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Phase Equilibria for Aqueous Systems Containing Salts and Carbon Dioxide. Application of Pitzer's Theory for Electrolyte Solutions[†]

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The semiempirical specific-interaction model developed by Pitzer is applied to aqueous salt solutions that also contain a dissolved nonelectrolyte. Pitzer's model is used to describe phase equilibria for aqueous solutions containing either sodium chloride and carbon dioxide to 600 bar or sodium sulfate and carbon dioxide to 200 bar at several temperatures. In contrast to predictions reported by previous authors, we find that, over wide ranges of pressure and temperature, Pitzer's equations provide an excellent description of salt solubilities in these ternary systems.

Introduction

The semiempirical specific-interaction model (SSIM) of Pitzer[1] has been used extensively to describe the thermodynamic properties of ionic aqueous solutions over wide ranges of concentration, including the region near saturation. For several electrolytes, Pitzer coefficients are available as a function of temperature and pressure.[2] For aqueous mixtures of electrolytes, the Pitzer formalism provides a useful predictive tool because it provides the properties of multicomponent mixtures using only information on the binary systems.

However, aqueous mixtures containing both ionic and nonionic solutes have been studied only rarely within the framework of the Pitzer approach. Pitzer[2] has discussed the dissolution of silica in salt-water systems in terms of the SSIM, and recently, Maeda et al.[3] have calculated ionic-strength effects on the dissociation constant of ammonia. Unfortunately in both cases the concentration of the nonionic species is very small and the electrolyte plays the major role. To the best of our knowledge, only Barta and Bradley[4] have used the SSIM to describe gas solubilities in high-temperature brines. These authors also use the SSIM approach to predict the effect of dissolved gases on the solubility of sodium chloride in water.

Recently,[5] we have measured the effect of a dissolved gas on the solubility of electrolytes in aqueous solutions. We studied the system CO_2–Na_2SO_4–H_2O at 50 and 75 °C; changes in the solubility of the salt due to CO_2 were described by use of a simple thermodynamic-consistency procedure that relates this change in salt solubility to the Setschenow constant, that is, to the salting out of the gas by the salt. In addition to some simplifying assumptions, that procedure requires also information on the ternary system to obtain the derivative of the activity coefficient for the dissolved CO_2 with respect to salt concentration.

The previously published procedure is capable of describing the observed solubility changes to high CO_2 pressures (150 bar). At higher pressures, the procedure fails, probably because the simplifying assumptions are no longer valid for relatively high concentrations of CO_2 in the aqueous solution.

The previously published procedure was also applied to the system CO_2–$NaCl$–H_2O; the solubility of the salt as a function of CO_2 pressure was predicted at several temperatures in the range 50–250 °C. Predictions at 50 °C were confirmed experimentally. However, the estimated solubilities disagree with those calculated by Barta and Bradley,[4] who predicted that dissolved CO_2 increases $NaCl$ solubility below 100 °C and also above 250 °C, while in the range 150–200 °C, dissolved CO_2 decreases $NaCl$ solubility. Our data at 50 °C show that dissolved CO_2 decreases $NaCl$

solubility, and our predictions indicate that this decrease should also be observed at higher temperatures. The discrepancy between our calculated results and those calculated by Barta and Bradley with the SSIM approach prompted us to study the applicability of the SSIM to phase equilibria for aqueous systems containing ions and gaseous nonelectrolytes. Our aim in this work is to predict the effect of dissolved CO_2 on the solubility of salts in aqueous solutions using Pitzer parameters obtained from the effect of a dissolved salt on the solubility of CO_2.

Solubility Equilibria in Gas–Salt–Water Systems

We use in this work essentially the same notation as that used previously:[5] 0, solvent (water); 1, gas (CO_2); and 2, electrolyte (which dissociates into ν_+ cations and ν_- anions).

The effect of a dissolved salt on the solubility of a gas (salting in/out) can be described in terms of the activity coefficient γ_{1x} of the solute, which is given by[6]

$$\ln \gamma_{1x} = \ln \frac{y_1 \phi_1 P}{x_1 H_1^\dagger} - \int_{P^{sat\dagger}}^{P} \frac{\bar{v}_1}{RT} \, dP \qquad (1)$$

Subscript x indicates that γ_{1x} is defined by using mole fractions. Here $H_1^\dagger$ is the Henry's constant for solute 1 in salt-free water ($m_2 = 0$), x_1 is the mole fraction of solute 1 in the solution (calculated on the basis of total salt dissociation), y_1 is the mole fraction of component 1 in the vapor phase, $\bar{v}_1$ is the partial molar volume of solute 1 in aqueous solution at infinite dilution, $P^{sat\dagger}$ is the vapor pressure of the solvent, and ϕ_1 is the vapor-phase fugacity coefficient of component 1. Comparing the activity coefficient of solute 1 in salt-free water with that in the electrolyte solution, for the same fugacity of the gas in the vapor, we get

$$\ln \frac{\gamma_{1x}}{\gamma_{1x}^\dagger} = \ln \frac{x_1^\dagger}{x^1} - \int_{P^{sat\dagger}}^{P} \frac{(\bar{v}_1 - \bar{v}_1^\dagger)}{RT} \, dP \qquad (2)$$

where superscript † denotes thermodynamic properties in the absence of salt. Activity coefficients are converted from the mole-fraction scale to the molal scale through

$$\gamma_1 = \gamma_{1x} \frac{1 - x_1}{(1 + \nu(MW)m_2)} \qquad (3)$$

(1) Pitzer, K. S. *J. Chem. Phys.* **1973**, 77, 268.
(2) Pitzer, K. S. *Rev. Mineral.* **1987**, 17, 97.
(3) Maeda, M.; Hisada, O.; Ito, K.; Kinjo, Y. *J. Chem. Soc., Faraday Trans. 1* **1989**, 85, 2555.
(4) Barta, L.; Bradley, D. J. *Geochim. Cosmochim. Acta* **1985**, 49, 195.
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(6) Prausnitz, J. M.; Lichtenthaler, R. M.; de Azevedo, E. G. *Molecular Thermodynamics of Fluid Phase Equilibria*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1986.

where m is molality, $\nu = \nu_+ + \nu_-$ is the number of ions produced by the dissociation of the salt, and MW is the molecular weight of the solvent. In the remainder of this work all activity coefficients are based on the molal scale.

Equation 2 can be compared to the well-known Setschenow equation

$$\ln (x_1^\dagger/x_1) = k_{21}m_2 \qquad (4)$$

where k_{21}, the Setschenow coefficient, indicates the effect of salt (solute 2) on the solubility of solute 1.

The equilibrium condition for salt solubility is

$$\mu_2^s(T,P) = \mu_2^0(T,P) + \nu RT \ln (Qm_2\gamma_2)^{sat} \qquad (5)$$

where μ_2^s denotes the chemical potential of solid salt, $Q = (\nu_+^{\nu_+}\nu_-^{\nu_-})^{1/\nu}$, and μ_2^0 is the chemical potential of the electrolyte in the standard state. For the aqueous electrolyte, we use the hypothetical standard state of an ideal dilute solution at unit molality at the pressure and temperature of the solution. Using this standard state, the activity of the electrolyte in the saturated solution, $(Qm_2\gamma_2)^{sat}$, is a function of pressure and temperature but it is independent of the concentration of any other solute.

From (5) it follows that the solubility of the salt in a solution containing a nonionic solute can be obtained if we have a method of estimating γ_2. The SSIM provides a simple expression for the activity coefficients of the components in solution.

Pitzer Equations

Pitzer[7] has presented equations for the activity coefficients of the ionic and nonionic components of an aqueous mixture. For the electrolyte, the mean activity coefficient is given by

$$\ln \gamma_2 = \ln \gamma_2^* + \frac{2}{\nu}m_1(\nu_+\lambda_{1+} + \nu_-\lambda_{1-}) + \frac{3}{\nu}m_1^2(\nu_+\tau_{11+} +$$
$$\nu_-\tau_{11-}) + \frac{2\nu_+\nu_-}{\nu}m_1m_2\left(6\tau_{1+-} + 3\left|\frac{z_-}{z_+}\right|\tau_{1++} + 3\left|\frac{z_+}{z_-}\right|\tau_{1--}\right) \quad (6)$$

where λ and τ are two-body and three-body interaction parameters, respectively, and where γ_2^* is the activity coefficient of the aqueous electrolyte in the absence of solute 1 ($m_1 = 0$), given by

$$\ln \gamma_2^* = |z_-z_+|f^\gamma + \frac{2\nu_+\nu_-}{\nu}m_2B^\gamma + \frac{2(\nu_+\nu_-)^{3/2}}{\nu}m_2^2C^\gamma \quad (7)$$

where

$$B^\gamma = 2\beta^0 + \frac{2\beta^1}{\alpha I}\left(1 - \left(1 + \alpha I^{1/2} - \alpha^2\frac{I}{2}\right)\exp(-\alpha I^{1/2})\right) \quad (8)$$

$$f^\gamma = -A_\phi\left(\frac{m^{1/2}}{1 + bm^{1/2}} + \frac{2}{b}\ln (1 + bm^{1/2})\right) \quad (9)$$

Here A_ϕ is the Debye–Hückel slope for the osmotic coefficient, I is the ionic strength, $\alpha = 2.0$, and $b = 1.2$. β^0, β^1 and C^γ are temperature- and pressure-dependent Pitzer parameters reported in the literature.[8]

To simplify notation, we define

$$\Lambda_{12} = (\nu_+\lambda_{1+} + \nu_-\lambda_{1-}) \qquad (10)$$

$$\Gamma_{112} = (\nu_+\tau_{11+} + \nu_-\tau_{11-}) \qquad (11)$$

$$\Gamma_{122} = \left(2\tau_{1+-} + \left|\frac{z_-}{z_+}\right|\nu_1^{++} + \left|\frac{z_+}{z_-}\right|\tau_{1--}\right) \qquad (12)$$

The mean activity coefficient of the electrolyte in the mixture is then given by

$$\ln \gamma_2 = \ln \gamma_2^* + \frac{2}{\nu}m_1\Lambda_{12} + \frac{3}{\nu}m_1^2\Gamma_{112} + \frac{6\nu_+\nu_-}{\nu}m_1m_2\Gamma_{122} \quad (13)$$

For the nonionic solute, the activity coefficient is given by

$$\ln \gamma_1 = \ln \gamma_1^\dagger + 2m_2\Lambda_{12} + 6m_1m_2\Gamma_{112} + 3m_2^2\nu_+\nu_-\Gamma_{122} \quad (14)$$

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(7) Pitzer, K. S. *Activity Coefficients in Electrolyte Solutions*; CRC Press, in press.

T, °C	m_2^{sat}(calc)	m_2^{sat}(expt)	γ_2^{sat}
25	6.145	6.146	1.006
50	6.279	6.275	1.022
75	6.355	6.460	0.977
100	6.650	6.680	0.919
150	7.207	7.198	0.724
200	7.959	7.973	0.503
250	9.073	8.989	0.299

where $\gamma_1^\dagger$ is the activity coefficient of the nonionic solute in salt-free water ($m_2 = 0$), given by

$$\ln \gamma_1^\dagger = 2m_1\lambda_{11} + 3m_1^2\tau_{111} \qquad (15)$$

Activity coefficients γ_1 and $\gamma_1^\dagger$ are obtained from solubility data for the nonionic solute in the salt-containing solution and in salt-free water, respectively, through (1)–(3).

Sources of Experimental Data and Evaluation of Parameters

To calculate γ_2^*, we use published parameters[8] for ionic interactions in binary aqueous electrolyte solutions of NaCl and Na_2SO_4.

Pitzer et al.[8] have given an equation for the chemical potential of solid NaCl as a function of temperature and pressure. That equation, coupled with the SSIM equation for the chemical potential of aqueous NaCl, yields the solubility of NaCl in water, as shown in Table I. The solubilities at saturation pressure are in good agreement with those reported in the literature. However, because the differences are in some cases close to the limits of the experimental error, we prefer to report the effect of pressure on the solubility through the ratio

$$\Delta m_2^P = \frac{m_2(T,P,m_1=0)}{m_2^\dagger(T,P^{sat},m_1=0)}$$

Similarly, we report the effect of concentration of dissolved CO_2 through the ratio

$$\Delta m_2^C = \frac{m_2(T,P,m_1)}{m_2^\dagger(T,P,m_1=0)}$$

For aqueous Na_2SO_4, Holmes and Mesmer[11] have reported the temperature dependence of B^γ and C^γ at high temperatures and for the entire range of concentrations at the saturation pressure. Pabalan and Pitzer[12] have published activity coefficients at high temperatures and 200 bar obtained from heat-capacity measurements. However, the volumetric properties of aqueous sodium sulfate derived from these values are not in agreement with those found in the literature;[13-15] for example, at 50 °C, the reported values of γ_2 for a 3 m aqueous solution of Na_2SO_4 give an excess volume of 8 cm³ mol⁻¹, while direct measurements indicate that it should be about 28 cm³ mol⁻¹. We therefore prefer to calculate the pressure dependence of γ_2 from the experimental information available for the partial molar volume of Na_2SO_4 in aqueous solutions.

We use solubility data for CO_2 in salt-free water reported by Houghton et al.,[16] Gillespie and Wilson,[17] Wiebe and Gaddy,[18,19] and Zawisza and Malesinka.[20] These investigators cover different

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(9) Linke, W. F. *Solubilities*; Washington, DC, 1965.

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(18) Wiebe, R.; Gaddy, V. L. *J. Am. Chem. Soc.* **1939**, *61*, 315.

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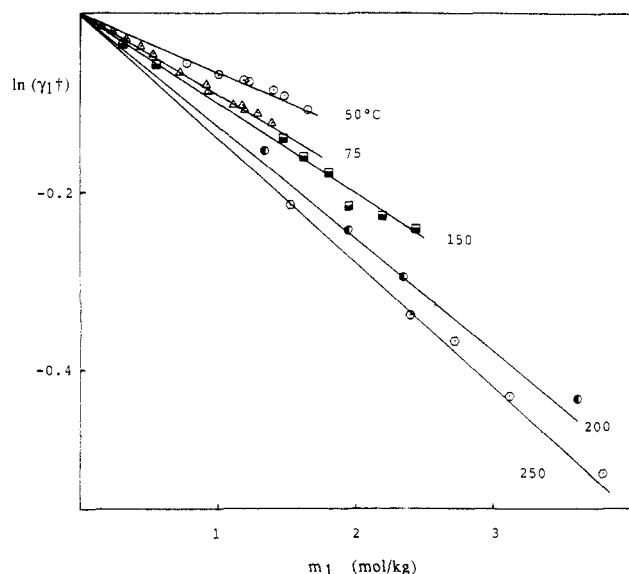(20) Zawisza, A.; Malesinska, B. *J. Chem. Eng. Data* **1981**, *26*, 388.

Figure 1. Concentration dependence of the activity coefficient of dissolved CO_2 in water at several temperatures.

ranges of pressure and temperature; agreement among them is generally good except for the data of Zawisza and Malesinka, which depart from the other data in a nonsystematic way. Malinin[21] has analyzed most of these data and our conclusions agree with his. All the volumetric data required for calculating the activity coefficients of CO_2 in water and in NaCl solutions are taken from Malinin[21] and Moore et al.[22]

To calculate the fugacity of CO_2 in the vapor phase, we use available data for vapor-phase composition at the dew point. Recently, Patel et al.[23] have reported virial coefficients for CO_2-H_2O mixtures to 200 °C and pressures to 100 bar at compositions near saturation; these virial coefficients reproduce accurately the data by Wiebe and Gaddy[24] and by Gillespie and Wilson;[17] therefore, we use them for our calculations.

In the range of temperature and pressure where virial coefficients for the CO_2-H_2O mixture are not available, we use the Lewis-Randall rule along with fugacity coefficients obtained from an equation of state for pure CO_2.[25]

For the solubility of CO_2 in aqueous NaCl solutions, we use data reported by Malinin et al.[26,27] and by Takenouchi and Kennedy.[28] These data cover the ranges of pressure and temperature analyzed in this work. A few data by Cramer[29] were discarded because of their poor precision.

The solubility of CO_2 in aqueous Na_2SO_4 solutions has been studied at low temperatures;[30,31] recently, we reported data at 50 and 75 °C.

Calculation of Pitzer Parameters

To obtain Henry's constants in salt-free water, we use solubility, fugacity, and volumetric data for the system CO_2-H_2O. The function

$$\ln\left(\frac{y_1\phi_1 P}{x_1}\right) - \int_{P^{sat}}^{P}\frac{\bar{v}_1}{RT}\,dP$$

(21) Malinin, S. D. *Geokhimiya* **1974**, *10*, 1523.

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(31) Yasunishi, A.; Yoshida, F. *J. Chem. Eng. Data* **1979**, *24*, 11.

TABLE II: Henry's Constant and Binary Interaction Parameter for the System CO_2-H_2O at Several Temperatures

T, °C	$H_1^{\dagger}$, bar^{-1}	λ_{11}, kg mol^{-1}
25	1655 ± 3	−0.0108 ± 0.0028
50	2948 ± 3	−0.0335 ± 0.0017
75	4239 ± 12	−0.0460 ± 0.0027
100	5335 ± 15	−0.0500 ± 0.0025
150	6490 ± 20	−0.0501 ± 0.0070
200	5840 ± 20	−0.0635 ± 0.0124
250	4420 ± 20	−0.0695 ± 0.0023

TABLE III: Pitzer Parameters for Two Systems CO_2-H_2O-Salt at Several Temperatures

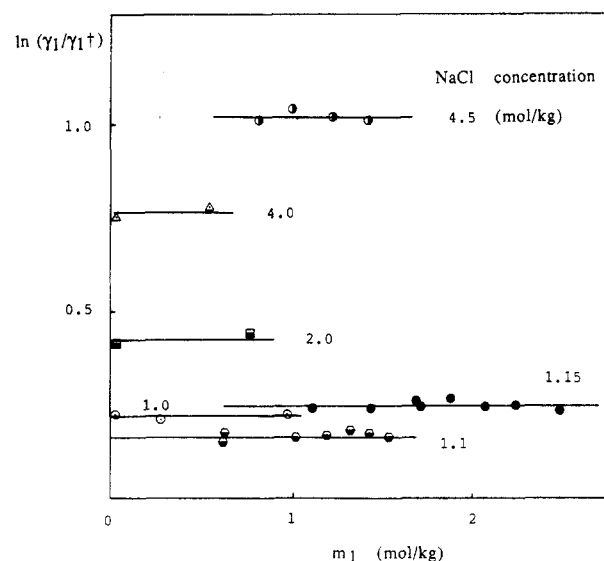| T, °C	Λ_{12}, kg mol^{-1}	Γ_{122}, kg mol^{-1}	σ	ref
		NaCl		
25	0.114 ± 0.002	−0.0028 ± 0.0003	0.011	19
50	0.109 ± 0.001	−0.0019 ± 0.0002	0.001	17, 18
75	0.101 ± 0.003	−0.0029 ± 0.0005	0.010	18, 19
100	0.103 ± 0.004	−0.0036 ± 0.0005	0.018	18
150	0.084 ± 0.007	−0.0008 ± 0.0011	0.042	21–28
200	0.106 ± 0.002	−0.0008 ± 0.0011	0.011	21–28
250	0.091 ± 0.006	−0.0035 ± 0.0009	0.021	21–28
		Na_2SO_4		
50	0.278 ± 0.022	−0.0034 ± 0.0025	0.059	5
75	0.272 ± 0.016	−0.0032 ± 0.0018	0.048	5

Figure 2. $\ln\,(\gamma/\gamma_1^{\dagger})$ as a function of CO_2 concentration in aqueous electrolyte solutions at several NaCl concentrations.

is plotted against $(1 - x_0^2)$; $\ln H_1^{\dagger}$ is obtained from extrapolation to $(1 - x_0^2) = 0$. Equations 1 and 3 are then used to calculate $\gamma_1^{\dagger}$ as a function of CO_2 molality, as shown in Figure 1.

Because $\ln\,(\gamma_1^{\dagger})$ is a linear function of m_1 and because the accuracy of the solubility data is not sufficient to determine both parameters in (15), we follow Barta and Bradley[4] and set τ_{111} to zero. Table II summarizes Henry's constants and λ_{11} for the range 25–250 °C.

Next, we analyze the available solubility data for CO_2 in aqueous electrolyte solutions. Equations 2 and 3 are used to calculate $\ln\,(\gamma_1/\gamma_1^{\dagger})$. Below 100 °C, we assume that the partial molar volume of the dissolved gas in the electrolyte solution remains equal to that in water (i.e., $\bar{v}_1 = \bar{v}_1^{\dagger}$), so that the second term in (2) can be neglected. Above 100 °C, we use the volumetric data reported by Malinin.[21] From these data, $(\bar{v}_1 - \bar{v}_1^{\dagger})$ is fixed at −5, −9, and −10 cm^3 mol^{-1} for 150, 200, and 250 °C, respectively.

There is an important difference between our analysis and that of Barta and Bradley.[4] To eliminate explicit m_1 dependence, these authors transformed (14) for the activity coefficient of the nonelectrolyte solute (γ_1) and proposed an expansion in terms of the ratio $(y_1\phi_1 P/m_1)$. However, the coefficients appearing in these authors' transformed equation for $\ln\,(\gamma_1)$ depend on m_1.

TABLE IV: Gibbs Energy of Solution (Divided by RT) of NaCl in Water at Several Temperatures (°C) and Pressures (bar)

					P				
T	P^{sat}	50	100	150	200	300	400	500	600
25	3.644	3.671	3.692	3.713	3.723	3.761	3.797	3.832	3.865
50	3.718	3.740	3.757	3.773	3.783	3.815	3.845	3.874	3.903
75	3.652	3.675	3.693	3.702	3.721	3.749	3.779	3.811	3.834
100	3.625	3.642	3.659	3.676	3.691	3.723	3.753	3.783	3.812
150	3.306	3.326	3.350	3.373	3.394	3.437	3.478	3.519	3.557
200	2.776	2.801	2.837	2.871	2.904	2.969	3.030	3.090	3.146
250	1.997	2.010	2.069	2.126	2.181	2.284	2.380	2.469	2.554

TABLE V: Partial Molar Volume of Na_2SO_4 at Infinite Dilution (cm³/mol) and Gibbs Energy (Divided by RT) of Solution of Na_2SO_4 in Water at Several Temperatures (°C) and Pressures (bar)

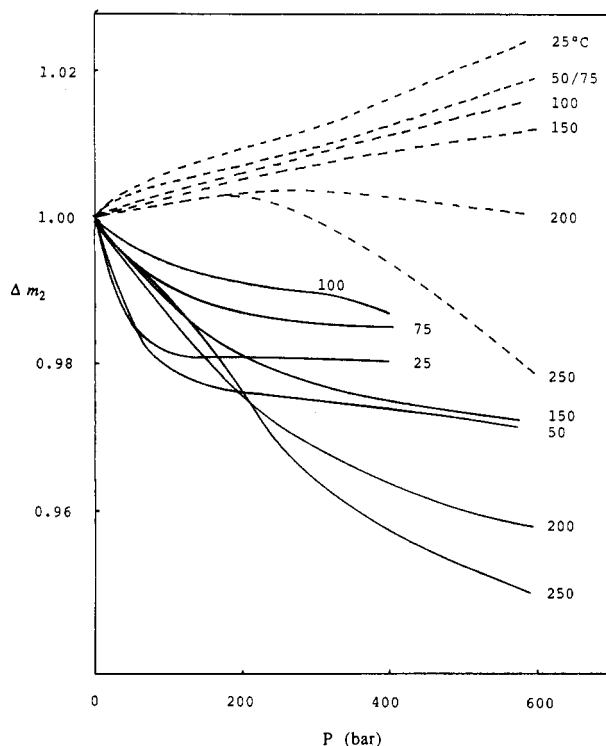|	T	P^{sat}				P		
			25	50	75	100	150	200
$\bar{v}_2$	50	15.0	15.2	15.4	15.6	15.8	16.1	16.4
$\Delta G°/RT$	50	0.9193	0.8852	0.8501	0.8154	0.7810	0.7129	0.6458
$\bar{v}_2$	75	13.9	14.35	14.8	15.25	15.7	16.6	17.5
$\Delta G°/RT$	75	1.2159	1.1822	1.1491	1.1173	1.0859	1.0256	0.9684

Figure 3. Calculated effects of pressure (- - -) and concentration of dissolved CO_2 (—) on the solubility of NaCl for the system $NaCl/CO_2/H_2O$ at several temperatures. - - -, $\Delta m_2^P = [m_2(T,P,m_1=0)]/[m_2^\dagger(T,P^{sat},m_1=0)]$. —, $\Delta m_2^C = [m_2(T,P,m_1)]/[m_2^\dagger(T,P,m_1=0)]$.

Since the modifications proposed by Barta and Bradley modify the way in which gas concentration is accounted for in the calculation of the activity coefficient of the electrolyte solute (13), we prefer to maintain the original virial expansion in m_1 for the activity coefficient of the nonelectrolyte solute, with pressure-dependent virial coefficients. When the pressure dependence of these coefficients is analyzed, we find that, for fixed values of electrolyte concentration, the activity coefficient of CO_2 is independent of m_1, as indicated in Figure 2. Therefore, parameter Γ_{112} in (14) can be set to zero.

Finally, parameters Λ_{12} and Γ_{122} in (14) are adjusted by a least-squares regression of the results for $\ln(\gamma_1/\gamma_1^\dagger)$ as a function of m_2. Table III gives parameters for the two ternary systems studied here along with the standard deviation of the fit (σ).

Results for the System $CO_2-NaCl-H_2O$

Table IV shows the values of the Gibbs energy of solution $\Delta G°_{sol}$ for NaCl calculated from the equations given by Pitzer et al.[8] The mean activity coefficient of NaCl in carbon dioxide free water is also calculated from these sources; the solubilities of the salt
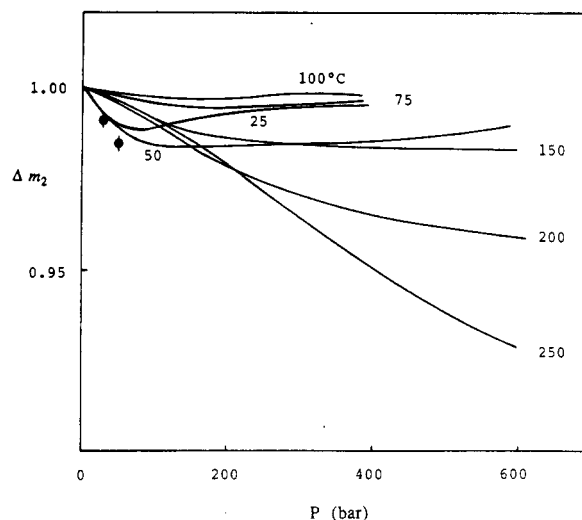

Figure 4. Calculated solubility of NaCl in the ternary system $NaCl/CO_2/H_2O$ at several temperatures. The points show experimental data at 50 °C [ref 6]. —, $\Delta m_2 = [m_2(T,P,m_1)]/[m_2^\dagger(T,P^{sat},m_1=0)]$.

in the ternary mixture at several temperatures and pressures are calculated using

$$\Delta G°_{sol} = \mu_2^0(T,P) - \mu_2^s(T,P) = -\nu RT \ln(Qm_2\gamma_2)^{sat} \quad (16)$$

by an iterative procedure. Figure 3 shows the effect of pressure on salt solubility. Figure 3 also shows the total, combined effect of pressure and dissolved gas on salt solubility. The curves shown if Figure 3 are calculated with (13) and parameters given in Table III.

While rising pressure increases the solubility of the salt (except above 200 °C and high pressure), rising concentration of the nonelectrolyte solute decreases the solubility of the gas. Figure 4 shows the combined effect of CO_2 on the solubility equilibria. Between 75 and 100 °C, the effect is smaller than that at other temperatures, but it is always negative; that is, part of the NaCl in solution precipitates as the pressure of CO_2 rises. The experimental points in Figure 4 correspond to our measurements[5] at 50 °C; they seem to indicate an underestimation of the CO_2 effect on the solubility, but they also indicate that the SSIM approach predicts the right sign for the effect. This conclusion disagrees with Barta and Bradley's assessment[4] that CO_2 increases the solubility of NaCl at low temperatures.

Moreover, the present results predict that with rising CO_2 pressure the decrease of salt solubility is even larger at temperatures above 150 °C. These results are in sharp disagreement with those of Barta and Bradley, who predict that rising CO_2 pressure increases salt solubility for temperatures above 250 °C.

The different predictions follow from different procedures used to evaluate parameters. The differences in prediction are not due

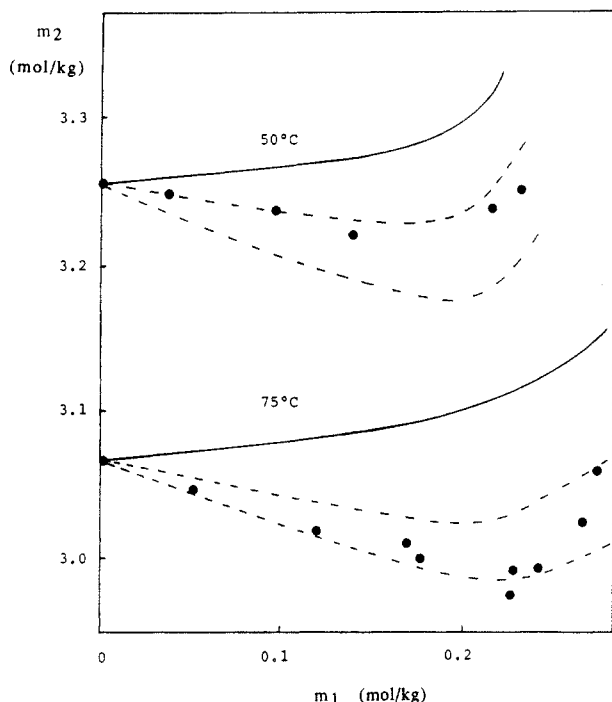**Figure 5.** Predicted and measured solubility of Na_2SO_4 for the system $Na_2SO_4/CO_2/H_2O$ at 50 and 75 °C. The solid curves show the pressure effect. The region bounded by the dashed lines corresponds to the predictions of the SSIM method (with the estimated uncertainty). The solid points show experimental data [ref 5].

to different sources of experimental data.

Results for the System CO_2–Na_2SO_4–H_2O

This system has been studied experimentally at 50 and 75 °C.[5] Table V presents the volumetric properties of the system and the calculated Gibbs energy of solution of the salt. The procedure for calculation of solubilities is the same as that for the previous system.

Figure 5 shows the effect of pressure on the solubility of Na_2SO_4 and the predicted combined effect of pressure and dissolved CO_2 on the solubility of the salt. These predictions are obtained with parameters given in Table III. Taking into account the uncertainties in the SSIM parameters, the observed solubilities are well reproduced by the equations given here over the entire range of pressure (0–200 bar).

Conclusions

Equations 2, 4, and 14 can be combined and rearranged to yield an expression for the Setschenow constant in terms of Pitzer's SSIM formalism. Pitzer's equation for the activity coefficient of the nonelectrolyte solute (14) has three parameters, but we find that, for the systems studied here, one of these (Γ_{112}) can be set to zero. As shown in Table III, one of the remaining two parameters, Λ_{12}, is much larger than the other, Γ_{122}. It follows that Λ_{12} is the Pitzer parameter that can most easily be related to the Setschenow constant for the solubility of a salt in a nonionic aqueous solution. This parameter is positive for electolytes that drive the gas out of solution and for gaseous solutes that decrease salt solubility.

The predictions of a previous thermodynamic analysis of solubility coefficients[5] are consistent with those reported in this work, except for the high-pressure region where the SSIM approach is superior.

Registry No. CO_2, 124-38-9; Na_2SO_4, 7757-82-6; NaCl, 7647-14-5.

Asymptotic Theory of the Chemical Bond in H_2^+ Based on a Simple Physical Model

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The Coulomb, exchange, and overlap integrals appearing in the Murrell–Shaw, Musher–Amos (MSMA) theory to second order are calculated for the $1s\sigma_g$ and $2p\sigma_u$ states of H_2^+ by use of a number of simple models. For the Coulomb integral a simple classical model is shown to provide a direct way to derive an expression for the term by term damping of the usual induction series as well as for the spherical induction term. The asymptotic behavior at small and large distances of the exchange and overlap integrals is analyzed in an analogous way. The simple expression for the total potentials is compared with the exact results and they agree to better than 5% over the entire range of distances. Compared with the exact second-order MSMA theory, the present model actually gives much better results when the internuclear distance is less than 2 au.

I. Introduction

The H_2^+ molecule is the simplest of all molecules. Although it contains only one electron, it incorporates all the basic physical features of a chemically bonded system. In H_2^+ the polarization induction series may be considered analogously to the dispersion interaction between the constituents of a neutral bonded system. Thus the treatment of H_2^+ also requires a correct description of exchange and its coupling to the polarization interaction. This problem has been extensively studied,[1-3] but until recently no

entirely satisfactory formulation could be developed. On the other hand, despite its apparent simplicity an exact calculation of the total energy is only possible via a numerical computation. For this reason a large number of attempts have been made to develop

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