[b] Cruz and Renon (1978).

the ion-molecule interaction contribution to excess Gibbs free energy can be negligible. In addition, $\beta^{(1)}$ can be estimated as functions of $\beta^{(0)}$ as a convenient approximation as suggested by Pitzer and Mayorga (1973). The expressions adopted in this study are

$$\beta^{(1)}_{1\text{-}1} = 0.125 + 1.172\beta^{(0)}_{1\text{-}1} \qquad (30\text{-}a)$$

$$\beta^{(1)}_{1\text{-}2} = 0.947 + 2.021\beta^{(0)}_{1\text{-}2} \qquad (30\text{-}b)$$

For each system, a suitable sum of squares objective function is chosen, depending on the form of the available data. This includes a choice of the variables to be fit and a choice of weighting. Adjustable parameters are varied, using a Gauss-Newton algorithm, to minimize the objective function. Each functional evaluation during data correlation requires a solution of the liquid phase equations discussed in the previous section. To save computer time, previous calculated results from the solution of the liquid phase equations are saved and used as initial guesses for the next solution of the liquid phase equations.

HCl AQUEOUS SOLUTION SYSTEM

Complete experimental data (t, p, x, y) for hydrochloric acid concentration up to 18 molal were obtained from Vega and Vera (1976). The temperature of the experimental data, 298.15°K, is below the critical point of hydrogen chloride. In the gas phase, hydrogen chloride and water are present. In the liquid phase, there are hydrogen, hydroxide and chloride ions. The following reactions occur in the liquid phase.

$$HCl \rightleftharpoons H^+ + Cl^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

The adjustable parameters of the extended Pitzer equation for this system are $\overset{(0)}{\beta}_{HCl}$, $\overset{(1)}{\beta}_{HCl}$, C_{HCl}, $D_{HCl,HCl}$ and $\lambda_{HCl,HCl}$. In addition, the Henry's constant for hydrogen chloride was treated as an adjustable parameter. Ideal gas behavior was assumed for the vapor phase, since the system pressures never exceed atmospheric pressure.

The sum of squares objective function used for data correlation was

$$S = \sum_{i=1}^{n} (y^{calc}_{HCl,i} - y^{exp}_{HCl,i})^2 + \sum_{i=1}^{n} \left(\frac{P_i^{calc} - P_i^{exp}}{P_i^{exp}} \right)^2 \qquad (31)$$

The results of the correlation are given in Table 2.

The same data was previously correlated with the same objective function by Cruz and Renon (1978), using a model for solutions of a partially or completely dissociated electrolyte in an undissociated solvent. This model was not based on the Pitzer equation. It assumes a known dissociation constant and has six adjustable parameters. The Nothnagel et al. (1973) correlation is used to represent the vapor phase, and the fugacity coefficients differed from unity by less than 1%. Their results are compared with those of the present work in Table 2.

To use the extended Pitzer equation for the subcritical solute hydrogen chloride it was necessary to introduce a Henry's constant, defined as the saturated vapor pressure of a subcritical molecular solute, multiplied by 55.55, times the symmetric activity coefficient of that solute at infinite dilution in the binary system with water. This approach is suitable as long as the subcritical component concentration is not very high. When this is not the case, a more suitable way to handle subcritical molecular solutes would be to consider the molecular solutes and the water as a mixed solvent. In principle, the Pitzer equation can be modified for mixed solvent electrolyte systems. However, practical application of the Pitzer equation involves empirical expressions for interactions among solutes in the solvent, water; required empirical expressions are not available for mixed solvent. The present

TABLE 3. REPRESENTATION OF VAPOR-LIQUID EQUILIBRIUM OF NH_3-CO_2 AQUEOUS SOLUTION SYSTEM (VAN KREVELEN ET AL., NH_3-CO_2-H_2O AT 293.15°K)

		$(N/m^2) \times 10^{-3}$			$(N/m^2) \times 10^{-3}$		
Normal A	R	$\overset{\text{exp}}{p_{NH_3}}$	calc p_{NH_3} this work	Van Krevelen	$\overset{\text{exp}}{p_{CO_2}}$	calc p_{CO_2} this work	Van Krevelen
1.96	0.347	1.25	1.20	1.16	0.111	0.116	0.133
1.99	0.246	1.73	1.70	1.61	0.033	0.038	0.044
2.01	0.271	1.67	1.59	1.49	0.051	0.051	0.057
1.00	0.298	0.757	0.714	0.720	0.160	0.065	0.068
1.00	0.48	0.393	0.389	0.387	0.367	0.368	0.373
1.00	0.59	0.231	0.247	0.253	1.05	0.97	1.00
1.00	0.685	0.165	0.158	0.160	2.35	2.21	2.27
1.00	0.89	0.040	0.041	0.040	15.28	15.77	15.33
2.00	0.415	0.941	0.929	0.907	0.307	0.242	0.280
2.00	0.56	0.484	0.452	0.467	1.13	1.18	1.20
2.00	0.743	0.157	0.158	0.167	6.94	7.50	6.67
2.00	0.956	0.023	0.024	0.023	89.17	85.57	99.99

$\beta^{(0)}_{NH_4HCO_3}$: −0.0275
$\beta^{(0)}_{(NH_4)_2CO_3}$: 0.8668
$\beta^{(0)}_{NH_4NH_2COO}$: 0.0155
$D_{NH_4HCO_3,NH_3}$: −0.0285
$D_{(NH_4)_2CO_3,NH_3}$: 0.1452
$D_{NH_4NH_2COO,NH_3}$: 0.1704

$S = 0.4625$ (excluding θ's)
$S = 0.4033$ (including θ's)

A: total ammonia concentration
R: ratio of total carbon dioxide concentration vs. total ammonia concentration

approach should be satisfactory for systems containing subcritical molecular solutes at low concentrations.

NH_3-CO_2 AQUEOUS SOLUTION SYSTEM

The data reported by Van Krevelen et al. (1949) at 293.15°K are used for data correlation. Ammonia, carbon dioxide and water are present in the vapor phase. In the liquid phase, hydrogen, hydroxide, ammonium, carbonate, bicarbonate, and carbamate ions are present in addition to ammonia and carbon dioxide molecular solutes. The following reactions occur in the liquid phase

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$$

$$HCO_3^- \rightleftharpoons CO_3^= + H^+$$

$$NH_3 + HCO_3^- \rightleftharpoons NH_2COO^- + H_2O$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

All ternary parameters are dropped from the proposed model, since the highest ammonia concentration is 2 normal. The three Setschenow constants for carbon dioxide are assumed negligible because ammonia is always in excess in Van Krevelen's data and carbon dioxide is almost completely dissociated. The ion-ion interaction parameters for salts containing hydrogen ion or hydroxide ion are assumed negligible. The system is a buffer solution and both hydrogen ion concentration and hydroxide ion concentration are small, compared to those of other solutes. Also excluded are the three binary ion-ion difference parameters because they are significant only where the concentrations of bicarbonate, carbonate, and carbamate ions are large compared to the concentrations of ammonia and ammonium ion. The remining adjustable parameters are the binary ion-ion interaction parameters and the Setschenow constants: $\beta^{(0)}_{NH_4HCO_3}$, $\beta^{(0)}_{(NH_4)_2CO_3}$, $\beta^{(0)}_{NH_4NH_2COO}$, $D_{NH_4HCO_3,NH_3}$, $D_{(NH_4)_2CO_3,NH_3}$, and $D_{NH_4NH_2COO,NH_3}$.

The equilibrium constants and Henry's constants used are given in Table 1. The Henry's constant for ammonia and the equilibrium constants are reported by Edwards et al. (1978) and Tsonopoulos (1976). Henry's constants for carbon dioxide were correlated from the work of Ellis and Golding (1963). They reported the solubility of CO_2 in water for temperatures up to 573.15°K. At the system pressures, vapor phase fugacity coefficients as predicted by the Nakamura et al. (1976) correlation are sufficiently close to unity to be neglected.

The sum of squares objective function used for data correlation was

$$S = \sum_{i=1}^{n} \left(\frac{\overset{\text{calc}}{p_{NH_3,i}} - \overset{\text{exp}}{p_{NH_3,i}}}{p^{\text{exp}}_{NH_3,i}} \right)^2 + \sum_{i=1}^{n} \left(\frac{\overset{\text{calc}}{p_{CO_2,i}} - \overset{\text{exp}}{p_{CO_2,i}}}{p^{\text{exp}}_{CO_2,i}} \right)^2 \quad (32)$$

The correlation results and calculated adjustable parameters are shown in Table 3, along with the correlated partial pressures given by Van Krevelen et al. (1949). In their model, activity coefficients were not taken into consideration and the correlation parameters were dependent on the ionic strength of the solutions. The mean of the absolute values of the relative deviations of partial pressure of carbon dioxide is 11% and for ammonia is 3.9%.

Three Setschenow constants dominate in the ammonia-rich region and the three ion-ion interaction parameters dominate in the ammonia-lean region. When the three binary ion-ion difference parameters were included in the correlation, the minimum sum of squares dropped only slightly. This tends to support the conclusion that these parameters are not significant.

The same system and the same least squares objective function have been studied by Beutier and Renon (1978). The ion-molecule interaction parameters were estimated using Debye-McAulay's electrostatic theory. The binary ion-ion interaction parameters were estimated from correlations with partial molar entropy of ions at infinite dilution. Two ternary ion-ion interaction parameters, $C^{\phi}_{NH_4HCO_3}$ and $C^{\phi}_{NH_4NH_2COO}$ were adjusted. The mean of the absolute values of the relative deviations of partial pressure of carbon dioxide was 16% and for ammonia was 5%. Edwards et al. (1978) also studied vapor-liquid equilibrium of a NH_3-CO_2 aqueous system at 373.15°K, using experimental data from Otsuka, et al. (1960). However, the accuracy of the fit was not reported quantitatively.

K_2CO_3-CO_2 AQUEOUS SOLUTION SYSTEM

The equilibrium data obtained by Tosh and coworkers (1959) were used for data correlation. The data have a temperature range from 343.15°K to 413.15°K, and a range from 20 to 40% equivalent concentration of potassium carbonate. "Equivalent concentration of potassium carbonate" refers to a solution in which only potassium carbonate and water are present. Thus, a 40% equivalent solution means a solution containing 40 g of potassium carbonate and 60 g of water, if all the bicarbonate in the system were converted back to carbonate. These equilibrium data cover the operating range of the Hot Carbonate scrubbing system for removing carbon dioxide from a gas mixture.

The stoichiometric equation for the carbon dioxide absorption by the potassium carbonate aqueous solution is

$$K_2CO_3 + CO_2 + H_2O \rightleftharpoons 2KHCO_3$$

In the gas phase, carbon dioxide and water molecules are present. In the liquid phase, there are two molecular solutes, water and carbon dioxide, and five ionic solutes: potassium ion, hydrogen ion, hydroxide ion, bicarbonate ion and carbonate ion. The three chemical equilibrium reactions occurring in the liquid phase are dissociation of carbonic acid, bicarbonate ion and water, respectively.

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

$$HCO_3^- \rightleftharpoons CO_3^= + H^+$$

$$H_2O \rightleftharpoons OH^- + H^+$$

Vapor phase fugacity coefficients were calculated using the model of Nakamura et al. (1976). Since no suitable model is available for partial molar volume, $\overline{V}$, it was approximated by the infinite dilute volume, $\overline{V}^{\infty}$. The correlation of Brelvi and O'Connell (1972) was used to estimate the latter.

The sum of squares objective function used for data correlation was

$$S = \sum_{i=1}^{n}\left(\frac{p^{calc}_{H_2O,i} - p^{exp}_{H_2O,i}}{0.1p^{exp}_{H_2O,i}}\right)^2 + \sum_{i=1}^{n}\left(\frac{p^{calc}_{CO_2,i} - p^{exp}_{CO_2,i}}{68.95 + 0.05p^{exp}_{CO_2,i}}\right)^2 \qquad (33)$$

TABLE 4. ORDER OF MAGNITUDE ANALYSIS FOR THE ADJUSTABLE PARAMETERS OF THE K_2CO_3-CO_2 AQUEOUS SOLUTION SYSTEM

Parameters	Contribution from molality of the corresponding solutes in equation (16)	Treatment
$\beta^{(0)}_{KOH}$	$<10^{-1}$ m^2	0.0
$\beta^{(0)}_{KHCO_3}$	0-77 m^2	adjusted
$\beta^{(0)}_{K_2CO_3}$	0-55 m^2	adjusted
$\beta^{(0)}_{HHCO_3}$	$<10^{-8}$ m^2	0.0
$\beta^{(0)}_{H_2CO_3}$	$<10^{-8}$ m^2	0.0
θ_{K^+,H^+}	$<10^{-8}$ m^2	0.0
θ_{OH^-,HCO_3^-}	$<10^{-1}$ m^2	0.0
$\theta_{OH^-,CO_3^=}$	$<10^{-1}$ m^2	0.0
$\theta_{HCO_3^-,CO_3^=}$	0-35 m^2	adjusted
C_{KOH}	$\simeq 1$ m^3	0.0
C_{KHCO_3}	0-800 m^3	adjusted
$C_{K_2CO_3}$	0-600 m^3	adjusted
C_{HHCO_3}	$<10^{-8}$ m^3	0.0
$C_{H_2CO_3}$	$<10^{-8}$ m^3	0.0
$\psi_{K^+,H^+,CO_3^=}$	$<10^{-7}$ m^3	0.0
ψ_{K^+,H^+,OH^-}	$<10^{-10}$ m^3	0.0
ψ_{K^+,H^+,HCO_3^-}	$<10^{-7}$ m^3	0.0
ψ_{K^+,HCO_3^-,OH^-}	<1 m^3	0.0
$\psi_{K^+,OH^-,CO_3^=}$	$<10^{-7}$ m^3	0.0
$\psi_{K^+,HCO^-,CO_3^=}$	0-385 m^3	adjusted
ψ_{H^+,HCO_3^-,OH^-}	$<10^{-10}$ m^3	0.0
$\psi_{H^+,HCO_3^-,CO_3^=}$	$<10^{-7}$ m^3	0.0
$\psi_{H^+,OH^-,CO_3^=}$	$<10^{-10}$ m^3	0.0
D_{KOH,CO_2}	$<10^{-3}$ m^2	0.0
D_{KHCO_3,CO_2}	<1 m^2	0.0
$D_{K_2CO_3,CO_2}$	<1 m^2	0.0
$\omega_{K^+H^+,CO_2}$	$<10^{-10}$ m^2	0.0
λ_{CO_2,CO_2}	$<10^{-2}$ m^2	$-0.4922 + 149.20$ $(1/T)$*

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* Obtained from Edwards, et al. (1978).

As shown in Table 4, there are many adjustable parameters in the proposed model for the K_2CO_3-CO_2 aqueous solution system. However, the approximate ranges of molalities of solutes in the K_2CO_3-CO_2 aqueous solution system for the Hot Carbonate Process are known to be

m_{K^+} : 3 − 11m $\qquad m_{HCO_3^-}$: 0 − 7 m

m_{H^+} : $< 10^{-9}$ m $\qquad m_{CO_3^=}$: 0 − 5 m

m_{OH^-} : $< 10^{-2}$ m $\qquad m_{CO_2}$: < 0.1 m

From Table 4 the parameters that should be considered in the vapor-liquid equilibrium data correlation of the system are $\beta^{(0)}_{KHCO_3}$, $\beta^{(0)}_{K_2CO_3}$, $\theta_{HCO_3^-,CO_3^=}$, C_{KHCO_3}, $C_{K_2CO_3}$, and $\psi_{K^+,HCO_3^-,CO_3^=}$. Other parameters were assumed to be zero unless numerical values were available from other sources.

Before fitting the data obtained by Tosh, $\beta^{(0)}_{KHCO_3}$, $\beta^{(0)}_{K_2CO_3}$, and $\theta_{HCO_3^-,CO_3^=}$ were adjusted to fit experimental activity coefficient data for bicarbonate and carbonate ions at ionic strength less than 0.5 molal at 298.15°K (Walker 1927). The inclusion of θ as adjustable parameters improves the data fitting significantly, as shown in Table 5.

TABLE 5. COMPARISON BETWEEN REPRESENTATIONS OF DATA† ON $\ln \overset{\bullet}{\gamma}_{HCO_3^-}$ AND $\ln \overset{\bullet}{\gamma}_{CO_3^=}$ (WALKER ET AL., 1927), A) WITHOUT θ, B) WITH θ

	$\overset{(0)}{\beta}_{KHCO_3}$	$\overset{(0)}{\beta}_{K_2CO_3}$	$\theta_{HCO_3^-,CO_3^=}$	$\sigma_{\ln\gamma^*}$	# of data points
a)	−0.4398	0.0125	—	0.0469	16
b)	0.1695	0.4530	−0.0724	0.0077	16

† Data are interpolated or taken directly from Walker, et al. (1927). Sum of squares objective function is

$$S = \sum_{i=1}^{n} \left(\ln \overset{\text{calc}}{\overset{\bullet}{\gamma}}_{HCO_3^-} - \ln \overset{\text{exp}}{\overset{\bullet}{\gamma}}_{HCO_3^-} \right)^2 + \sum_{i=1}^{n} \left(\ln \overset{\text{calc}}{\overset{\bullet}{\gamma}}_{CO_3^=} - \ln \overset{\text{exp}}{\overset{\bullet}{\gamma}}_{CO_3^=} \right)^2$$

Also, θ is of the same order of magnitude as $\beta^{(0)}$. This implies that Brönsted's principle of specific ion interaction is not valid for the system.

The inclusion of ternary ion-ion interaction parameters in the fitting of Tosh's data is justified by the comparison between representations of the data, as shown in Table 6. This table also shows that the six parameters selected from Table 4 are the significant ones. Adding less significant parameters does not give better representation of the data. As further justification for the inclusion of ternary ion-ion interaction parameters, an examination of the fitted parameter correlation matrix in Table 7 shows the ternary parameters to be substantially statistically independent of the binary parameters. It is also interesting

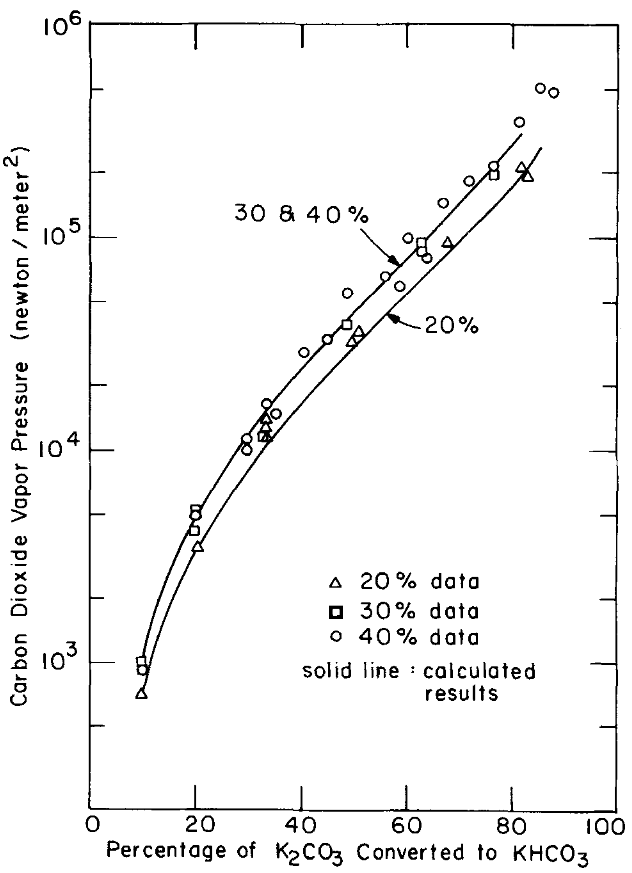

Figure 1. Equilibrium pressure of carbon dioxide at 383.15°K over 20, 30 and 40% equivalent potassium carbonate solution.

TABLE 6. COMPARISON OF REPRESENTATIONS OF TOSH'S DATA* WITH A) 3 PARAMETERS, B) 6 PARAMETERS, C) 9 PARAMETERS

	$\overset{(0)}{\beta}_{KHCO_3}$	$\overset{(0)}{\beta}_{K_2CO_3}$	$\theta_{HCO_3^-,CO_3^=}$	C_{KHCO_3}	$C_{K_2CO_3}$	$\psi_{K^+,HCO_3^-,CO_3^=}$	D_{KHCO_3,CO_2}	$D_{K_2CO_3,CO_2}$	S
a)	0.0466	0.2076	−0.0189						11.68
b)	0.0722	0.2349	−0.0219	0.0026	−0.0092	0.0040			8.50
c)	0.0725	0.2349	−0.0231	0.0025	−0.0091	0.0039	0.01156	0.3380	8.46

* 383.15°K, 40 data points.

TABLE 7. PARAMETER CORRELATION MATRIX OF REPRESENTATION OF TOSH'S DATA AT 383.15°K

	$\overset{(0)}{\beta}_{KHCO_3}$	$\overset{(0)}{\beta}_{K_2CO_3}$	$\theta_{HCO_3^-,CO_3^=}$	C_{KHCO_3}	$C_{K_2CO_3}$	$\psi_{K^+,HCO_3^-,CO_3^=}$
$\overset{(0)}{\beta}_{KHCO_3}$	1.0000					
$\overset{(0)}{\beta}_{K_2CO_3}$	0.9895	1.0000				
$\theta_{HCO_3^-,CO_3^=}$	0.0643	0.0486	1.0000			
C_{KHCO_3}	−0.5157	−0.5219	−0.1685	1.0000		
$C_{K_2CO_3}$	0.3588	0.3941	0.1344	−0.9675	1.0000	
$\psi_{K^+,HCO_3^-,CO_3^=}$	−0.4338	−0.4488	−0.3858	0.9669	−0.9556	1.0000

TABLE 8. REPRESENTATION OF VAPOR-LIQUID EQUILIBRIUM OF K_2CO_3-CO_2-H_2O SYSTEM A) 343.15°K, B) 363.15°K, C) 383.15°K, D) 403.15°K, E) ALL TEMPERATURES (DATA FROM TOSH ET AL.)

	$\overset{(0)}{\beta}_{KHCO_3}$	$\overset{(0)}{\beta}_{K_2CO_3}$	$\theta_{HCO_3^-,CO_3^=}$	C_{KHCO_3}	$C_{K_2CO_3}$	$\psi_{K^+,HCO_3^-,CO_3^=}$	# of data points	S
a)	0.0689	0.2669	−0.0742	0.0084	−0.0187	0.0119	18	3.61
b)	0.0978	0.3071	−0.0441	0.0093	−0.0221	0.0118	17	5.22
c)	0.0722	0.2349	−0.0219	0.0026	−0.0092	0.0040	40	8.50
d)	0.0879	0.2759	−0.0704	0.0057	−0.0124	0.0082	32	8.94
e)	0.0688	0.2560	−0.0267	0.0076	−0.0159	0.0084	107	67.66

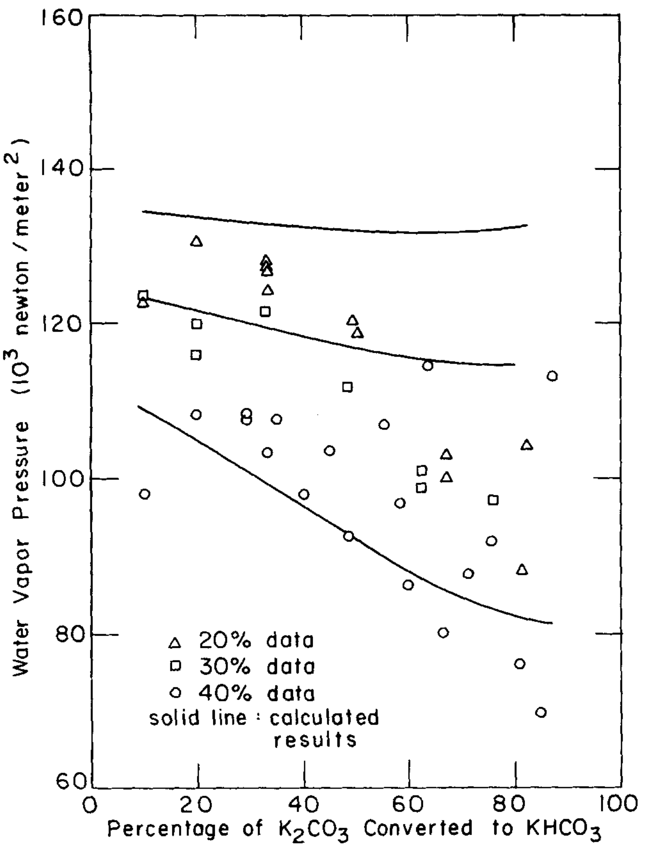

Figure 2. Equilibrium pressure of water at 383.15°K over 20, 30 and 40% equivalent potassium carbonate solution.

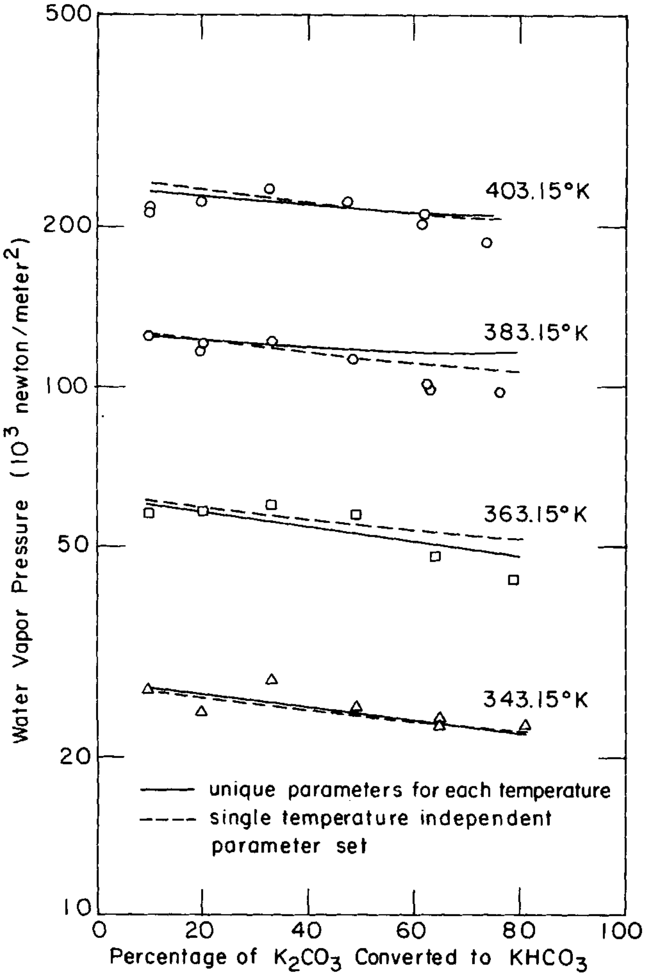

Figure 4. Equilibrium pressure of water of 30% equivalent potassium carbonate solution, at 343.15, 363.15, 383.15 and 403.15°K.

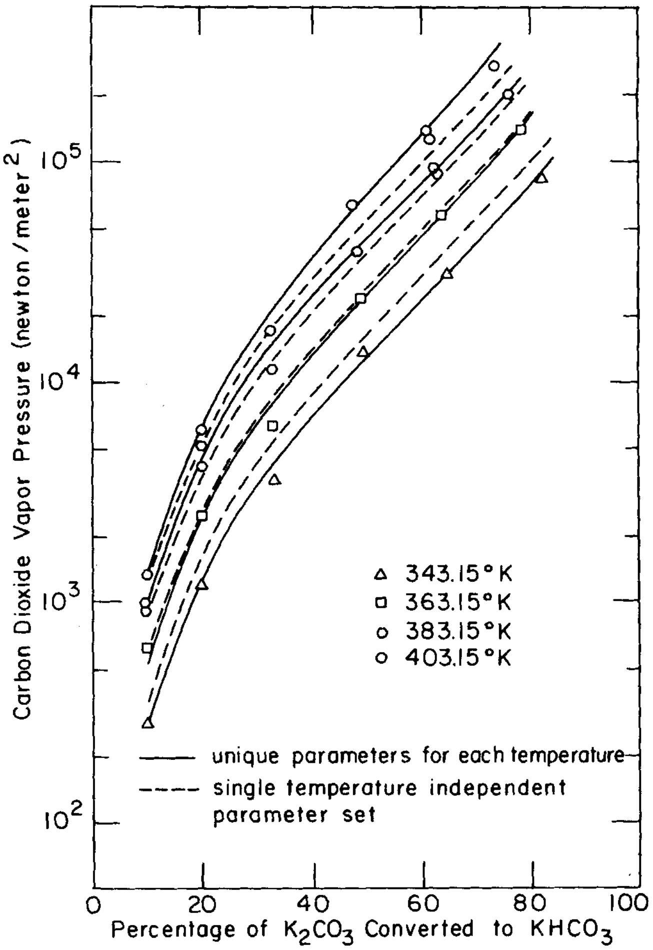

Figure 3. Equilibrium pressure of carbon dioxide of 30% equivalent potassium carbonate solution at 343.15, 363.15, 383.15 and 403.15°K.

that θ is substantially independent of the other parameters, consistent with the conclusion in the previous paragraph, that Brönsted's principle of specific ion interaction is not valid for the system.

The strong mutual correlation within the binary and ternary parameter subsets does not necessarily indicate that any single binary or ternary parameter should be dropped. Rather, it means that, locally, some linear combination of the correlated parameters is contributing to the goodness of fit. The correlation further implies that the parameters within a subset can not be individually well-determined. This could account for the lack of smoothness of the variation of the parameters with temperature.

Figure 1 shows experimental data and correlation results for equilibrium partial pressure of carbon dioxide at 383.15°K, for solutions of various concentrations. Since the data are widely scattered and unreliable, less weight is given to the data for equilibrium water vapor pressure during correlation. Correlation results for water vapor pressure are, however, acceptable.

All of the adjustable parameters in the extended Pitzer equation may be temperature dependent. To study the significance of this dependence, data at 343.15, 363.15, 383.15, and 403.15°K were fit independently. In addition, the data from these four temperatures are lumped together and fit, assuming no temperature dependence. The resulting parameters are shown in Table 8. No significant temperature trend was suggested. Figures 3 and 4 give the experimental data and the correlation results of equilibrium partial pressure of carbon dioxide and water at those temperatures for 30% equivalent potassium carbonate aqueous solution. Solid lines are the correlation results for data at each temperature fit independently. Dotted lines are from the data at all four temperatures lumped together.

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NOTATION

A_{ej} = stoichiometric number of element e in solute j
A_ϕ = Debye-Hückel constant for the osmotic coefficient
B_{ca} = binary ion-ion interaction parameter
C_{ca} = ternary ion-ion interaction parameter
$D_{ca,m}$ = binary salt-molecule interaction parameter or Setschenow constant
G^{ex} = excess Gibbs free energy
H = Henry's constant (atm · kg/g-mole)
I = ionic strength $(= 1/2 \sum_i m_i Z_i^2)$
K = dissociation equilibrium constant
P = pressure N/m^2
PK = cologarithm of dissociation constant
R = gas constant
S = sum of squares of objective functions
T = temperature (°K)
$\overline{V}$ = partial molar volume (cm^3/mole)
W_{el} = Debye-McAulay electrostatic work
Z = absolute value of ionic charge
a = activity
b_e = molality of element e (a constant)
m = molality (g-mole/kg of solvent)
m_j = molality of any solute j
n_w = number of kg of the solvent, water
x = liquid phase mole fraction
y = vapor phase mole fraction

Greek Letters

$\beta^{(0)}$, $\beta^{(1)}$ = parameters of the empirical expression of $B(I)$
γ = activity coefficient
$\delta P/P$ = relative error of P, in percentage

$$100\left[\frac{1}{n}\sum_{i=1}^{n}\left(\frac{p_i^{\text{calc}} - p_i^{\text{exp}}}{p_i^{\text{exp}}}\right)^2\right]^{1/2}$$

δy = absolute error of y, in percentage

$$100\left[\frac{1}{n}\sum_{i=1}^{n}(y_i^{\text{calc}} - y_i^{\text{exp}})^2\right]^{1/2}$$

θ = binary ion-ion difference parameter
λ = second virial coefficient of the basic Pitzer equation
μ = third virial coefficient of the basic Pitzer equation
ν = stoichiometric coefficient
σ = standard deviation
Φ = vapor phase fugacity coefficient
ϕ = osmotic coefficient
ψ = ternary ion-ion difference parameter
ω = binary salt-molecule difference parameter

Superscripts

s = saturation
$*$ = unsymmetric convention
∞ = infinite dilution
calc = calculated
exp = experimental

Subscripts

a, a' = anion
c, c' = cation
i, j, k = solute
m = molecular solute
w = water
1-1 = univalent-univalent electrolyte
1-2 = univalent-divalent electrolyte

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Calculation of Sulfate and Nitrate Levels in a Growing, Reacting Aerosol

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The temporal variation of particle size and chemical composition of a marine aerosol exposed to SO_2, NH_3, NO, NO_2, H_2SO_4 and H_2O vapor is studied to determine the effect of these parameters on the sulfate and nitrate levels in the particle. Results show that, for gas phase SO_2 oxidation to sulfate, and liquid phase nitrate formation, those parameters that enhance sulfate formation tend to inhibit nitrate formation, and vice versa. Further, for the situation considered, the ratio predicted for sulfate and nitrate ions to ammonium ions is very nearly that found if all these ions were present in the form of NH_4NO_3 and $(NH_4)_2SO_4$. This compares favorably with data on sulfate, nitrate and ammonium levels in the Los Angeles area. The model used is capable of representing a general growing, reacting aerosol; other cases studied by this approach are briefly outlined. Limitations of its use are discussed.

SCOPE

The influence of atmospheric aerosols on human health and visibility depends on particle size and chemical composition. Three major particulate pollutants found in most urban regions are sulfates, nitrates and particulate hydrocarbons. These species are not, in general, emitted directly into the atmosphere, but rather are a consequence of chemical reactions involving emitted gaseous pollutants to form particulate species. These reactions take place by a number of mechanisms, such as homogeneous gas phase chemistry, heterogeneous solution chemistry, or surface catalyzed chemistry at the gas-particle interface. When condensation of water vapor accompanies these reactions, both the size and chemical composition of the aerosol may change.

Prediction of the size and chemical composition of a growing, reacting aerosol (given the primary particle size and composition and the concentration of various reactive gaseous pollutants) is central to the ability to mathematically model air pollutant behavior. Of particular importance is the ability to predict secondary sulfate and nitrate levels in the aerosol, since these are two of the major particulate components in both the urban and non-urban atmosphere. They appear in particles as a consequence of chemical reactions involving gaseous NO_x and SO_2. In this article, a model capable of predicting size and chemical composition of a growing, reacting aerosol particle is used to calculate the sulfate and nitrate levels of an initial marine aerosol, exposed to gaseous air pollutants.

CONCLUSIONS AND SIGNIFICANCE

Sulfate and nitrate levels in aqueous atmospheric aerosol particles, as well as particle size, are predicted as a function of exposure time for various ambient conditions. By considering a liquid phase nitrate formation mechanism and a gas phase sulfate formation mechanism, the following observations can be made:

1. Equilibrium conditions dictate that the ratio of nitrate and sulfate to ammonium ion, when all ions are present, is nearly that found in NH_4NO_3 and $(NH_4)_2SO_4$.

2. For the size range considered (0.05-2.0 μm radius), particle pH increases with particle size, the smallest particles being the most acidic. Particle pH ranges from approximately 1.75-3.0.

3. Those conditions which tend to increase sulfate concentration cause a decrease in nitrate concentration, and

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