

VAPOR-LIQUID EQUILIBRIUM IN AQUEOUS
SOLUTIONS CONTAINING WEAK
AND STRONG ELECTROLYTES

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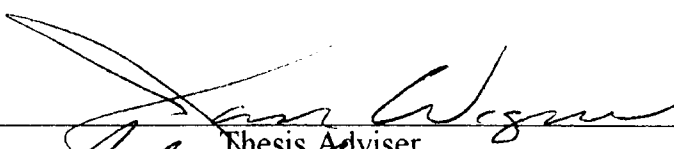
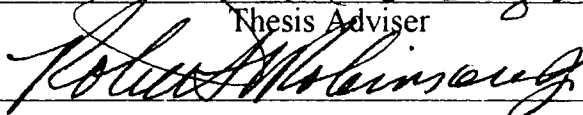
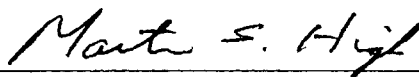
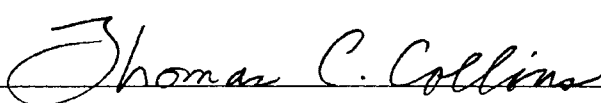
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CHAPTER I

INTRODUCTION

Electrolyte solutions, especially aqueous electrolyte solutions, play an important role in environment and industrial processes. The thermodynamic properties of electrolyte solutions must be known in many chemical and petroleum separation processes. The design of separation equipment could be achieved with more confidence by a model that is capable of describing wide ranges of temperature, pressure and concentration in electrolyte solutions. Because the applications are numerous and important, there are growing interests in the correlation and prediction of thermodynamic properties of weak as well as strong aqueous electrolyte solutions.

A new approach developed by Chen (1993) and Chen and Wagner (1994) successfully describes phase equilibrium in aqueous solutions containing weak electrolytes. One of the purposes of this study is to extend Chen (1993) work to phenol and hydrogen cyanide systems. Phase-equilibrium and chemical dissociation equations for these systems are incorporated into the model for bubble point calculations. Model predictions

are tested against multicomponent vapor-liquid equilibrium data.

The main object of this work is to revise the Chen and Wagner model to aqueous weak electrolyte solutions containing strong electrolytes. The new approach should have a minimum number of adjustable model parameters which must be easily fitted from single salt ternary experimental data. The correlation data base would be carefully selected based on their reliability and salt concentration ranges. The model predictions in single and multisalt systems will be tested against experimental data base as complete as possible. The new model should contain the simplicity, reliability and predictability features of the Chen and Wagner model development.

CHAPTER II

LITERATURE REVIEW

The literature review will consist of three segments. In the first segment, models to calculate the activity coefficients of strong electrolytes in aqueous solutions will be reviewed. Because currently available statistically based thermodynamic models are valid only for dilute solutions, attention will be focused on the semiempirical methods which are usually preferred in phase equilibria calculations of electrolyte solutions. In the second segment, the methods to describe the weak volatile electrolyte gases in aqueous solutions based on the liquid phase activity coefficient models and equation-of-state models will be reviewed. In the third segment, the methods that have been used to correlate the thermodynamic properties in weak electrolytes in the presence of strong electrolytes will be discussed.

Models for Description of Phase Equilibrium of Strong Electrolytes in Aqueous Solutions

Electrolyte solutions are characterized by both molecular and ionic species resulting in three different types of interactions: ion-ion, molecule-molecule, and

ion-molecule. Thermodynamic properties in electrolyte solutions are strongly dependent not only on long-range electrostatic forces between the ions but also on short-range forces between the ions, solvent molecules, and undissociated electrolytes (Prausnitz, 1969).

The modern electrolyte theory was established by Debye and Huckel (1923). Since then, numerous attempts to extend the Debye-Huckel equation have been published by adding semiempirical correction terms. The ion interaction model of Pitzer (1973) has been widely applied in chemical industries. An alternate approach based on the local composition concept was proposed by Cruz and Renon (1978) as well as Chen et al. (1982). The hydration models introduced by Stokes and Robinson (1948) combine ion-ion interactions with the ion solvation concept. Furthermore, the non-primitive models using mean spherical approximation (MSA) proposed by Planche and Renon (1981) more precisely describe both long and short range forces.

Debye-Huckel Law and Direct Extensions

Debye and Huckel (1923) established the modern electrolyte theory of interionic attraction which has been the basis for developing semiempirical models. The model only incorporated long-range forces to account for deviations from ideal activity coefficients in dilute solutions. A simple expression for mean ionic activity

coefficient which is called the Debye-Huckel limiting law was derived as follows:

$$\ln \gamma_{\pm} = -A |z_+ z_-| \sqrt{I}$$

where the I is the ionic strength of the solution:

$I = 1/2 \sum m_i z_i^2$; m_i is molality of component i , z_i is the charge number of ion, and the coefficient A is temperature dependent. The equation is valid only at low electrolyte concentrations up to about 0.001 molality. Better agreement with experimental results for solutions up to 0.1 molality can be achieved when the finite sizes of the ions are introduced into the Debye-Huckel equation (Robinson and Stokes, 1948):

$$\ln \gamma_{\pm} = -\frac{A |z_+ z_-| \sqrt{I}}{1 + B d \sqrt{I}}$$

where d is the hard sphere diameter of the ions and B stands for the solvent properties related to the dielectric constant.

Meissner and Tester (1972) found a plot of the reduced mean activity coefficient ($\gamma_{\pm}^{1/(z_+ + z_-)}$) as a function of total ionic strength of the solution at 25 °C forms a family curves for single strong electrolyte solutions. This graphical method enables us to estimate mean activity coefficients based on a family curves at certain ionic strengths when given one single experimental value of mean activity coefficient at a known ionic strength for a single electrolyte solution. Later, Meissner and Kusik (1972) extended their graphical approach to multisalt

solutions at high temperatures and developed algebraic equations for the family curves with one parameter for each strong electrolyte. The agreement with experimental data varying from 3 to 15 molality has been found to be within 20% error.

Bromley (1972, 1973) developed a model combining the Debye-Huckel term with an additional empirical term involving a single parameter known as β . He found that the individual values for the β parameter could be estimated by assuming the sum of individual ion values for cations and anions. The procedure is correlated with experimental results of strong electrolytes up to about 6 molality with one single parameter for each salt. The model provides a quite effective, yet less accurate, way to estimate activity coefficients when no experimental data have been measured.

Pitzer (1973) developed a system of virial type equations by expanding the Debye-Huckel equation to represent the thermodynamic properties of electrolyte solutions. The most important contribution of his work was to take the effect of short-range forces into account. Pitzer proposed an expression for excess Gibbs free energy:

$$\frac{G^E}{R \cdot T \cdot n_w \cdot M_w} = f(I) + \sum_i \sum_j m_i \cdot m_j \cdot \lambda_{ij}(I) + \sum_i \sum_j \sum_k m_i \cdot m_j \cdot m_k \cdot \tau_{ijk}.$$

The first term is a modified Debye-Huckel equation expressing the effect of the long-range electrostatic

forces. The correction for short-range binary interactions between ions is taken into account by parameter $\lambda_{ij}(I)$ which is the ionic strength dependent second virial coefficient. The ternary parameter τ_{ijk} is the correction term for triple ion interactions and is assumed independent of ionic strength.

The model yields excellent agreement with experimental results from dilute solutions up to 6 molality in single strong electrolyte solutions. The model also shows some flexibility in terms of the ternary adjustable parameters. The third virial coefficient can be neglected at electrolyte concentration less than 2 molality. The equation is subject to all the limitations of a virial equation. Moreover, it is not applicable to mixed solvent systems because the parameters are unknown functions of solvent composition. The model has been developed extensively by regression of a large amount binary and ternary experimental data.

Models Based on Local Composition Concept

Other extensions of the Debye-Huckel equation, combining local composition models such as the Nonrandom Two-Liquid (NRTL) equation and Universal Quasi-Chemical (UNIQUAC) equation, were developed by Cruz and Renon (1978), Ball et al. (1985a), Chen and Evans (1982, 1986), and Lu and Maurer (1993).

Cruz and Renon (1978) expressed the excess Gibbs free energy as the sum of the contributions of long-range interionic forces and the corrections for the short-range forces. One of the deficiencies in the Debye-Huckel law is that the effect caused by the decrease of dielectric constant D of the solution with the increase of ionic concentration is neglected. Therefore Cruz and Renon expressed the long-range interaction as Debye-Huckel term plus a Debye-McAulay term, cited by Harned and Owen (1958), which takes into account the "salt effect" caused by a change in the dielectric constant with ionic concentration. The NRTL local composition model of Renon and Prausnitz (1968) is introduced to account for the short range forces. The NRTL model is able to represent the nonideality of equilibrium properties in nonelectrolyte solutions and requires only binary adjustable parameters for extension to multicomponent systems. The model requires six adjustable parameters to represent single electrolytes if partial dissociation is assumed. It also involves one additional adjustable parameter for each new ionic specie.

The modified version by Ball et al. (1985a) used only two adjustable NRTL parameters for representation of strong single electrolyte properties up to 6 molality, while no new adjustable parameter is needed for mixtures. This was achieved by introducing a new expression for the Debye-McAulay term to estimate the dielectric constant.

Another extended NRTL theory was proposed by Chen et al. (1982, 1986). Similar to the Cruz and Renon model, the excess Gibbs free energy is a sum of two contributions: long-range interionic contributions and short-range contributions. In contrast to the Cruz and Renon method, Chen et al. proposed two basic assumptions: (1) the local composition of cations around a central cation is zero, and (2) the distribution of cations and anions around a central molecule leaves the net local ionic charges as zero. This results in only two binary energy interaction parameters associated with solvent-solvent pairs, solvent-salt pairs, and salt-salt pairs. It was also found that in mixed-solvent electrolyte systems, the long-range contribution due to the Pitzer-Debye-Huckel term was negligible, leaving only the local interaction term. Good agreement with experimental data was obtained for isopropanol-water-LiCl and methanol-water-CaCl₂ systems. However, this model requires ternary systems to obtain the salt-salt energy parameters.

The most recent model developed by Lu and Maurer (1993) combined the solvation equilibrium (mentioned later) between the solvated and unsolvated ions with physical models (Debye-Huckel law and UNIQUAC local composition concept by Abrams and Prausnitz, 1975). The model requires five parameters: two binary interaction parameters between each cation and anion, and three solvation parameters per ion. The model correlates well

for concentrated electrolytes from 3 to 29 molality. The model shows comparable results with other activity models suitable for extremely concentrated electrolyte solutions. The extension to mixed electrolytes requires no high order parameters.

Non-primitive Models

Planche and Renon (1981) and Ball et al. (1985b) started from a statistical thermodynamic expression for the interparticle potentials by introducing both long-range coulombic forces and short-range forces between all species. The analytical solution of the radial distribution function is obtained using the mean spherical approximation and the mathematical tool known as Fourier transformation. Thermodynamic properties such as Helmholtz energy and chemical potential are derived from the analytical solution. The equation of state is obtained by differentiation of the Helmholtz free energy, A , based on the fundamental thermodynamic relationship:

$$P = -(\partial A / \partial V)_T$$

With only one adjustable parameter for each salt, the model successfully correlated the osmotic coefficients of strong electrolytes up to 6 molality. The prediction of mixture electrolytes requires no additional parameters. However, the only calculations reported were for osmotic coefficients of salts in water at 25 °C.

Similar work done by Copeman and Stein (1987) presented the contributions to Helmholtz free energy as an electrostatic term, a repulsive term, and an attractive term. The model was tested on 18 strong electrolytes at 25 °C limited to near atmosphere pressure. For highly concentrated systems, two binary parameters are needed.

Raatschen et al. (1987) expressed the Helmholtz free energy in terms of six contributions with three terms related to the presence of ions. Their work focused mainly on mixed solvent solutions such as the LiBr-methanol-water ternary system. The model requires three cation-anion binary parameters per electrolyte. However, some of the expressions for ion contributions, for instance molecule-ion interaction terms, are not suitable for extension to supercritical components at high pressure, as pointed out by Harvey and Prausnitz (1989).

Furst and Renon (1993) developed a successful one-parameter Redlich-Kwong-Soave type equation of state from the Helmholtz free energy derived from mean spherical approximation. While the model agreed well with halide systems up to 6 molality, the extension to other nonhalide systems by assuming Pauling diameters for anions shows relative large errors.

Hydration Theory

Hydration models explain the deviation from the ideal mixtures as the result of ion-solvent hydration or solvation. It is well known that the ionic species present in the solution have a strong interaction with water in the close neighborhood. The solvation model was established by Stokes and Robinson (1948) and latter modifications have been proposed to correct the thermodynamic inconsistency of the original model (Kawaguchi et al., 1981; Nesbitt, 1982; Ghosh and Patwardhan, 1990).

Stokes and Robinson (1948) proposed the hydration theory in which the Debye-Huckel model for long-range interionic forces was combined with ionic hydration concept. The correction to the Debye-Huckel model led to a simple hydration model with two adjustable parameters: the hydration number in the solvent shell and the effective size of the solutes. The activity coefficients of the electrolytes can be represented accurately for strong electrolytes in dilute and moderately concentrated solutions up to 4 molality. However, the formulation of the model has an inadequacy because the hydration number of an electrolyte is assumed independent of the concentration of solution. This results in failure of the model at high concentrations.

Kawaguchi et al. (1981) described an extension of the Stokes and Robinson hydration equation by applying

the Analytical Solutions of Groups (ASOG) model of Wilson and Deal (1962) to account for the non-electrostatic contributions and by assuming total hydration of ions. Nesbitt (1982) proposed a correction for the hydration model based on the assumption that H_2O molecules reside in two separate environments: the hydration shell and bulk solvent environment. This assumption allows the hydration number to decrease gradually in concentrated solution. The model can be extended to concentrations up to 5 molality using two parameters.

A similar hydration model developed by Ghosh and Patwardhan (1990) shows good accuracy over a large range of concentrations, up to 20 molality for 150 electrolytes. The excess Gibbs free energy is expressed as the sum of ion-ion electrostatic contributions and ion-water contributions. Although there are no terms accounting for short-range ionic interactions, Ghosh and Patwardhan suggested the hydration term as an alternative to replace the virial terms proposed by Pitzer. The aqueous solution of LiBr was selected as a reference electrolyte because of its highly hydrated feature and available high-concentration experimental data. The model only involves two empirical parameters related to the hydration number and the energy of hydration for each strong electrolyte. Unfortunately, the model is not extended to multielectrolyte solutions.

Volatile Weak Electrolyte Gases in Aqueous Solutions

In contrast to the great amount of work done for aqueous strong electrolyte systems, limited work has been reported on weak electrolyte solutions due to the complexity of the problem. Weak electrolytes in the liquid phase can form ionic species by partial dissociation. Interactions between molecules and ionic species have a strong effect on dissociation equilibrium which affects distributions of unreacted molecules in the vapor and liquid phases. Phase equilibrium calculations may be difficult if chemical and phase equilibria are present at the same time. Several models have been developed by introducing a mixing rule combined with the activity coefficient models into a cubic equations of state (e.g. Huron and Vidal, 1979; Wong and Sandler, 1992; and Michelsen, 1990). However, none of these models account for the presence of ions.

Edwards et al. (1975, 1978) made a major contribution to development of the basic thermodynamic framework to correlate and predict the vapor-liquid equilibrium for volatile weak electrolyte solutions based on liquid phase activity models. Many researchers (Beutier and Renon, 1978; Pawlikowski et al., 1982, 1983; Chen and Evan, 1986; and Kawazuishi and Prausnitz, 1987) have focused on the improvement of liquid phase activity correlations, which are believed to be the major

reason for the poor performance of the models. Another model developed by Wilson et al. (1978, 1990) includes no expression for activity coefficients but correlates the dissociation constants and Henry's constants as a function of composition and ionic strength. However, a large number of parameters, including quaternary parameters, are required for model correlation. Alternative approaches which combine an equation of state that successfully describes high pressure phase equilibrium in nonaqueous systems with electrolyte effects have been proposed by Daumn et al (1986), Friedemann (1987), and Jin and Donohue (1988a, b).

Liquid Phase Activity Models

Edwards et al. (1975) established the basic thermodynamic framework to correlate vapor-liquid equilibrium for dilute aqueous electrolyte solutions containing one or more volatile weak electrolytes in the temperature range from 0 to 100 °C. The equilibrium between the vapor and liquid phase is described by applying the concept of Henry's constants for the solubility of molecular solute:

$$y_i \phi_i P = H_i m_i \gamma_i$$

where y_i , P , H_i and m_i designate the mole fraction of component i in vapor phase, the total pressure, Henry's constant for a gas i in pure water and molality of component i in liquid phase. The vapor phase fugacity

coefficient ϕ_i is calculated from a truncated virial equation. The liquid phase activity coefficient γ_i is obtained from a modified Debye-Huckel equation:

$$\ln \gamma_i = -\frac{\alpha z_i^2 \sqrt{I}}{1 + \sqrt{I}} + 2 \sum_{k \neq w} \beta_{ik} m_k$$

where w stands for water, α is the Debye-Huckel factor, and β_{ik} is the interaction parameter for species i and k . The limitation of this activity model is that it is not valid at ionic strengths higher than 0.1 molality.

The chemical reactions between dissociated and undissociated species have a strong influence on the solubility of gases:

$$K = \frac{m \cdot m \cdot \gamma_z^2}{m_i \gamma_i}$$

where K is the dissociation constant and γ_i is the activity coefficient of the molecular form of the weak electrolyte. Additionally, an overall mass balance in the liquid and vapor phase as well as the condition of charge balance must be taken into account. A system of nonlinear equations is solved for total pressure with specified temperature and overall liquid phase composition. The original model is able to predict multisolute systems without ternary parameters.

Edwards et al. (1978) modified vapor phase fugacity coefficient and the liquid activity coefficient models to extend the temperature range to 170 °C and ionic strengths to 6 molality. The model uses the extended

Pitzer activity model but neglects the contribution from ternary interactions. A large number of binary ion-ion and molecule-ion parameters are required in multisolute systems because the Pitzer model takes into account the contributions of ion-molecule interactions, as well as ion-ion interactions. For example, considering the ammonia-carbon dioxide-water system, there are two molecular solute species (NH_3 and CO_2) and six ionic species (NH_4^+ , H^+ , OH^- , HCO_3^- , $\text{CO}_3^{=}$, and NH_2COO^-). Even if the parameters are assumed symmetric, there remain 72 binary parameters. Obviously, the number of parameters must be reduced through simplification. The temperature and ionic strength range of the model are limited by accuracy of equilibrium constants, Henry's constants, and the liquid activity model. Later developments were concerned mainly with these three areas.

Pawlikowski et al. (1982) revised the Edwards et al. model by fitting ternary experimental data to obtain new interaction parameters. A computer program, TIDES, was developed by Pawlikowski (1981) to correlate vapor-liquid equilibrium data for NH_3 - CO_2 - H_2O at 100 and 150 °C. Good results were obtained at 100 °C for Pawlikowski's data (16% errors for CO_2 partial pressure and 13% errors for NH_3 partial pressure). However, the model correlation gives generally poorer agreement with other experimental results in ternary and quaternary systems (see Tables V and VI in Daumn et al., 1986). The model

involves a large number of parameters. For the $\text{CO}_2\text{-NH}_3\text{-H}_2\text{O}$ ternary system, for example, the model requires 14 ternary interaction parameters plus 25 binary interaction parameters.

Beutier and Renon (1978) used the thermodynamic framework established by Edwards et al. and modified the liquid activity equation to extend their model to higher electrolyte concentrations. They presented a modified Pitzer equation by splitting the excess Gibbs free energy into three terms including additional molecule-molecule interactions. Unlike the method of Edwards et al., ternary parameters are also included in Pitzer activity coefficient equation. Generally the model provides similar agreement and limitations with experimental data as the model of Edwards et al. (1978).

Chen et al. (1986) modeled weak electrolyte systems by introducing the NRTL local composition concept as discussed earlier. The highly concentrated $\text{NH}_3\text{-H}_2\text{S-H}_2\text{O}$ system was examined at temperatures of 80 and 120 °C. With more than 7 binary temperature-dependent adjustable parameters, the fitting results had 9 percent average relative deviation of the partial pressure of ammonia. The reported results were less extensive than those of Edwards et al. (1978) and Beutier and Renon (1978). For example, no calculations were provided for systems containing SO_2 and CO_2 .

Equation-of-State Approach

Very little attention has been given to the extension of equations of state to electrolyte solutions. The equation-of-state approach does not suffer the limitations of activity models at high pressure and temperature. Furthermore, it has the advantage of simple computational procedures with fewer adjustable parameters without sacrificing the ability to correlate the experimental data.

The perturbed-hard-chain equation of state which applies successfully to polar mixtures at high pressure was extended by Daumn et al. (1986) to aqueous weak electrolyte solutions. The model requires two temperature dependent parameters per binary system and two additional binary-pair parameters fitted from ternary systems. The prediction results were comparable with models of Edwards et al. (1978) and Wilson (1978) for the quaternary $\text{CO}_2\text{-NH}_3\text{-H}_2\text{S-H}_2\text{O}$ system. The average relative deviation in the partial pressures were approximately 30 % for all the models. The Daumn et al. method fails in low pressure and dilute regions because the model neglects the dissociation of weak electrolytes.

Friedemann (1987) applied the Redlich-Kwong-Soave equation of state to calculate the fugacity coefficients in liquid phase. The thermodynamic framework is the same as the Edwards et al. (1978). The major drawback in Friedemann's approach is that the activity coefficients for

all species are assumed to be unity, whereas the nonideality in weak electrolyte systems results activity coefficients deviating from unity. The biggest advantage of the model is its simplicity and ability to predict multicomponent systems with few parameters from binary data reduction. The prediction results are compared with the more complex Edwards et al. (1978) liquid activity models and Daumn et al. (1986) equation of state model for ternary $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ and $\text{NH}_3\text{-H}_2\text{S-H}_2\text{O}$ systems. The prediction results of Friedemann are approximately equivalent with other complex model correlation results at high temperatures and pressures (see Tables IV and V in Friedemann, 1987).

Recently, a new equation of state based on perturbation theory was derived by Jin and Donohue (1988a, b; 1991). The Helmholtz free energy contains up to ten terms taking into account molecule-molecule interactions, ion-ion interactions, and ion-molecule solvation effects. The equation of state requires one adjustable parameter per anion-cation pair. This model shows less than 6% average absolute errors with experimental mean ionic activity coefficients at 25 °C for single strong electrolyte solutions up to 6 molality. The model was also used to predict vapor pressures of binary weak electrolyte systems. The model gave good agreement with the limited experimental data for aqueous CO_2 , SO_2 , and H_2S systems in moderate temperature and

concentration ranges. Unfortunately, extension from binary to multicomponent systems is still not reported.

Volatile Weak Electrolyte Gases in Aqueous Solutions Containing Strong Electrolytes

While useful methods have been developed in phase equilibrium calculation in mixed electrolyte solution, less progress has been made in the mixed solvent systems with one or more dissolved salts. It is well known that the solubility of a gas in a salt solution can be less or greater than that in pure water. The solubility decrease or increase is referred to as "salting out" or "salting in" phenomena. This behavior has been attributed to the interactions between ions and water molecules which have a direct impact on the solubility of nonpolar or slightly polar gases in water. Mock et al. (1986) and Sander et al. (1986) developed models to calculate the phase equilibrium for multiple-solvent electrolyte solutions, but they do not include noncondensable gases. A detailed comparison for these two models has been presented by Jansson et al. (1989). For noncondensable supercritical gases at high pressure, activity coefficient models can not be used because there is no standard state for supercritical components.

Harvey and Prausnitz (1989) developed a new model applied at high pressure where conventional activity coefficient models are not suitable. The Helmholtz free

energy is split as the sum of three contributions: a nonelectrolyte contribution, a contribution from charging the ions, and a contribution to account for ion-ion interaction described by Mean Spherical Approximation (MSA). The model requires four pure component parameters for nonelectrolytes, four pure component parameters for ions, and three binary parameters for gas-water plus an additional salt-solvent parameter. The results only qualitatively agreed with experiment. The salting-out effect for high salt concentrations is significantly underpredicted for all the systems tested.

Aasberg-Petersen et al. (1991) proposed an equation for fugacity at low pressure containing two contributions:

$$\ln \phi_i = \ln \phi_i^{\text{EOS}} + \ln \gamma_i^{\text{EL}}$$

where the first term is a nonelectrolyte contribution calculated by a conventional equation of state. The second term is an electrostatic contribution calculated by a modified Debye-Huckel equation. The model requires three binary gas-water interaction parameters and an additional ternary electrolyte interaction parameter regressed from gas-water-salt experimental data at low pressure. While the model agrees with CO₂-H₂O-NaCl system, it overestimates the total pressure of CO₂ at 30 wt% CaCl₂ concentration.

Rumpf and Maurer (1993a, b, c, 1994) used a modified Pitzer equation to correlate experimental data. Excellent agreement was obtained with their measured

data (for example, 1.6 % average relative errors in total pressure for CO₂-Salt-H₂O). The model also yields good agreement with data of Corti et al. (1990). The average deviation in total pressure is 14.2% at pressures less than 100 bar. Again, one has to face a problem of fitting a large number of parameters including ternary parameters. Furthermore, the model is not applicable at high concentrations of weak electrolytes and pressures greater than 100 bar.

CHAPTER III

PHASE EQUILIBRIA IN AQUEOUS VOLATILE WEAK ELECTROLYTE SOLUTIONS

Introduction

A new approach by Chen (1993) and Chen and Wagner (1994) has been developed for predicting phase equilibrium in weak electrolyte aqueous solutions. The new model shows its simplicity, reliability and accuracy in predicting phase equilibria of ammonia, carbon dioxide, sulfur dioxide and hydrogen sulfide in aqueous binary and multicomponent systems over a wide range of temperature, pressure, and concentration. The model prediction in multicomponent systems are as good as, and in many cases better than, correlation results from more complex activity coefficient models (Edwards et al., 1975, 1978; Pawlikowski et al., 1982, 1983; and Beutier et al., 1978), or equation-of-state model (Daumn et al., 1986), or correlations for Henry's and dissociation constants (Wilson et al., 1990). This study extends the Chen (1993) work to phenol and hydrogen cyanide aqueous systems. Phase-equilibrium and chemical dissociation equations for hydrogen cyanide and phenol are incorporated into the

model for bubble point calculations. Model predictions are tested against multicomponent experimental results for phenol as well as recent published data for the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ ternary.

Thermodynamic Framework

The model approach is based on the rigorous thermodynamic framework established by Edwards et al. (1975). The framework is constructed so that it provides a convenient, thermodynamically consistent method for calculating of multicomponent vapor-liquid equilibrium in volatile weak electrolyte aqueous solutions. For ionic species, which only exist in the liquid phase, the model is based upon four principles:

a) Vapor-liquid equilibrium for the molecular solutes like HCN , and $\text{C}_6\text{H}_5\text{OH}$.

b) Chemical dissociation equilibrium between the undissociated and dissociated weak electrolytes.

c) Mass balances on the electrolytes in the liquid phase.

d) Bulk electroneutrality in the liquid phase.

The vapor-liquid phase equilibrium calculations are based on a modified Soave-Redlich-Kwong (SRK) equation of state (Graboski and Daubert, 1979):

$$p = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)}$$

$$a = 0.42747 \frac{R^2 T_c^2}{P_c}$$

$$b = 0.08664 \frac{RT_c}{P_c}$$

$$\alpha = [1 + (0.48508 + 1.55171\omega - 0.15163\omega^2)(1 - T_r^{0.5})]^2$$

$$T_r = \frac{T}{T_c}$$

$$a\alpha = \sum \sum X_i X_j (a\alpha)_{ij}$$

$$(a\alpha)_{ij} = (1 - C_{ij}) [(a\alpha)_i (a\alpha)_j]^{0.5}$$

$$C_{ij} = C_{ij}^o - \frac{C_{ij}^1}{T}$$

$$b = \sum \sum X_i X_j b_{ij}$$

$$b_{ij} = 0.5(1 - D_{ij})(b_i + b_j)$$

where T_c and P_c are pure component critical temperature and pressure respectively, the ω is the pure component eccentric factor, and X_i is the mole fraction of i -th molecular component in the mixture.

The GPA*SIM-II program by Wagner (1994) performs the phase equilibrium calculations based on the fugacity coefficients obtained from the SRK equation of state:

$$\ln \phi_i = \frac{\sum X_j b_{ij}}{b} (Z - 1) - \ln \left[Z \left(1 - \frac{b}{V} \right) \right] + \frac{aa}{bRT} \left[\frac{\sum X_j b_{ij}}{b} - \frac{2}{aa} \sum X_j (a\alpha)_{ij} \right] \ln \left(1 + \frac{b}{V} \right)$$

where Z is the compressibility of the fluid mixture obtained from the SRK equation of state.

A modified Debye-Huckel type activity coefficient model is used to calculate the activity coefficient for ionic species:

$$\ln \gamma_{\pm} = |z_{+} z_{-}| f^{\gamma}$$

$$f^{\gamma} = -A_{\phi} \left(\frac{\sqrt{I}}{1 + 1.2\sqrt{I}} + \frac{2}{1.2} \ln(1 + 1.2\sqrt{I}) \right)$$

$$A_{\phi} = -61.44534 \exp\left(\frac{T - 273.15}{273.15}\right) + 2.864468 \left[\exp\left(\frac{T - 273.15}{273.15}\right) \right]^2 +$$

$$183.5379 \ln\left(\frac{T}{273.15}\right) - 0.6820223(T - 273.15) +$$

$$0.0007875695(T^2 - 273.15^2) + 58.95788 \left[\frac{273.15}{T} \right]$$

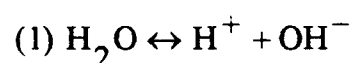
where correlation of A_{ϕ} is due to Chen et al (1982); I is the ionic strength of the electrolyte solution.

Chemical dissociation equilibrium constants, K , which describe the ratio of the molecule to the ionic concentration of the electrolytes are expressed by activities:

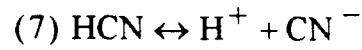
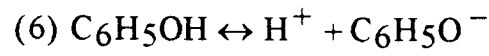
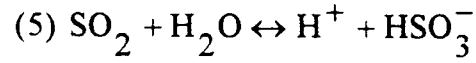
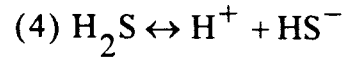
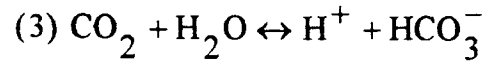
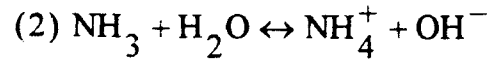
$$K = \frac{a_{+} a_{-}}{a}$$

where activity a is related to molality through the activity coefficient, γ : $a_i = \gamma_i m_i$. The following chemical dissociations for weak electrolytes in aqueous solutions take place:

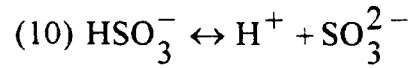
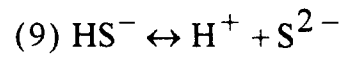
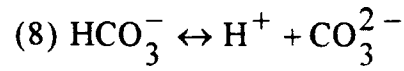
Dissociation of water:



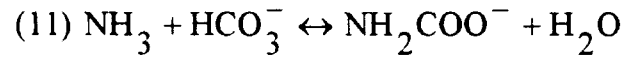
Dissociation of molecular species:



Second dissociation of ionic species:



Carbamate reaction:



The temperature-dependent dissociation equilibrium constants of NH_3 , CO_2 , SO_2 and H_2S are obtained from Maurer (1980) and those for HCN and $\text{C}_6\text{H}_5\text{OH}$ from Tsonopoulos et al. (1976).

The overall mass balance in the liquid phase results in six additional equations:

$$m_{\text{NH}_3} + m_{\text{NH}_4^+} + m_{\text{NH}_2\text{COO}^-} = M_{\text{NH}}$$

$$m_{\text{CO}_2} + m_{\text{HCO}_3^-} + m_{\text{NH}_2\text{COO}^-} = M_{\text{CO}}$$

$$m_{\text{H}_2\text{S}} + m_{\text{HS}^-} + m_{\text{S}^{2-}} = M_{\text{HS}}$$

$$m_{\text{SO}_2} + m_{\text{HSO}_3^-} + m_{\text{SO}_3^{2-}} = M_{\text{SO}}$$

$$m_{\text{HCN}} + m_{\text{CN}^-} = M_{\text{CN}}$$

$$m_{\text{C}_6\text{H}_5\text{OH}} + m_{\text{C}_6\text{H}_5\text{O}^-} = M_{\text{C}_6\text{H}_5\text{O}}$$

where the M_i is the stoichiometric concentration of the weak electrolyte, m_i is the molecular concentration of the weak electrolyte, m_i^+ and m_i^- are the concentrations of the cation and anion, respectively.

The charge balance in the liquid phase is expressed as:

$$\sum_{\text{ion}} Z_i m_i = 0$$

where Z_i is ionic charge of ion i .

The numerical implementation for solving the set of non-linear equations is based on the computational procedure outlined by Friedemann (1987).

Binary Parameter Regression

For the phenol-water binary, two adjustable interaction parameters, C_{ij} for the molecule-molecule interaction term and D_{ij} for the molecular volume term, take into account the molecule-molecule forces through the mixing rule of the SRK equation of state. For hydrogen cyanide, only a single parameter, C_{ij} , is required. The adjustable parameters are determined from binary vapor-liquid equilibrium data by minimizing the following objective function:

$$OBJ = \sum_i^{NPT} \left[\left(\frac{y_i^{cal} \cdot P_{tot}^{cal} - P_i^{exp}}{P_i^{exp}} \right)^2 \right]$$

where P_i is the partial pressure of component i , and P_{tot} is the total pressure. The difference between experimental and calculated total pressure is minimized when partial pressures are not available. The parameters fitted from binary data as well as the data base used in the regression are listed in Table I. Note that C_{ij} is temperature dependent.

Binary Regression Data Base

To estimate the interaction parameters for hydrogen cyanide-water and phenol-water, reliable experimental vapor-liquid equilibrium data are needed. In Table I, the data base used in determining binary adjustable parameters, C_{ij} and D_{ij} , are given.

Literature data for hydrogen cyanide-water are scarce. Miles and Wilson (1975) measured total and partial pressures for the HCN binary at 323, 363 and 393 K. Rumpf and Maurer (1992) measured the total pressure of HCN at temperatures from 293 to 413 K and pressures up to 250 bar. Considering the fact that the experimental data by Rumpf and Maurer covers the larger temperature and pressure range and appears to have best accuracy, it is selected for the regression data base.

For phenol-water binary, experimental measurements for total pressure from many researchers only covered low

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For phenol-water binary, experimental measurements for total pressure from many researchers only covered low

Table I
Results of Binary Interaction Parameter Fitting

Solute	No. of Points	Temp K	Pressure Bar	AAPD P _{tot}	C _{ij} ⁰	C _{ij} ¹	D _{ij}
HCN	86	291-413	0.1-5	10.0	-0.0063	35.8	0
C ₆ H ₅ OH	76	317-433	0.01-1	12.8	0.309	-141	0.404

AAPD is average absolute percentage deviation

P_{tot} is the total pressure

$$C_y = C_y^o + \frac{C_y^1}{T}$$

Experimental data sources:

HCN-H₂O: Rumpf and Maurer (1992)

C₆H₅OH-H₂O: Weller et al. (1963), and Schreinemakers (1900)

pressure region up to 1 bar. Since the measurements by Weller et al. (1963) and Schreinemakers (1900) were of best quality based on experimental data evaluation results of Onken et al. (1981), it is decided to include their experimental results in the regression data base.

Results for Binary Systems

The binary experimental data used in the regression are chosen very carefully as discussed above because the accurate performance in this region is essential for the prediction of multicomponent systems. As one can see from Table I, the experimental total pressure for HCN binary deviate from the model correlation by 10%, and 14% for C_6H_5OH binary. Considering the experimental uncertainty of most binary data sets is frequently around 10% to 20% as pointed out by Chen (1993), the model approach based on the SRK equation of state is adequate for the present work.

Figure 1 shows the model correlation for the hydrogen cyanide-water binary compared with the experimental total pressure by Rumpf and Maurer (1992). The model correlation systematically underestimates total pressures from experimental data at high concentrations, but is very accurate at molalities less than 3.0.

Prediction for Multicomponent Systems

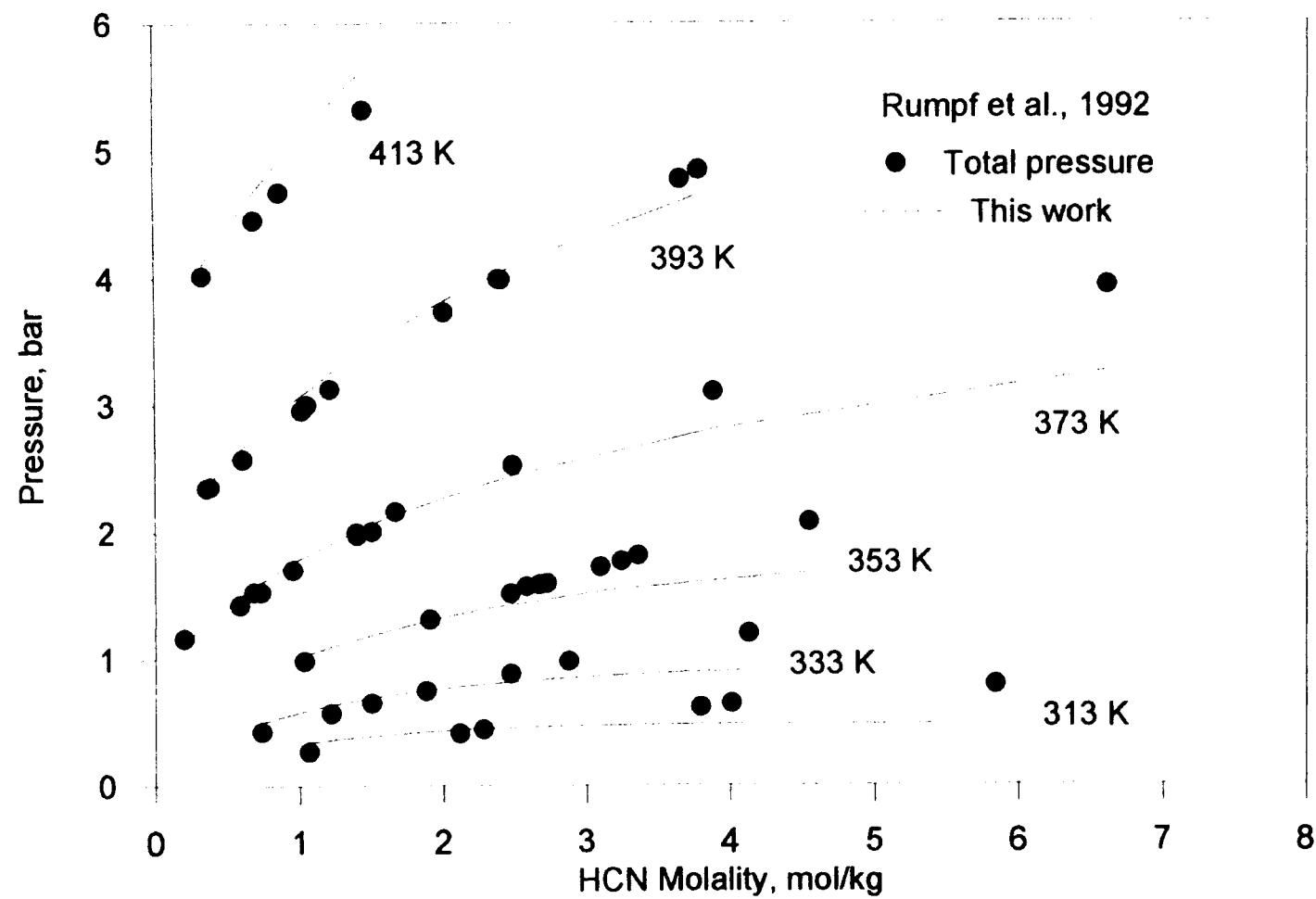


Figure 1. Total pressure for the HCN-H₂O system

Binary systems discussed so far are used to correlate the adjustable parameters from experimental vapor-liquid equilibrium data. Extension to multicomponent systems is purely predictive.

NH₃-C₆H₅OH-H₂O Ternary System

There is only one data set available in the open literature by Pawlikowski et al. (1983). They measured NH₃ partial pressure at 373 and 423 K at fixed concentrations of phenol. Figure 2 shows the predicted NH₃ partial pressures compared with the experimental data. This model prediction agrees very well with the experimental data, 8.1% absolute average deviations. At 373 K and 32.3 NH₃ molality, the model prediction results yield only 0.1% relative deviation from experimental data value. As one can see from the plot, the model predictions show large temperature effects on solubilities of NH₃.

NH₃-CO₂-H₂O Ternary System

More recent data reported by Muller and Maurer (1988) and Goppert and Maurer (1988) cover a wide range of temperature, pressure and solutes concentrations (up to 26 molality of NH₃ and 13.3 molality of H₂S). A detailed comparison of predictions of this model and correlation results of Gas Processors Sour Water (GPSWAT) model (Wilson et al. 1990) are compared in Table II. This model

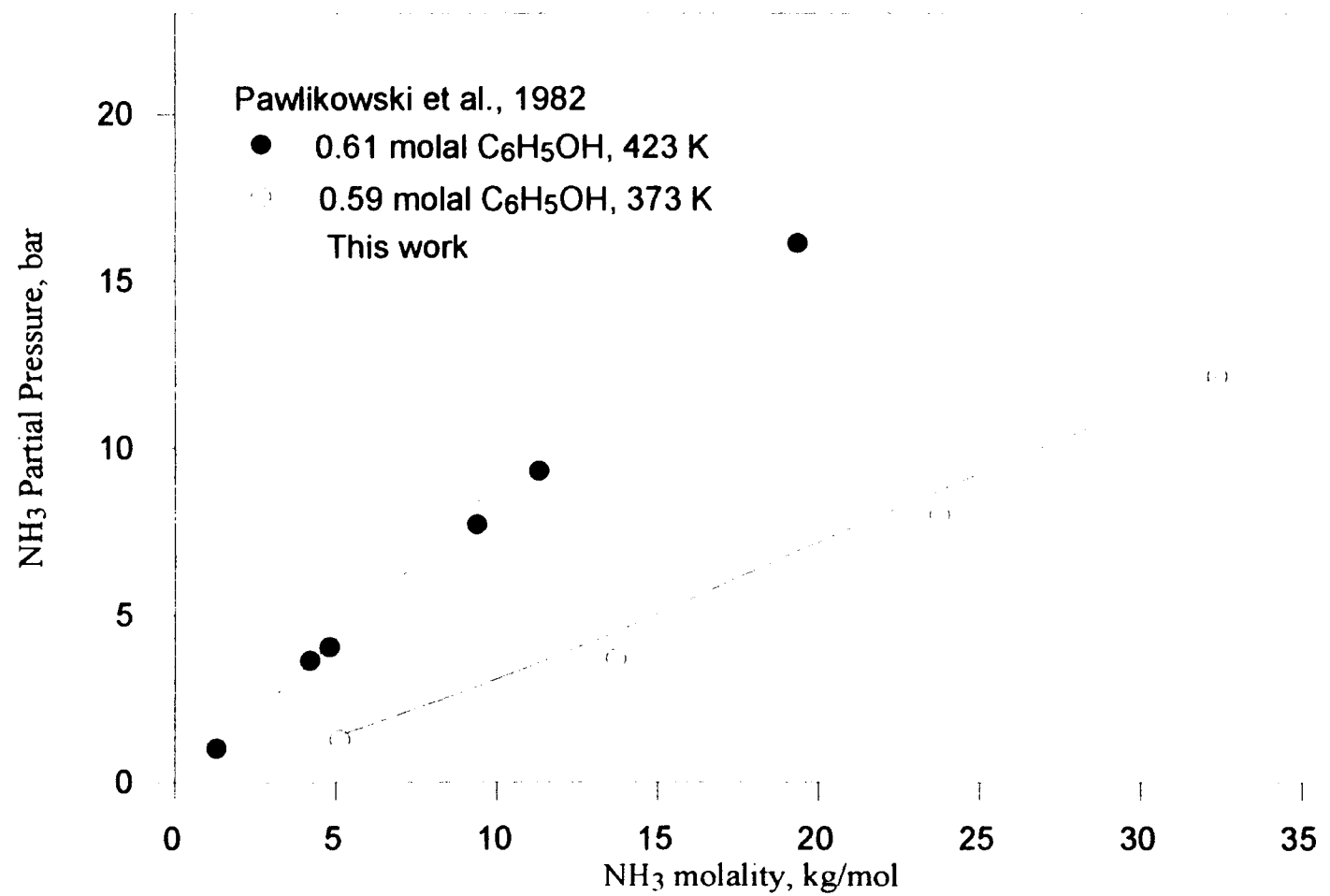


Figure 2. Partial pressure of NH₃ for the NH₃-C₆H₅OH-H₂O system

Table II
Average Errors in Partial Pressure Calculated By Different Models
For The $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ System

Temp K	NH_3 Molality	CO_2 Molality	Ptot Bar	No. points	Solute	AAPD % GPSWAT	AAPD % his Work
373-a	3.8-26.0	0.26-13.3	1.9-9.4	61	Ptot	8	8
				61	CO_2	31	16
				61	NH_3	16	15
393-a	2.84-25.9	0.22-12.7	3.3-27.3	42	Ptot	8	10
				42	CO_2	36	19
				42	NH_3	102	87
413-a	2.5-25.3	0.22-11.3	5.8-46.6	72	Ptot	14	11
				72	CO_2	52	17
				72	NH_3	58	59
433-a	2.7-24.6	0.25-9.2	10.5-67.6	40	Ptot	20	10
				40	CO_2	89	19
				40	NH_3	17	17
453-a	2.5-12.6	0.19-3.8	16.5-79.5	23	Ptot	9	8
				23	CO_2	25	13
				23	NH_3	10	10
473-a	2.4-10.7	0.26-1.6	29.1-83.4	11	Ptot	13	3
				11	CO_2	20	6
				11	NH_3	4	3
333-b	1.0-11.7	0.6-12.7	0.8-70.3	85	Ptot	33	46
				85	CO_2	34	48
				9	NH_3	110	75
353-b	0.6-12.2	0.4-11.4	1.3-70.3	93	Ptot	19	10
				93	CO_2	21	12
				32	NH_3	19	17
360-b	0.5-16.5	0.6-13.5	1.3-68.6	183	Ptot	14	5
				183	CO_2	59	39
				137	NH_3	94	62
373-b	1.0-14.3	0.4-10.4	2.3-69.2	117	Ptot	12	8
				98	CO_2	29	19
				97	NH_3	71	62
393-b	0.7-12	0.2-7.4	2.8-50.0	72	Ptot	8	10
				72	CO_2	41	30
				62	NH_3	66	61

prediction performs better than GPSWAT in all the temperature regions. The only exception is for data at 333 K (Goppert and Maurer, 1988) where both models agree badly with experimental results. In general, this model yields excellent prediction results in experimental total pressure with less than 10% errors and good to fair results for CO₂ partial pressure. The GPSWAT model also gives satisfactory correlation results for total pressure. However, for partial pressure of NH₃, the results from both models are generally poor.

Summary

A new model by Chen and Wagner (1994) for the vapor-liquid equilibrium calculation in volatile weak electrolyte solutions is extended to hydrogen cyanide and phenol systems. The model prediction for NH₃-C₆H₅OH ternary systems yields excellent results compared with experimental data. This model predictions perform better than the GPSWAT correlations for the NH₃-CO₂-H₂O systems compared with recent experimental data by Muller and Maurer (1988) and Goppert and Maurer (1988).

The new model is less complex, in terms of its number of adjustable parameters, than the more complex activity coefficient models and equation of state models. For the CO₂-NH₃-H₂O ternary system, for instance, the revised Edwards et al. (1978) model by Pawlikowski et al. (1982) requires 62 parameters which are determined from

binary and ternary data. The Daumn et al. (1986) model requires 12 binary and ternary parameters. The GPSWAT model requires even more parameters associated with the Henry's constants and dissociation constants fitted from binary, ternary experimental data. This model only involves three binary parameters including one temperature dependent parameter, a dramatic reduction in the total number of model parameters compared to other models.

The biggest advantage of the new model is its purely prediction feature for multicomponent systems. Only binary molecule-molecule interaction parameters from the regression of the binary data are involved in the model predictions. Considering the available models for aqueous weak electrolyte solution, only this model and Edwards et al. (1975, 1978) are predictive in nature for ternary systems.

The new model describes phase behavior for multicomponent systems about as good as, or in most cases better than the correlations obtained with more complicated activity coefficient models. The deviation of the model predictions are frequently on the order of the experimental uncertainty.

CHAPTER IV

PHASE EQUILIBRIA IN AQUEOUS WEAK ELECTROLYTE SOLUTIONS CONTAINING SALTS

Model Development

Ionic species dissociated from strong electrolytes have an important effect on vapor-liquid equilibrium. The thermodynamic properties become more difficult to describe when the solvent is not water alone. Even greater difficulty arises for systems containing noncondensable gases at high pressure. The existing activity coefficient models which satisfactorily describe low-pressure, single-solvent systems are not suitable for multisolvent electrolyte systems at high pressure. An alternate approach for high pressure phase equilibrium is based on an equation of state to calculate the fugacities of molecular species in the vapor and liquid phases. Equations of state, such as the cubic Soave-Redlich-Kwong (SRK), have been successfully applied to nonelectrolyte systems. As demonstrated in Chapter III, by introducing a molecule-molecule interaction parameter, C_{ij} , and molecular volume parameter, D_{ij} , into the SRK equation of state mixing rule, the new model is able to

describe phase behavior of strong polar weak electrolyte systems. The problem for salt containing systems is to superimpose properly the salting effects on an EOS for nonelectrolytes and weak electrolyte gases.

With increasing ionic strength, the contributions of ion-ion and ion-molecule forces become significant, and consequently, should be included in the vapor-liquid equilibrium calculation. For weak electrolyte solutions the model correlation from the Chen and Wagner (1994) work shows systematic deviations below experimental total pressures. In Figure 3, error distributions of system pressures for SO₂ binary are given as the function of ionic strength of liquid solution. As one can see from the plot, negative deviations of total pressure become significant with increasing of ionic strength of solutions. In the present work molecule-ion interactions are taken into account by introducing a single additional ionic strength dependent salting effect parameter E_{ij} into the mixing rule of equation of state:

$$C_{ij} = C_{ij}^o + \frac{C_{ij}^1}{T} + E_{ij} \cdot I$$

where C_{ij}^o and C_{ij}^1 are the same values as obtained from gas-water binary systems; an empirical salting effect parameter E_{ij} is determined from the gas-salt-water ternary systems for each weak electrolyte. No improvement is obtained by introducing a higher order salting effect parameter. Furthermore, it is assumed that

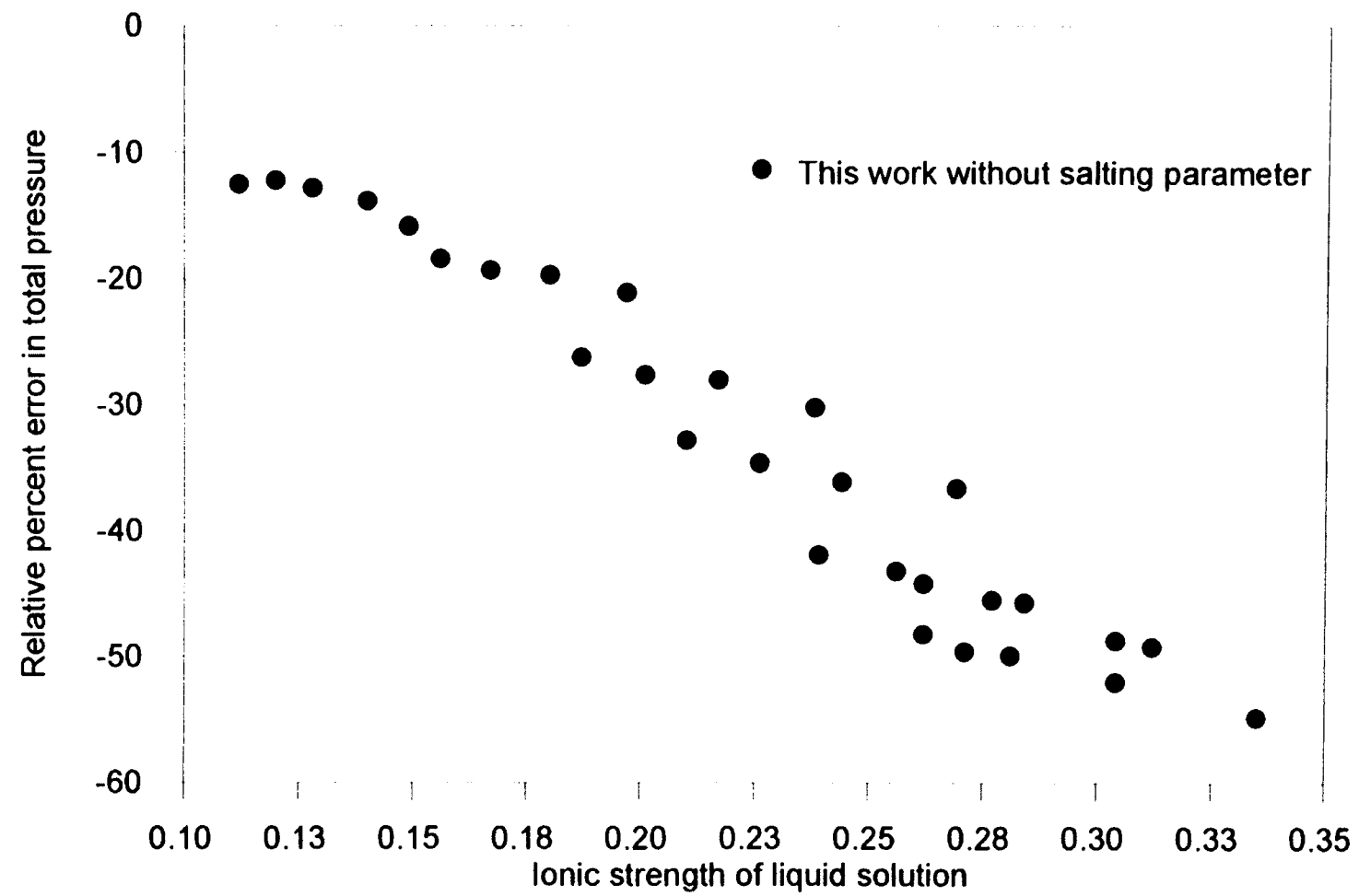


Figure 3. Error distribution for total pressure in the $\text{SO}_2\text{-H}_2\text{O}$ system (Wright and Maass, 1932)

the ion-ion interactions are zero to simplify calculation at present stage of model development. The thermodynamic framework of present work is identical to the previous model.

Regression Data Base

To estimate the salting effect parameters, E_{ij} , for ammonia, carbon dioxide, sulfur dioxide, and hydrogen sulfide reliable experimental vapor-liquid equilibrium ternary data are needed. In Table III, the data base used in determining salting effect adjustable parameters are given.

CO₂-Salt-H₂O ternary systems have been extensively studied experimentally by Rumpf and Maurer (1993c, 1994), Corti et al. (1990), Yasunishi et al. (1979), Markham and Kobe (1941), Nighswander et al. (1989), Takenouchi et al. (1965) and Prutton and Savage (1945). Considering the fact that the experimental measurements by Rumpf and Maurer (1994) covers the largest concentration range of salt, up to 6 molality, it is selected in the regression data base.

For NH₃-salt-H₂O systems, only two data sets are available in the open literature. Perman (1901) measured solubilities of ammonia in dilute aqueous sodium sulfate solutions at temperatures from 298 to 319 K. Rumpf and Maurer (1993a) measured total pressure for aqueous ammonium sulfate solutions at temperatures up to 433 K

Table III

Results of Salting Effect Interaction Parameter Fitting

Aqueous System	No. of Points	Temp K	Pressure bar	Solute mol/kg	Salt mol/kg	AAPD /Ptot Eij=0	Eij	
CO ₂ -NaCl	63	313-433	1.5-96.4	0.05-0.55	4.0-6.0	13.8	5.1	0.00966
NH ₃ -(NH ₄) ₂ SO ₄	83	333-433	0.2-29.9	1.10-23.7	2.0-4.0	22.2	6.4	0.00721
SO ₂ -(NH ₄) ₂ SO ₄	19	333-363	0.4-6.4	0.21-2.1	2.0-4.0	22.5	16.9	-0.00128
H ₂ S-NaCl	238	297-368	1.01	0.01-0.09	1.0-5.0	14.9	4.2	0.00606

AAPD is average absolute percentage deviation

Ptot is the total pressure

$$C_{ij} = C_{ij}^o + \frac{C_{ij}^1}{T} + E_{ij} \cdot I$$

where I is ionic strength

Experimental data sources:

CO ₂ -NaCl-H ₂ O	Rumpf et al. (1994)
NH ₃ -(NH ₄) ₂ SO ₄ -H ₂ O	Rumpf et al. (1993a)
SO ₂ -(NH ₄) ₂ SO ₄ -H ₂ O	Rumpf et al. (1993b)
H ₂ S-NaCl-H ₂ O	Barrett et al. (1988)

and pressures up to 300 bar. It is believed that the Perman measurements are not as accurate as Rumpf and Maurer results because the molality of ammonia in experiments could not be determined properly (Rumpf and Maurer, 1993a). Since salt concentrations from Rumpf and Maurer studies range up to 4 molality, their experimental data are used as the regression data base.

Data from Rumpf and Maurer (1993b) and Hudson (1925) are the only two literature data sources for SO_2 -salt- H_2O system. Hudson investigated the salting effect of potassium chloride and sodium sulfate in the temperature range from 293 to 323 K and at total pressures near one atmosphere. The experimental data from Rumpf and Maurer (1993b) are included in the regression data base because they measured the solubilities of sulfur dioxide in aqueous solutions of ammonium sulfate at temperatures from 313 to 393 K and pressures up to 35 bar.

The open literature data for H_2S -salt- H_2O is extremely scarce. Only Barrett et al. (1988) reported a large set data for the solubilities of hydrogen sulfide in aqueous solutions of NaCl at temperatures between 298 and 368 K and at pressures near one atmosphere. Their measurements are believed reliable because two different analytical methods as volumetric method and gravimetric method were used to cross-check the experimental data.

Ternary System Regression Results

As shown in Table III, the regression results compared with experimental data for system pressures are generally very good, except the sulfur dioxide ternary system. Table III also lists relative deviations with and without adjustable salting parameters. By introducing a salting effect parameter, significant improvements are obtained for CO_2 , NH_3 and H_2S ternary systems.

The influence of temperature on the solubility of CO_2 at constant concentrations of sodium sulfate in aqueous solutions is shown in Figure 4 and 5. This model correlates total pressure very well at temperatures below 393 K, whereas the model underestimates total pressure at 433 K with 11% errors.

Figure 6 is a more detailed comparison between the correlation results and Rumpf and Maurer (1993a) data for solubility of NH_3 in ammonium sulfate aqueous solutions at temperatures from 353 to 433 K and NH_3 concentrations up to 23 molality. The salting-out effects at 1 and 2 molalities are correlated very well at each isotherm.

Excellent agreement between correlated and experimental results is obtained with only 4.2% absolute average deviation for the H_2S - NaCl - H_2O system. Error distributions for correlated and experimental results are shown in Figure 7. It also gives the calculation results

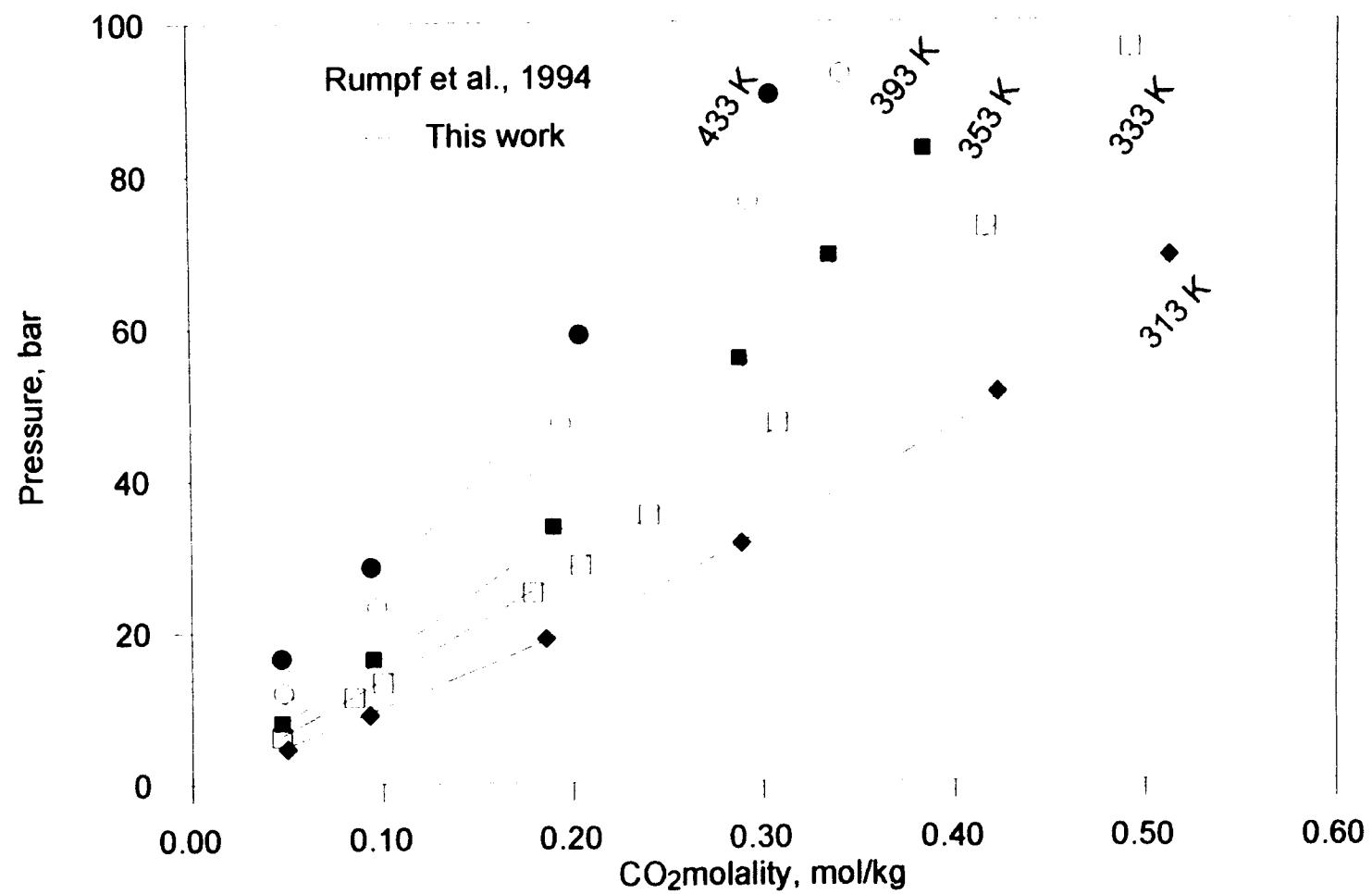


Figure 4. Total pressure for the CO₂-NaCl-H₂O system at 4 NaCl molality

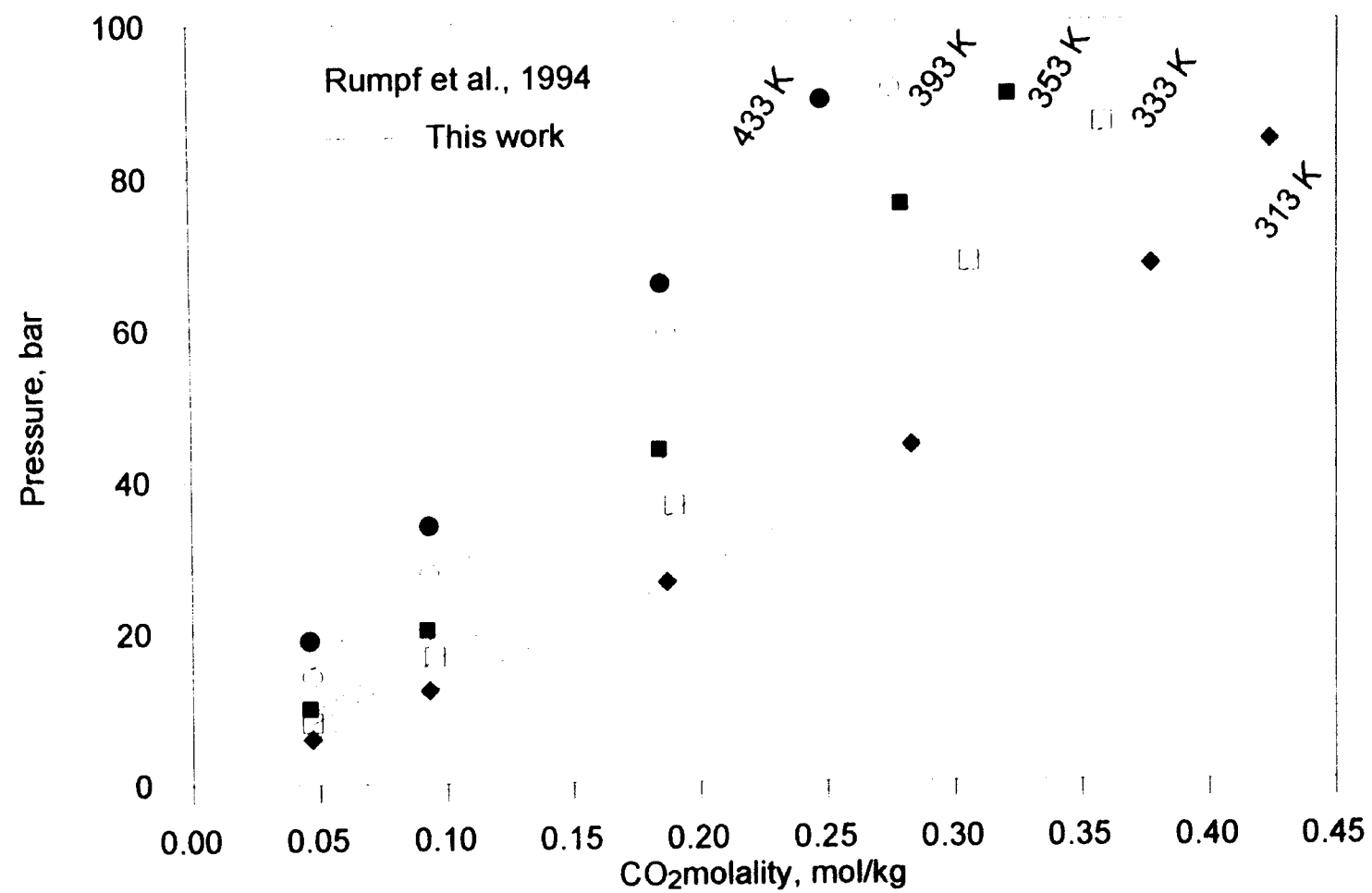


Figure 5. Total pressure for the CO₂-NaCl-H₂O system at 6 NaCl molality

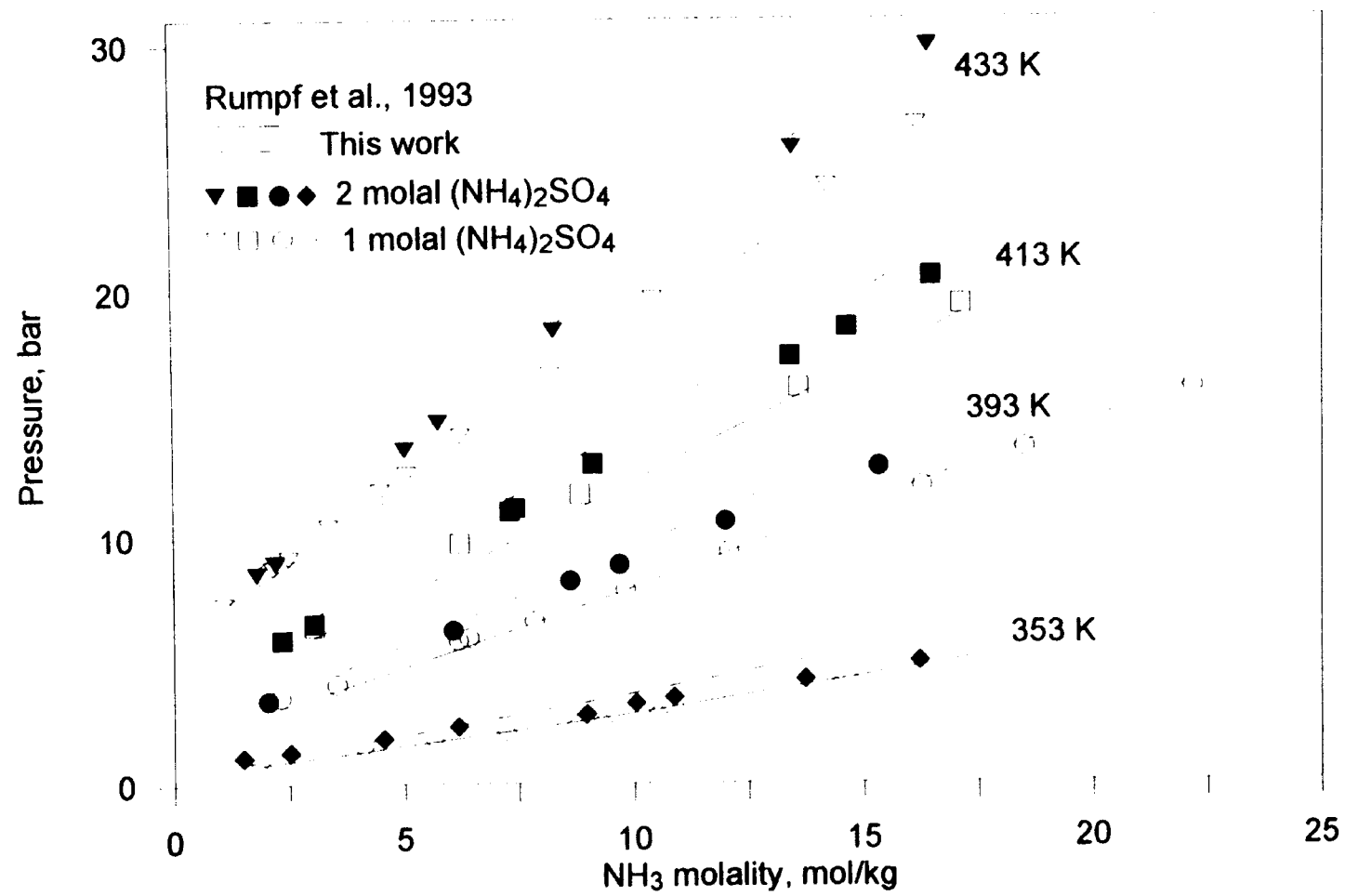


Figure 6. Total pressure for the NH₃-(NH₄)₂SO₄-H₂O

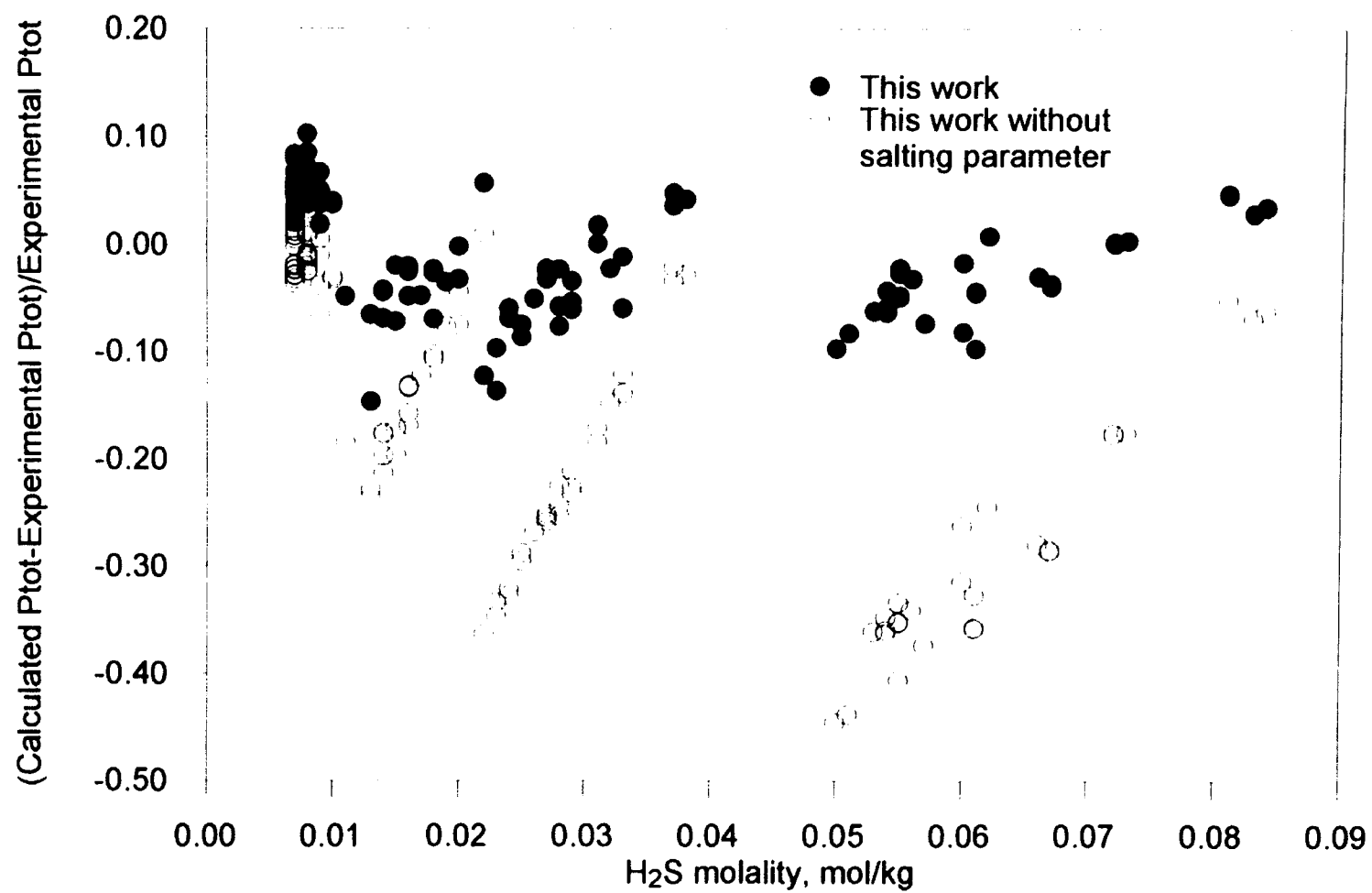


Figure 7. Error distribution for total pressure in the H_2S - NaCl - H_2O system (Barrett et al. 1988)

without the salting effect parameter which results in systematic underestimates of system pressure with errors up to 45%. It is clear that by introducing the salting out parameter, the new model is able to accurately describe the salt containing aqueous solutions.

Predictions for Gas-Salt-H₂O Ternary Systems

Incorporating the salting parameters determined from the regression data base, the new model is tested against the other vapor-liquid equilibrium data over a wide range of temperature, pressure, and salt concentration. The following discussion examines the model predictions system by system.

CO₂-Salt-H₂O Ternary System

This aqueous system has been extensively investigated by many researchers. The predicted and measured results are compared in Table IV, which shows average absolute deviations in total and partial pressures over the entire range of published experimental results.

Rumpf and Maurer (1993c) provided extensive measurements for the solubilities of CO₂ in aqueous solutions of sodium sulfate and ammonium sulfate in the temperature range from 313 to 433 K, total pressures up to 100 bar, and salt concentrations up to 4 molality. The effect of salts on gas solubility are predicted very well.

Table IV

Average Errors in Total and Partial Pressure for the CO₂-Salt -H₂O
System Calculated by This Work

Aqueous System	Experimental Data Sources	No. of Points	Temp K	Pressure bar	Molality		AAPD %	
					CO ₂	Salt	P _{tot}	P _{CO2}
CO ₂ -Na ₂ SO ₄	Rumpf and Maurer(1993c)	102	313-433	0.2-97.1	0.05-0.7	1-2	4.4	--
CO ₂ -(NH ₄) ₂ SO ₄	Rumpf and Maurer (1993c)	90	313-433	0.4-93.7	0.05-0.7	2-4	5.8	--
CO ₂ -Na ₂ SO ₄	Corti et al. (1990)	24	323-348	1-197	0.04-0.3	3.0-3.3	2.9	--
CO ₂ -Na ₂ SO ₄	Yasunishi et al. (1979)	26	288-308	1.01	0.008-0.03	0.3-1.76	14.8	--
CO ₂ -(NH ₄) ₂ SO ₄	Yasunishi et al. (1979)	31	288-308	1.01	0.007-0.04	0.3-3.87	15.0	--
CO ₂ -Na ₂ SO ₄	Markham and Kobe (1941)	8	298-313	1.01	0.01-0.03	0.3-1.5	--	15.5
CO ₂ -NaCl	Nighswander et al. (1989)	34	353-473	21.1-102	0.1-0.9	0.18	8.6	--
CO ₂ -NaCl	Takenouchi et al. (1965)	81	423-673	100-1400	0.4-10	1.1-4.3	2.5	--
CO ₂ -CaCl ₂	Prupton and Savage (1945)	116	349-394	15-885	0.05-1.1	2-5.8	3.1	--

AAPD is average absolute percentage deviation

P_{tot} is the total pressure

P_{CO2} is the partial pressure of CO₂

The average deviations in the total pressure are less than 5.8%.

Corti et al. (1990) reported 24 measurements of solubility for CO₂ in aqueous sodium sulfate solutions at 323 and 348 K. The data up to 200 bar are compared with the present work. This model accurately reproduces salting out effect for experimental data with only 2.9% average error.

The new model agrees fairly well with the results reported by Yasunishi et al. (1979) at low temperature and dilute solutions of CO₂ with sodium sulfate and ammonium sulfate.

Markham and Kobe (1941) studied the CO₂-Na₂SO₄-H₂O system at fixed partial pressure of carbon dioxide. The present work yields fair agreement with their results.

Nighswander et al. (1989) investigated the CO₂-NaCl-H₂O system in the temperature range from 353 to 473 K. The predictions of this work agree very well with their data up to 100 bar total pressure.

High temperature and pressure experimental data for the CO₂-NaCl-H₂O system as well as the CO₂-H₂O binary were measured up to 1400 bar and up to 673 K at constant salt molality by Takenouchi et al. (1965). Prutton and Savage (1945) also reported 116 data points at high pressure for the CO₂-CaCl₂-H₂O system. The predictions of this work compare very well with these two data sets. The relative errors in total pressure are only 2.5 and 3.1%

respectively. Note that the low pressure $\text{CO}_2\text{-H}_2\text{O}$ binary data of Takenouchi et al. are used in the C_{ij}^0 and C_{ij}^1 parameters fit.

Figure 8 shows the salting-out effect of ammonium sulfate on the solubility of carbon dioxide. This work clearly demonstrates influence of salt on the solubility of carbon dioxide. For example, the total pressures at 0.2 molality carbon dioxide and 393 K are 27, 39, and 59 bar corresponding to the salt free, 2 molality and 4 molality ammonium sulfate concentration, respectively. The system pressure is doubled at 4 molality salt compared to the salt-free solutions.

The influence of ammonium sulfate and sodium sulfate at different temperatures, pressures, and concentrations are shown in Figure 9 and Figure 10. Again, the new model predictions are in excellent agreement with experimental results at temperatures below 393 K, whereas the model somewhat underestimates the system pressure of CO_2 at 433 K.

Figure 11 demonstrates the capability of the new model to predict effects of salt and temperature on the carbon dioxide solubility at temperatures to 623 K and total pressures to 1400 bar (Takenouchi et al., 1965). The dashed lines show the calculated results of this work for salt free $\text{CO}_2\text{-H}_2\text{O}$ binary system. The salting out effect of sodium sulfate in water is clearly shown in the figure. The predicted results of salting out effect and

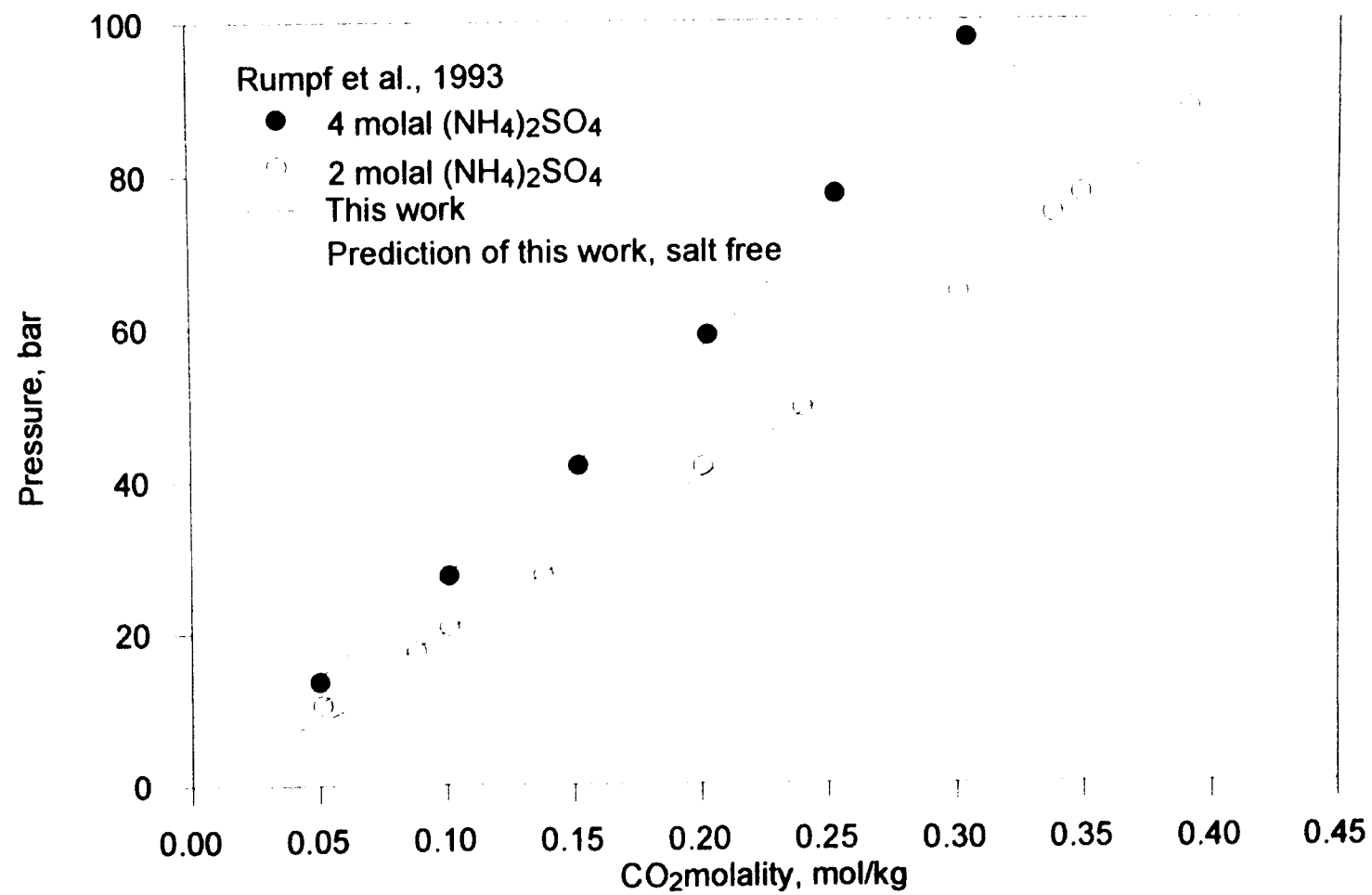


Figure 8. Total pressure for the CO_2 - $(\text{NH}_4)_2\text{SO}_4$ - H_2O system at 393 K

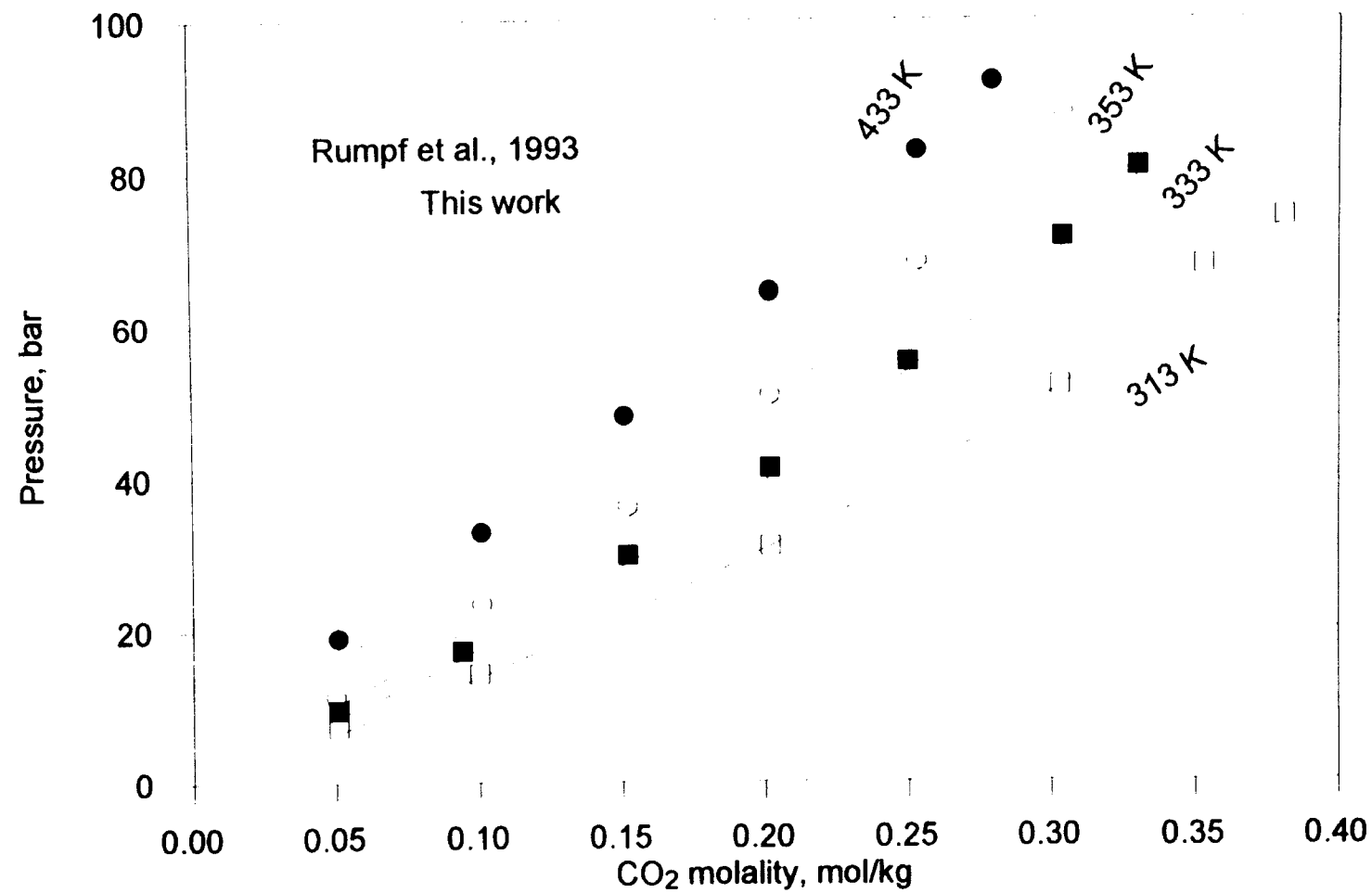


Figure 9. Total pressure for the CO₂-Na₂SO₄-H₂O system at 2 Na₂SO₄ molality

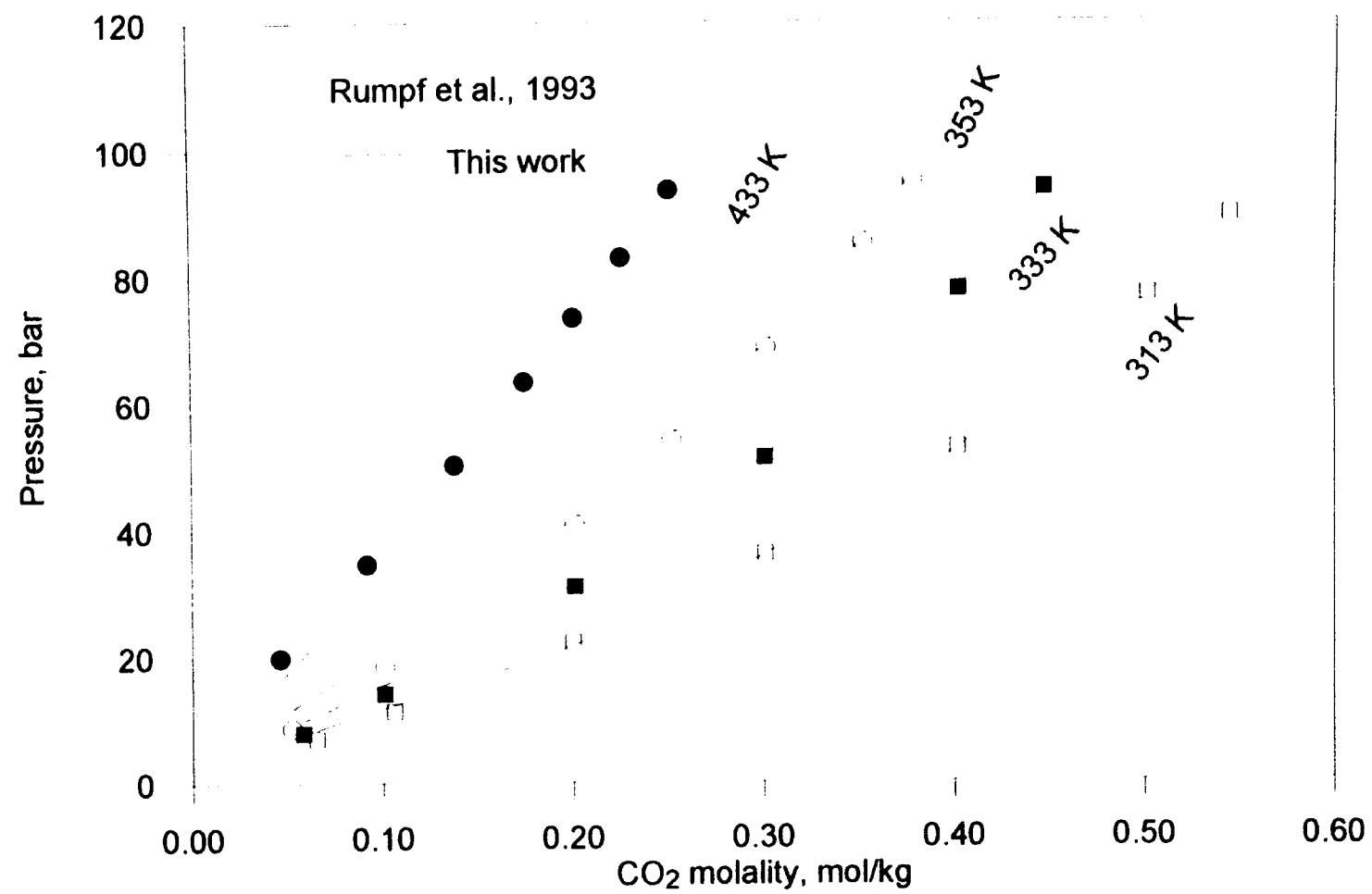


Figure 10. Total pressure for the CO₂-(NH₄)₂SO₄-H₂O system at 4 (NH₄)₂SO₄ molality

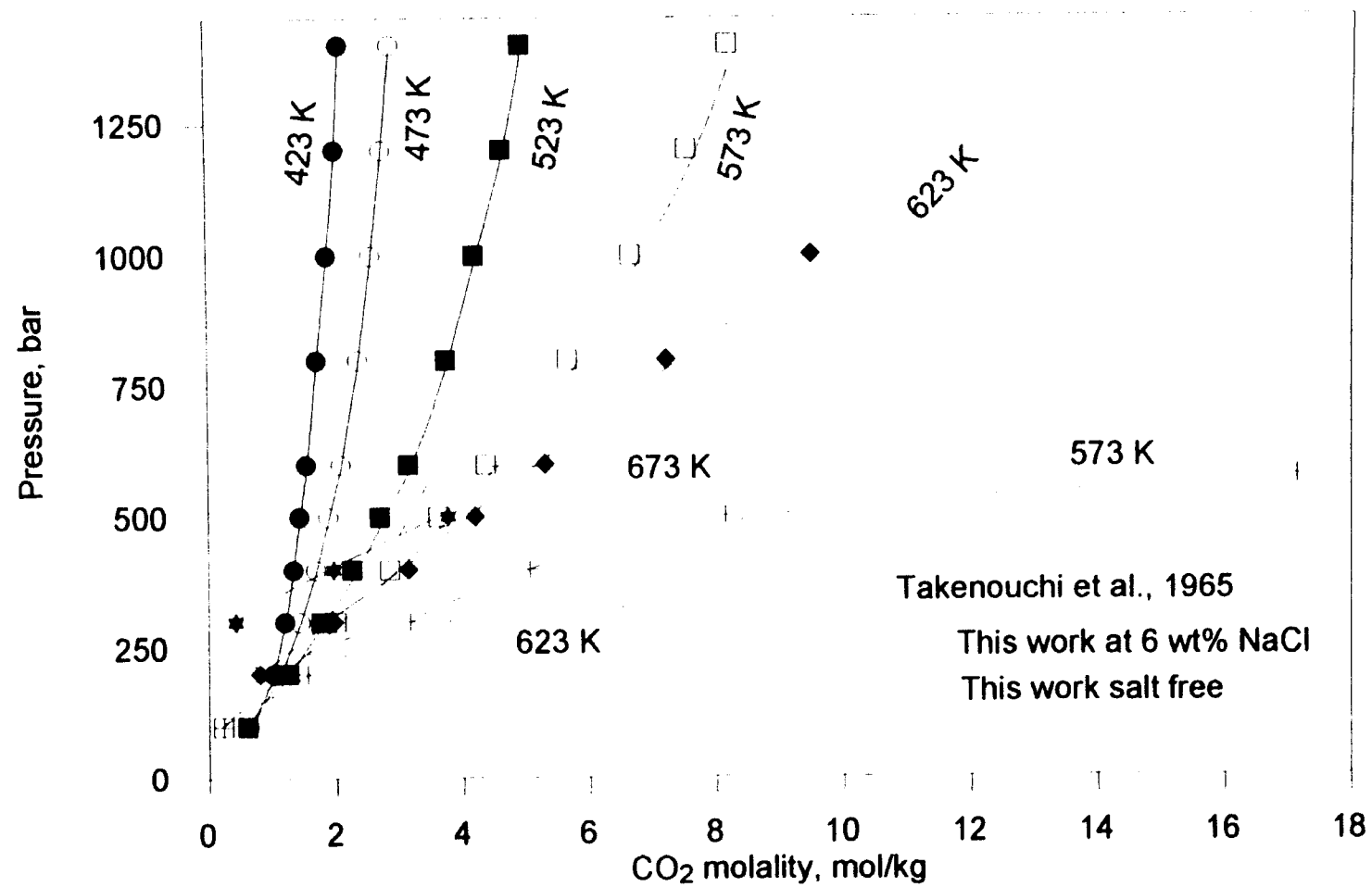


Figure 11. Total pressure for the CO₂-NaCl-H₂O system at 6 wt% NaCl

temperature effect on total pressure of the system yield excellent agreement with the observed data. The solubility of CO_2 in water depends heavily on the concentration of salt. As a result, solubility of CO_2 decreases rapidly as the concentration of sodium sulfate increases, even at high system pressure.

NH_3 -Salt- H_2O Ternary System

Two data sets available in the open literature are reported by Rumpf and Maurer (1993a) and Perman (1901). Table V is a detailed comparison of calculated results with the Perman data at constant concentration of ammonia sulfate and sodium sulfate. The prediction results for system pressure are typically around 7% below Perman's results.

Figure 12 demonstrates the model prediction for solubility of ammonia in aqueous sodium sulfate solutions at each isotherm from 333 to 433 K. The model describes the system pressure nearly within the experimental uncertainties except at very high molalities of ammonia.

A summary comparison of the model and experimental results is shown in Table VI. In general, the model predictions show better agreement with Rumpf and Maurer (1993a) data.

Table V

Total pressure for the $\text{NH}_3\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$ system at
0.35 molality NH_3 and 6.08 molality Na_2SO_4

Temp K	Total Pressure, bar	
	Experimental ^a	This Work
302.5	0.224	0.210
304.3	0.245	0.228
306.6	0.270	0.252
308.0	0.288	0.268
309.7	0.310	0.289
311.1	0.328	0.306
313.3	0.362	0.336
316.3	0.414	0.381
319.4	0.470	0.433

^a Perman (1901)

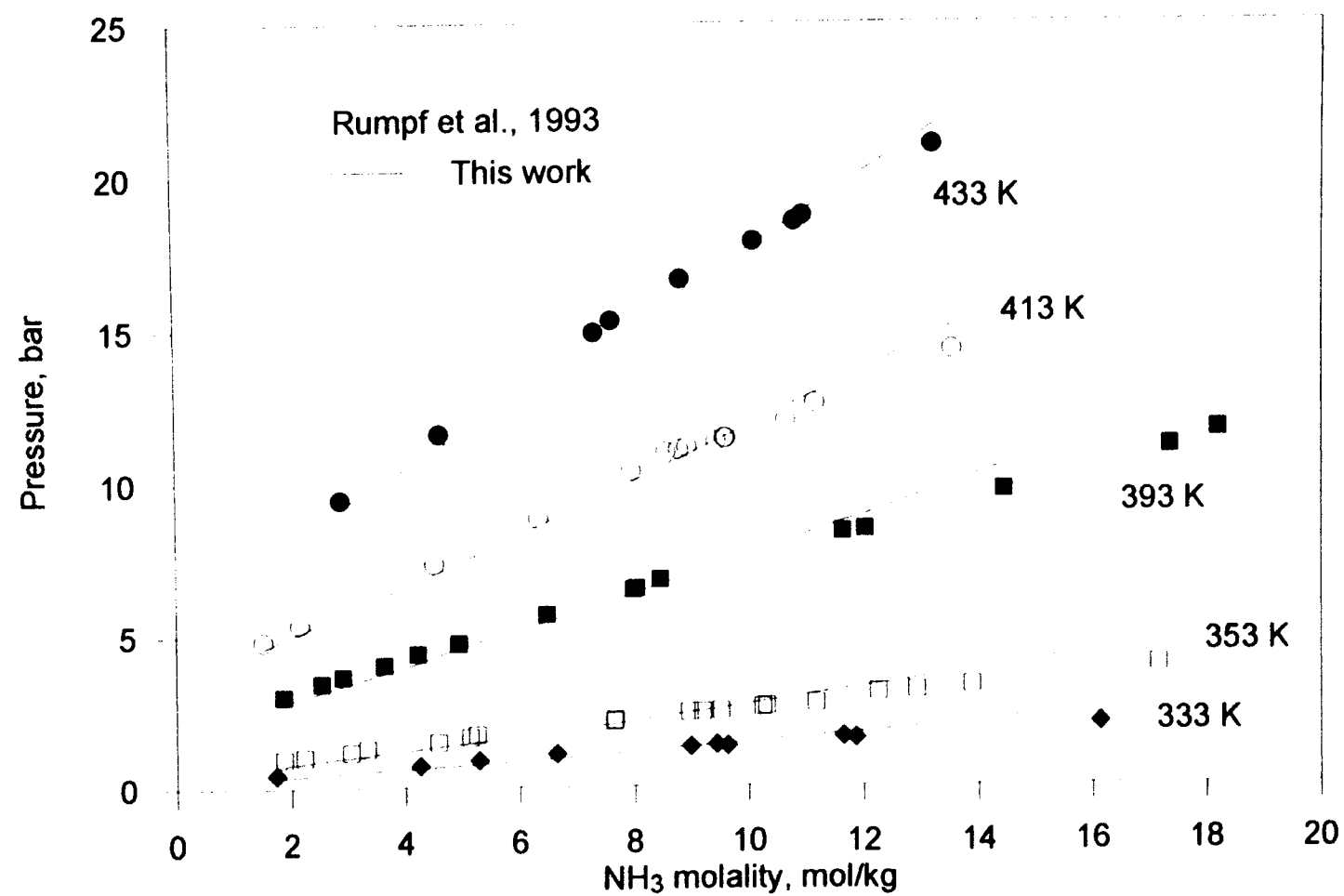


Figure 12. Total pressure for the NH₃-Na₂SO₄-H₂O system at 1 Na₂SO₄ molality

Table VI

Average Errors in Total Pressure for the NH_3 -Salt - H_2O
System Calculated by This Work

Aqueous System (Reference)	No. of Points	Temp K	Pressure bar	Molality		AAPD %	
				CO ₂	Salt	P _{tot}	
NH ₃ -Na ₂ SO ₄	-a	102	333-433	0.44-21.0	1.0-18.2	1-2	7.4
NH ₃ -Na ₂ SO ₄	-b	33	298-319	0.21-0.80	0.35-0.38	6.1-10.3	9.8

AAPD is average absolute percentage deviation
Ptot is the total pressure

Experimental data sources:

a Rumpf et al. (1993 a)

b Perman (1901)

SO₂-Salt-H₂O Ternary System

Rumpf and Maurer (1993b) and Hudson (1925) are the only two literature data sources for this system. In Table VII, the comparison between model results and two data sets is summarized. As one can see from the table, the prediction results for Rumpf and Maurer (1993b) data give poor performance with deviations frequently ranging from 10 to 20%. The predictions of this work show fair agreement with the Hudson (1925) data.

Although good agreement with experimental data of Rumpf and Maurer (1993b) is obtained at low ammonia concentration, this model systematically underestimates system pressure at sulfur dioxide concentrations higher than 1.5 molality as shown in the Figure 13.

Predictions for Multisalt Weak Electrolyte Systems

With parameters regressed from gas solubility in single salt ternary systems, the new model is used to predict the solubility of gases in multisalt solutions. Predictions are straightforward and no additional parameter adjustments are needed. The prediction results for multisalt systems are used to evaluate reliability and accuracy of new approach.

Rumpf and Maurer (1993 c) reported 35 data points for the solubility of CO₂ in an aqueous solution containing a mixture of sodium sulfate and ammonium

Table VII

Average Errors in Total and Partial Pressure for the SO₂-Salt -H₂O
System Calculated by This Work

Aqueous System (Reference)	No. of Points	Temp K	Pressure bar	Molality CO ₂	Salt	AAPD % P _{tot} P _{CO2}		
SO ₂ -Na ₂ SO ₄	-a	65	313-393	0.11-32.80	0.15-5.80	0.5-1.0	18.5	--
SO ₂ -Na ₂ SO ₄	-b	23	293-323	1.01	0.73-1.67	0.4-2.8	--	10.5
SO ₂ -KCL	-b	40	283-353	1.01	0.35-3.97	0.7-4.4	13.8	17.1

AAPD is average absolute percentage deviation

P_{tot} is the total pressure

P_{CO2} is the partial pressure of CO₂

Experimental data sources:

a Rumpf et al. (1993 b)

b Hudson (1925)

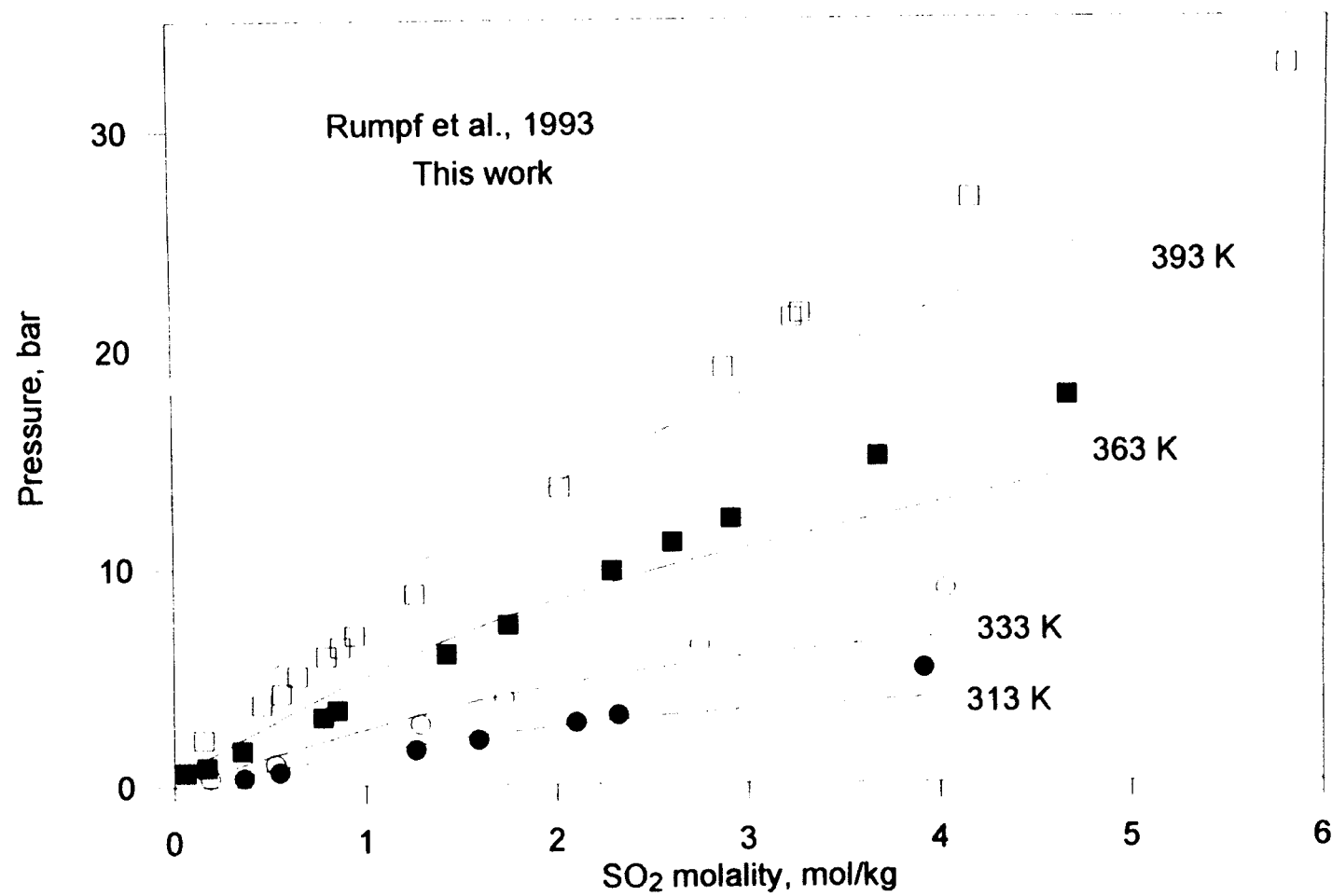


Figure 13. Total pressure for the SO₂-Na₂SO₄-H₂O system at 2 Na₂SO₄ molality

sulfate. Temperatures range from 313 to 433K and pressures from 3 to 91 bar. A comparison between the experimental data and predicted results yields an average absolute deviation in total pressure of 5.8%. The results are shown in Figure 14. The model predicts the solubility of CO₂ very well at 313, 333 and 353K, whereas the total pressures at 413 and 433K are typically underestimated by 10%.

Figure 15 shows the influence of ammonium sulfate and sodium sulfate on the solubility of carbon dioxide from the same data set. At fixed ionic strengths of about 2 molality and constant temperature at 393 K, the model predictions compare well with experimental data. At constant total pressure of 40 bar, for example, the solubility of carbon dioxide is 0.28 molality in salt-free water whereas it is only 0.17 molality in a 2 molality aqueous mixture of ammonium sulfate and sodium sulfate.

Discussion

The model correlations and predictions agree very well with vapor-liquid equilibrium data for carbon dioxide, ammonia, and hydrogen sulfide over a wide range temperature, pressure, and composition. Harvey and Prausnitz (1989) presents a new model to calculate phase equilibria for aqueous solutions containing gases and salts. Their model results only qualitative agreed with

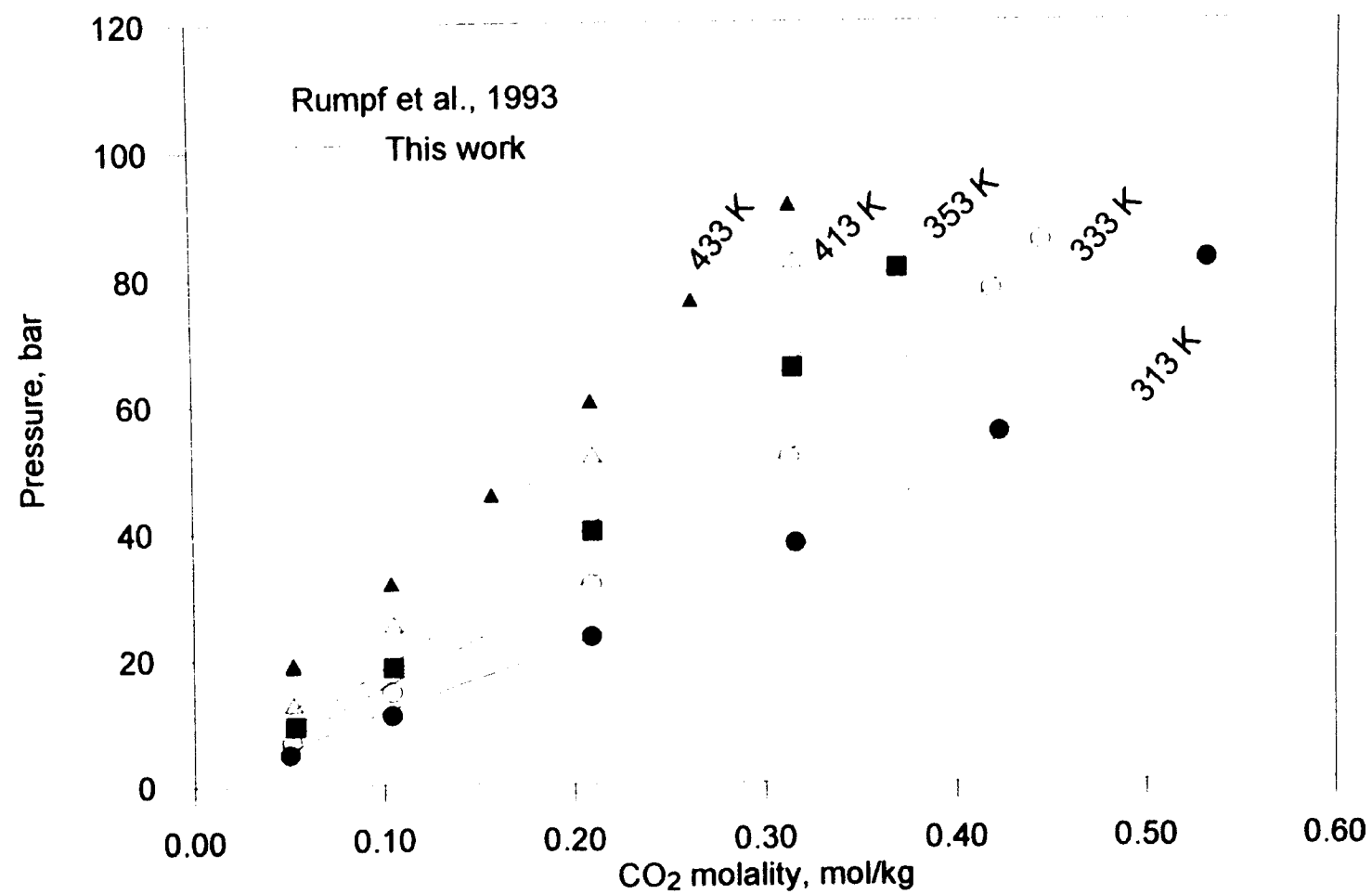


Figure 14. Total pressure for the CO₂-Na₂SO₄-(NH₄)₂SO₄-H₂O system at 1 Na₂SO₄ and 1 (NH₄)₂ SO₄ molality

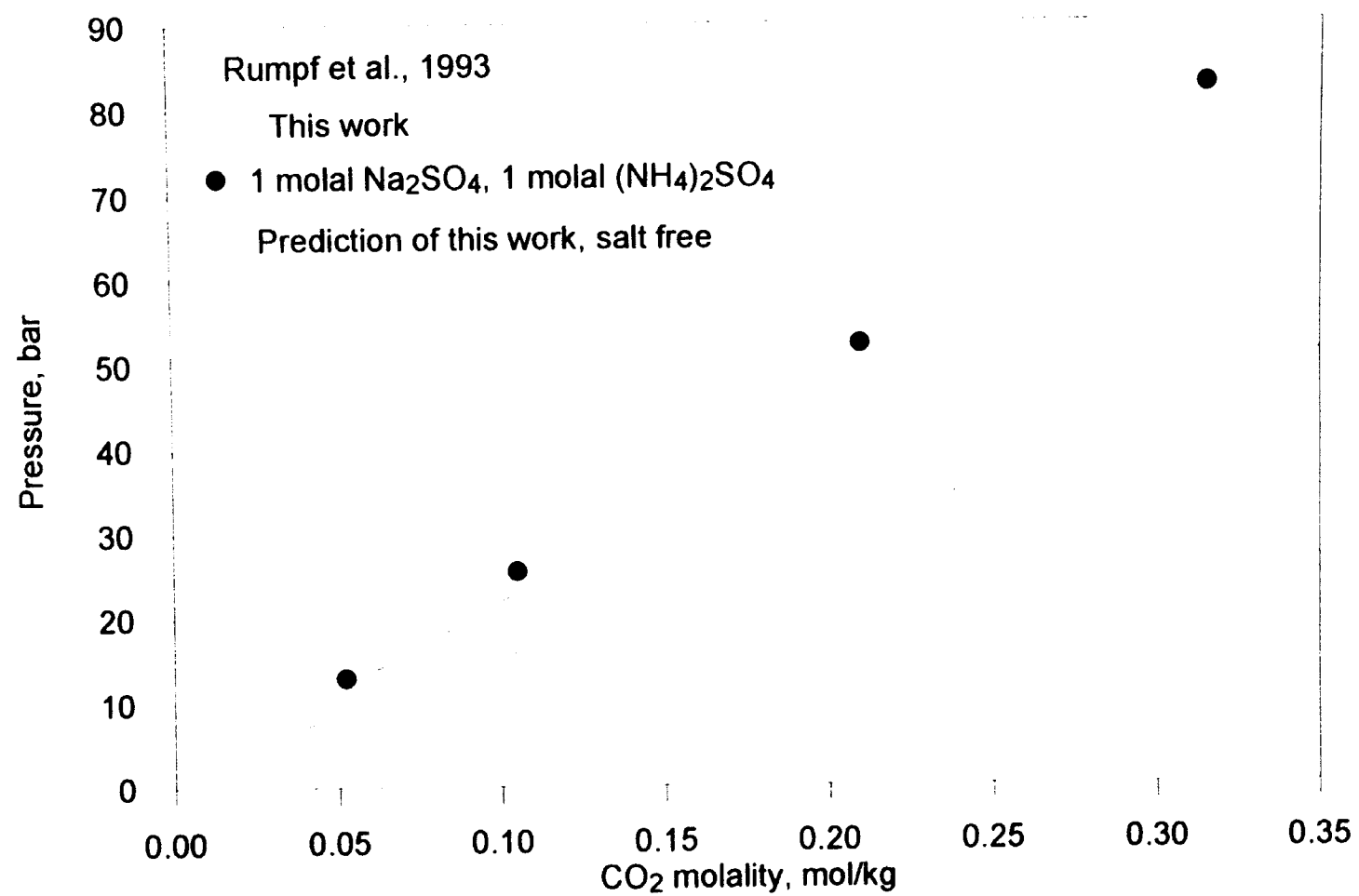


Figure 15. Total pressure for the CO₂-Na₂SO₄-(NH₄)₂SO₄-H₂O system at 393 K

experiment for CO_2 -salt- H_2O systems (Takenouchi et al., 1965, Prutton and Savage, 1945). The salting-out effect for high salt concentrations is significantly underpredicted for all the systems tested. Aasberg-Petersen et al. (1991) developed a new method to predict high pressure gas solubilities in aqueous solutions for which the interaction parameters are determined from low pressure experimental data. The model results agree fairly well with CO_2 - NaCl - H_2O system by Takenouchi et al. (1965) at low salt concentrations, but it significantly overestimates the total pressure of CO_2 at 30 wt% CaCl_2 concentration.

For sulfur dioxide system, the salting effect is significantly underpredicted at high salt concentrations for Rumpf and Maurer (1993) data. The systematic errors for Rumpf and Maurer data in the model calculations most likely arise from two sources: (1) The binary data from the same laboratory are not consistent with the data of Rabe and Harris (1963) which is the binary regression data base for this model. It is believed that Rabe and Harris data are the most reliable data source for this system as suggested by Goldberg and Parker (1985) in their evaluation for the SO_2 - H_2O system; (2) There is a strong possibility that the dissociation constants for SO_2 and HSO_3 may not be accurate. Sulfur dioxide strongly dissociates in water. The dissociation constant for SO_2 in water is about three to five order of magnitude larger

than those of NH_3 , CO_2 , and H_2S . The accuracy of dissociation constants of SO_2 and HSO_3^- may significantly impact the dissociation equilibrium between molecular and ionic species in liquid phase which in turn strongly affect phase equilibrium calculation.

The different effects of a salt on gas solubility can be attributed to difference in the gas-ion interactions or to the different hydration structure of solutions. The present model incorporates ionic charge and molality of salts to account for salting effect on solubilities of weak electrolyte gases. The present model is not able to distinguish between different ionic species. The good agreement between the model results and experimental measurements may suggest that the present model treatment successfully describes phase behavior of aqueous electrolyte solutions to a certain extent without going detailed into molecular structure of the solutions. To pursue this problem, it may be necessary to develop a suitable mixing rule for the SRK equation of state to incorporate additional ionic species information such as ionic radius to account for molecule-ion interactions for different salts.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

A new approach has been developed following the Chen and Wagner (1994) work for predicting vapor-liquid phase behavior of aqueous weak electrolyte solutions containing strong electrolytes. The approach is confined within the thermodynamic framework for aqueous weak electrolyte solutions outlined by Edwards et al. (1975). A Soave-Redlich-Kwong (SRK) equation of state (Soave, 1972) is used to obtain the fugacity coefficients of molecular species in both vapor and liquid phases. The activity coefficients of ionic species present in liquid phase are calculated by a modified Debye-Huckel equation.

In this work, an additional ionic strength dependent parameter is introduced to take into account salting effect. This adjustable salting effect parameter is determined from weak electrolyte gas-salt-water ternary systems. It should be pointed out that only one temperature and one ionic strength dependent parameter are required to predict the single gas solubility in

multisalt aqueous solutions for most solutes. NH_3 and $\text{C}_6\text{H}_5\text{OH}$ require an additional parameter for the volume term in the SRK equation of state.

Evaluation of the new approach using experimental total or partial pressures over a wide range of temperature and concentration indicates that the model performs very well for carbon dioxide, ammonia, and hydrogen sulfide systems. For example, total pressures for CO_2 -Salt- H_2O ternary have been calculated at temperatures from 288 to 673 K, pressures up to 1400 bar, and salt concentrations up to 6 molality with typically less than 10% average absolute deviation from experimental data. Predicted system pressures for CO_2 systems have been significantly improved compared to the models of Harvey and Prausnitz (1989) and Aasberg-Petersen et al. (1991).

The main objective of this work has been achieved in terms of simplicity, reliability and predictability.

Recommendations

There is still much room left for improvement of the model or its extended application. The following work is recommended to improve this model.

(1) Select an equation of state which is capable of accurate correlation phase equilibrium for aqueous binary weak electrolyte solutions.

(2) Conduct a detailed evaluation of all the chemical dissociation constants needed to model phase equilibrium of the aqueous weak electrolyte solutions with special emphasis on the SO_2 and HSO_3^- dissociation constants.

(3) Develop a suitable mixing rule for the SRK equation of state to incorporate additional ionic species information to account for molecule-ion interactions for different salts.

(4) Compile a detailed and extensive evaluation of the vapor-liquid equilibrium experimental data of the aqueous weak electrolyte binary and multicomponent systems and aqueous multisalt and gases systems.

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