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EFFECT OF A DISSOLVED GAS ON THE SOLUBILITY OF AN ELECTROLYTE IN AQUEOUS SOLUTION

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ABSTRACT

The solubility of Na_2SO_4 in aqueous CO_2 solutions has been measured at 50 and 75 ° C and pressures to 200 bars. To calculate the effect of gas concentration on the solubility of the salt, we use thermodynamic-consistency equations that relate the solubility of the salt to the Setschenow constant and other thermodynamic properties. The effect of pressure on the salt solubility is estimated from volumetric data for the aqueous electrolyte solution and for the solid salt. Calculated and experimental results are in good agreement. Using the thermodynamic-consistency analysis, predictions are made for the solubility of NaCl in aqueous solutions containing CO_2 or CH_4 , using available data for gas solubility in the respective binary electrolyte solutions. The predicted decrease of NaCl solubility with rising CO_2 concentration is confirmed experimentally at 50 ° C.

Introduction

Salting out of non-electrolytes from aqueous solutions has been studied for over a century[1-3]. The Setschenow equation is often used to describe the effect of a salt on the solubility of a gas. Unfortunately, experimental information is scarce at temperatures above 25 ° C. Only a few systems containing NaCl or CaCl_2 , and gases such as N_2 , CO_2 and CH_4 , have been studied at high temperatures and pressures.

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However, if we direct attention to the reverse effect, that is, to the effect of a gas on the solubility of an electrolyte, we find a severe lack of experimental information. This effect, however, may be important for technology because solid-liquid phase equilibria for aqueous salt-gas systems are found in a variety of chemical and geochemical processes. A classical example is provided by an aqueous electrolyte solution in boilers or heat exchangers where, in addition to water and salts, dissolved gases are present, often at elevated pressure.

In this work we report experimental studies of the ternary system water/carbon dioxide/sodium sulfate, with emphasis on the solubility of the electrolyte as a function of liquid-phase CO_2 concentration. Because the solubility of CO_2 in aqueous Na_2SO_4 is known only at 25 ° C, we have also measured it at 50 and 75 ° C.

The main goal of this work is to assess the effect of a dissolved gas on aqueous liquid-solid equilibria, using available experimental information for the effect of the salt on gas solubility. We present a classical thermodynamic discussion which predicts equilibrium conditions for the ternary system based on a few well-defined approximations.

We compare calculated results with experiment for the system $H_2O-CO_2-Na_2SO_4$. This particular system was chosen first, because the solubility of CO_2 in aqueous solutions is higher than that of other non-polar gases and second, because Na_2SO_4 produces a relatively large salting-out effect for aqueous CO_2 solutions.

Finally, we present estimates of the effect of dissolved CO_2 or CH_4 on the solubility of NaCl. Our estimates are based on available data for salting-out of these gases by the salt, and from some complementary thermodynamic data for the constituent binary systems.

Experimental

The apparatus shown in Figure 1 is designed to measure phase-equilibria for water-gas-salt mixtures for temperatures to 100 ° C and for pressures to 200 bar.

The equilibrium cell is a high-pressure stainless-steel Jerguson liquid-level gage, with an internal volume of approximately 150 cm^3 .

Mixing in the equilibrium cell is achieved by recirculating both phases; the top phase is drawn from the top and driven to the bottom of the cell by a Milton-Roy metering simplex minipump (3 in Figure 1). The bottom phase is drawn from the bottom and circulated through a cartridge containing the solid salt (5), then through a 15- μm NUPRO in-line filter (4), then through a VICI six-port switching valve (6), and finally through a Mettler-Paar vibrating-tube high-pressure densimeter before it is driven back to the top of the cell by a pump (2). To ensure saturation, the cartridge with the solid salt is used only when working with saturated electrolyte solutions. The filter prevents solids from reaching the sampling valve.

The equilibrium cell is located in a constant-temperature air-bath where the temperature is monitored and controlled by an Omega Engineering heater-controller. The temperature inside the densimeter cell is kept constant by a constant-temperature oil bath.

The pressure of the system is measured with a Heise bourdon-tube pressure gauge. The estimated accuracies of the temperature and pressure measurements are ± 0.1 K and ± 0.02 MPa, respectively.

The cell is initially evacuated. Having fed the water-electrolyte solution into the cell, liquid CO_2 is pumped into the cell by pump (1) until the desired pressure is reached. Both recirculation pumps are then operated for approximately four hours to ensure equilibrium. When equilibrium is attained, the density displayed by the densimeter remains stable. Once the system has equilibrated, a sample is collected by turning the switching valve.

Figure 2 shows a diagram of the sampling section. Samples are trapped in a sampling loop of calibrated volume. When the sampling valved is switched, the contents of the loop are flashed to atmospheric pressure. The amount of CO_2 is measured by displacement of a CO_2 -saturated aqueous solution. CO_2 volumes are measured with an accuracy of about 1%.

Having evacuated the CO_2 from the sample, the sampling lines are rinsed thoroughly with deionized water. Later, the water from the resulting solution is evaporated and the salt is dried at $125^\circ C$. The amount of electrolyte in the sample is measured gravimetrically. Electrolyte concentrations can be reproduced with an accuracy of about 1%.

The amount of water in the sample is calculated by difference from the known volume of the sample and from the measured density.

The volume of the sampling loop is approximately 1.3 cm^3 ; the exact value depends on the temperature. Volume calibration is accomplished, at each temperature, by sampling a saturated salt-water mixture of known composition and density.

Density determination is based on measuring the period of oscillation of a vibrating U-shaped sample tube through which the sample liquid flows continuously. The density, ρ , is related to the period, τ , by

$$\rho = A\tau^2 + B ,$$

where A and B are temperature-dependent instrument constants, determined by calibration with fluids of known density. In this work, we used CO_2 , water, ethylene glycol and saturated electrolyte solutions to calibrate the densimeter. Densities are measured with an accuracy of 0.0001 gcm^{-3} .

Thermodynamic Framework

Consider a ternary system containing n_0 moles of solvent (0), n_1 moles of non-electrolyte (1) and n_2 moles of electrolyte (2) at fixed temperature T and pressure P . In the

liquid phase, thermodynamic consistency [4] requires that chemical potentials μ_1 and μ_2 are related by

$$\left(\frac{\partial \mu_1}{\partial n_2} \right)_{T,P,n_1,n_0} = \left(\frac{\partial \mu_2}{\partial n_1} \right)_{T,P,n_2,n_0} \quad (1a)$$

which can be rewritten in the form

$$\left(\frac{\partial \mu_1}{\partial m_2} \right)_{T,P,m_1} = \left(\frac{\partial \mu_2}{\partial m_1} \right)_{T,P,m_2} \quad (1b)$$

where m_i is the molality of component i .

The effect of a second solute on the solubility of the first is expressed by a solubility coefficient, which can be obtained from solubility experiments. For our ternary system, there are two solubility coefficients, denoted by k_{12} and k_{21} ; these are defined by

$$k_{12} = - \left(\frac{\partial \ln m_1}{\partial m_2} \right)_{\mu_1} \quad (2a)$$

and

$$k_{21} = - \left(\frac{\partial \ln m_2}{\partial m_1} \right)_{\mu_2} \quad (2b)$$

The first coefficient, k_{12} , is Setschenow's constant [1], which is commonly used to describe the effect of a salt on the solubility of a non-electrolyte. If k_{12} is independent of m_2 , equation (2a) can be integrated to yield Setchenov's equation

$$\ln \frac{m_1^0}{m_1} = k_{12} m_2 \quad (3)$$

where superscript 0 designates absence of component 2. However, k_{12} is independent of m_2 only in the limit of infinite dilution of the electrolyte; Equation (3) is therefore a limiting relation [3]. For this reason, we must use equations (2a) and (2b), instead of equation (3), to describe the ternary system over a wide range of solute concentrations.

Mc Kay [4] and Friedman [5] have pointed out that the cross-differentiation relation [Equation (1)] can be used to obtain one of the solubility coefficients in terms of the other. To deduce such a relation, using standard calculus, Equations (2a) and (2b) are rewritten in the form

$$k_{12} = \frac{\left(\frac{\partial \mu_1}{\partial m_2} \right)_{m_1}}{m_1 \left(\frac{\partial \mu_1}{\partial m_1} \right)_{m_2}} \quad (4a)$$

$$k_{21} = \frac{\left(\frac{\partial \mu_2}{\partial m_1} \right)_{m_2}}{m_2 \left(\frac{\partial \mu_2}{\partial m_2} \right)_{m_1}} \quad (4b)$$

For the solutes, mean activity coefficients γ are related to μ by

$$\mu_1 = \mu_1^\infty(T) + RT \ln m_1 \gamma_1 \quad (5a)$$

$$\mu_2 = \mu_2^\infty(T) + \nu RT \ln m_2 \gamma_2, \quad (5b)$$

where standard-state chemical potentials μ_1^∞ and μ_2^∞ depend only on temperature, and ν is the number of particles produced by the dissociation of the electrolyte [5]. Substitution of Equations (5) into the derivatives appearing in Equation (1), gives

$$\left(\frac{\partial \mu_1}{\partial m_2} \right)_{m_1} = RT \left(\frac{\partial \ln \gamma_1}{\partial m_2} \right)_{m_1} \quad (6a)$$

and

$$\left(\frac{\partial \mu_2}{\partial m_1} \right)_{m_2} = \nu RT \left(\frac{\partial \ln \gamma_2}{\partial m_1} \right)_{m_2} \quad (6b)$$

It then follows that

$$\left(\frac{\partial \mu_1}{\partial m_2} \right)_{m_1} = RT k_{12} \left(1 + m_1 \left(\frac{\partial \ln \gamma_1}{\partial m_1} \right)_{m_2} \right) \quad (7a)$$

$$\left(\frac{\partial \mu_2}{\partial m_1} \right)_{m_2} = \nu RT k_{21} \left(1 + m_2 \left(\frac{\partial \ln \gamma_2}{\partial m_2} \right)_{m_1} \right). \quad (7b)$$

As indicated by Equation (1), Equations (7a) and (7b) must be equal; the effect of a non-electrolyte on the solubility of an electrolyte (k_{21}) can therefore be calculated from the generalized Setschenow constant, k_{12} . Here, generalized means that k_{12} is no longer assumed to be independent of the electrolyte concentration.

However, if the non-electrolyte is a gas, and if the solubility of this gas is known at different partial pressures and at different electrolyte concentrations, it is possible to calculate k_{21} according to

$$k_{21} = \frac{\left(\frac{\partial \ln \gamma_1}{\partial m_2} \right)_{m_1}}{\nu \left(1 + m_2 \left(\frac{\partial \ln \gamma_2}{\partial m_2} \right)_{m_1} \right)} \quad (8)$$

To arrive at Equation (8), we first substitute Equation (7b) into the left side of Equation (1b), and we then substitute Equation (6a) into the right side.

To obtain k_{21} , which accounts for the effect of the non-electrolyte on the solubility of the salt, we need to know the derivatives appearing in Equation (8). To estimate these derivatives we make some reasonable simplifying assumptions.

Because we are interested in the case where the non-electrolyte is a gas, we assume that its solubility in the salt solution is low when compared to that of the salt. In that event, it is valid to assume that $\partial \ln \gamma_2 / \partial m_2$ at constant m_1 can be evaluated using only information for the binary solvent-electrolyte system. For aqueous solutions of electrolytes, this information is obtained from the concentration dependence of the activity coefficient of the electrolyte as given by Pitzer's Equation [6] (see Appendix); Further, Pitzer's equation can be used to obtain $\partial \ln \gamma_2 / \partial m_2$ at saturation.

The derivative $\partial \ln \gamma_1 / \partial m_2$ at constant m_1 can be calculated from the solubility of the non-electrolyte in the electrolyte solution using the Krichevsky-Ilinskaya equation [7]

$$\ln \gamma_{1x} = \ln \left(\frac{y_1 \phi_1 P}{x_1 H_1^\infty} \right) - \int_{P^\circ}^P \frac{\bar{v}_1^\infty}{RT} dP, \quad (9)$$

where y_1 is the mole fraction and ϕ_1 is the fugacity coefficient of component 1 in the vapor phase; x_1 is the mole fraction of component 1 in the liquid phase, H_1^∞ is Henry's constant for component 1 in the salt-free solvent, P° is the vapor pressure of the solvent at temperature T , and $\bar{v}_1^\infty$ is the partial molar volume of component 1 in solution at infinite dilution. We use the notation γ_{1x} to indicate that Equation (9) gives an activity coefficient based on mole fraction as opposed to molality. Strictly speaking, the non-electrolyte activity coefficient needed for Equation (8) should be in the molal scale. Here, however, we are only interested in its logarithmic derivative with respect to m_2 ; since the concentration of component 1 is so low, we can set $\partial \ln \gamma_{1x} / \partial m_2 = \partial \ln \gamma_1 / \partial m_2$.

Solubility coefficient k_{12} only accounts for the effect of a dissolved gas on the solubility of a salt. High pressures are needed to dissolve a significant amount of gas in the solvent. However, high pressure also affects salt solubility, even in the absence of a gaseous solute.

The pressure effect can be estimated from the volumetric properties of the salt in the solid and aqueous phases, and from the concentration dependence of the activity coefficient [8] according to

$$\left(\frac{\partial m_2}{\partial P} \right)_T = \frac{\bar{v}_2 - v_2^s}{vRT \left(\frac{1}{m_2} + \frac{\partial \ln \gamma_2}{\partial m_2} \right)} \quad (10)$$

where $\bar{v}_2$ is the partial molar volume of the salt in aqueous solution and v_2^s is the molar volume of the solid.

We assume that the pressure coefficient given by Equation (10) is independent of P and m_1 . Then

$$m_2^s(P, T, m_1=0) = m_2^s(P', T, m_1=0) + \left(\frac{\partial m_2}{\partial P} \right)_T (P - P') \quad (11)$$

where P' is the vapor pressure of the saturated electrolyte solution in the absence of dissolved gas.

Finally, to estimate the solubility of the salt in the presence of dissolved gas, we assume that the solubility coefficient k_{21} is independent of m_1 . Equation (2b) can then be integrated to give

$$m_2(P, T, m_1) = m_2^s(P, T, 0) \exp(-k_{21} m_1) \quad (12)$$

where $m_2^s(P, T, 0)$ is the solubility of the salt in water, at pressure P and temperature T , in the absence of a dissolved gas ($m_1 = 0$).

Equation (12) describes the joint effect of pressure and dissolved-gas on salt solubility. The pressure effect is taken into account through the pre-exponential factor of Equation (12), $m_2^s(P, T, 0)$, which is calculated using Equations (11) and (10). The dissolved-gas effect is taken into account through the exponential factor of Equation (12), where k_{21} is calculated with Equation (8) and m_1 is the experimental molality of the gas in the salt solution at pressure P and temperature T .

According to Equations (10) to (12), the effect of dissolved gases on salt solubility can follow four types of behavior, depending on the sign of k_{21} (positive for salting-out, and negative for salting-in) and on the sign of $\bar{v}_2 - v_2'$ (positive or negative pressure coefficient). Figure 3 schematically illustrates these four possibilities.

The binary systems water/carbon dioxide and water/sodium sulfate

For the binary systems water/carbon dioxide and water/sodium sulfate, published experimental data are available over a wide range of temperature and composition.

The volumetric properties of both solutes are known from density measurements. Malinin[9] has reported the partial molar volumes of CO_2 in aqueous solutions at high temperatures. For Na_2SO_4 , we have calculated the partial molar volume from the density data of Ellis[10] and Phutela et al.[11] and from our own results at saturation.

We assume that the partial molar volumes of both solutes in the ternary aqueous system are the same as those for the respective aqueous binary systems. For Na_2SO_4 , this is a reasonable assumption because the concentration of CO_2 is low. From solubility measurements for CO_2 in aqueous NaCl solutions [12], there is evidence that the partial molar

volume of CO_2 does not change significantly with salt concentration; we have therefore adopted the experimental value of $\bar{v}_1$ in water in the absence of electrolyte.

Henry's constants for CO_2 in salt-free water have been reported elsewhere[13]. Fugacity coefficients for CO_2 are taken from the compilation by Angus et al[14]. The solubility of CO_2 in Na_2SO_4 solutions of different concentrations has been measured in this work. These new data are used to calculate $\ln\gamma_1$ and its derivative with respect to m_2 .

Holmes et al. [15], and more recently Pabalan et al. [16], have measured the effect of temperature and salt concentration on the activity coefficient of Na_2SO_4 . The concentration dependence of $\ln\gamma_2$ is described by Pitzer's equation, whose coefficients have been tabulated as a function of temperature [24]. From Pitzer's equation we calculate $\partial\ln\gamma_2/\partial m_2$.

Table I shows the partial molar volumes and the activity coefficients, as well as the derivative of $\ln\gamma_2$ with respect to m_2 at the temperatures studied in this work.

Results

Table II shows measured solubilities for CO_2 and Na_2SO_4 , and the density of the ternary system at pressures from 0 to 200 bar, at 50 and 75 ° C.

For Na_2SO_4 , v_2' was fixed at 53.32 gcm^{-3} over the entire range of temperature. We have assumed that the presence of CO_2 has no appreciable effect on $\bar{v}_2$, γ_2 and $\partial\ln\gamma_2/\partial m_2$, and that the pressure effect on $\bar{v}_2$ can be neglected.

While the solubility of CO_2 increases monotonically with pressure, the salt solubility goes through a minimum, as indicated in Table II.

The solubility of Na_2SO_4 in the binary solution increases linearly with pressure, as indicated in the last column of Table II. However, when plotted against m_1 , the solubility of Na_2SO_4 increases sharply at high CO_2 concentrations because at high pressures CO_2 solubility deviates considerably from Henry's law, even when gas-phase fugacity coefficients are included.

We use Equations (8) to (12) to calculate the effect of m_1 on salt solubility; the denominator in Equation (8) is evaluated from data in Table I, while the numerator is calculated from our measurements of CO_2 solubility in aqueous Na_2SO_4 solutions, reported in Table III. For this system, $\ln\gamma_1$ is almost independent of CO_2 concentration.

Figure 4 shows the effect of salt concentration on $\ln\gamma_1$ at 50 ° and 75 ° C. Table IV gives $\partial\ln\gamma_1/\partial m_2$ and k_{21} .

Figures 5a and 5b show results for the solubility of Na_2SO_4 at 50 ° and at 75 ° C, respectively. The broken lines represent the separate effects of pressure and gas-concentration on Na_2SO_4 solubility. The joint effect of pressure and gas concentration is

calculated with Equation (12); the shaded bands represent the calculated solubility within our error estimates. The solid lines represent the smoothed experimental solubility. Agreement is satisfactory to $m_1 = 0.25$ ($P \sim 150$ bar), if we bear in mind the assumptions made for our calculations. At higher pressures the difference between measured and calculated solubilities increases, because of the simplifications made for our estimates.

Solubility predictions for water/gas/salt mixtures at high temperatures

The thermodynamic framework described above can be used for prediction of salt solubility in ternary water/gas/salt mixtures, when the solubility of the gas in the aqueous solution of the electrolyte is already known. A number of such ternary systems have been previously studied at high temperature and pressure.

To illustrate, we consider the system $\text{NaCl}-\text{CO}_2-\text{H}_2\text{O}$ which has been studied extensively. The solubility of CO_2 in aqueous NaCl solutions has been measured by various authors [17-19] over wide ranges of temperature, pressure and salt concentration. Here we are interested in the prediction of NaCl solubility; for our calculations, we use CO_2 solubility data in aqueous NaCl solutions, reported by Malinin et al. [12-19] and Takenouchi et al. [18].

Activity coefficients for concentrated NaCl solutions at high temperatures have been reported by Liu and Lindsay[20]; we have used their empirical equation for the concentration dependence of the activity coefficient to obtain $\partial \ln \gamma_2 / \partial m_2$. Volumetric properties for the binary electrolyte solutions were taken from the review by Rogers and Pitzer[21]. At each temperature, partial molar volumes were extrapolated to saturation.

Table V shows the values of k_{21} and $\partial m_2 / \partial P$ for this system at temperatures between 50° and 250° C. Figure 6 shows the estimated solubilities as a function of CO_2 partial pressure.

The pressure effect is positive for NaCl up to 150° C (case A in Figure 3). It changes sign, however, at 250° C and pressures above 200 bar (case C in Figure 3). As Figure 7 shows, the pressure effect is small when compared to the concentration effect up to 150° C and at low pressures; however, above 150° C and at high pressures, the effect of pressure becomes important.

The effect of CO_2 on NaCl solubility appears to be a minimum around 100° C. Dissolved CO_2 always produces a decrease in salt solubility. These findings are contrary to the salt-solubility estimates of Barta and Bradley [22], who predict that CO_2 increases NaCl solubility between 75° and 100° C and also between 250° and 300° C.

Figure 8 shows experimental and predicted salt solubilities for the system $\text{NaCl}-\text{CO}_2-\text{H}_2\text{O}$ at 50° C. Experiment and theory are in good agreement. Changes in the sign of the dissolved-gas effect on NaCl solubility are not expected for the range of

temperatures and pressures studied here.

Predictions for the system $\text{NaCl}-\text{CH}_4-\text{H}_2\text{O}$ were also performed using data for CH_4 solubility in aqueous NaCl solutions [23]. Henry's constants for the binary system $\text{CH}_4-\text{H}_2\text{O}$ were reported by Gillespie et al [13].

The predicted results are shown in Figure 9. It is important to note that the effect of CH_4 concentration is one order of magnitude lower than that of CO_2 ; it is overshadowed by the pressure effect which is positive for NaCl over the range of temperatures considered here.

A similar effect is expected for non-polar gases having solubilities in aqueous NaCl solutions similar to those of CH_4 . However, highly soluble gases such as NH_3 and H_2S are expected to have a significant effect on the solubility of electrolytes.

Conclusions

We have predicted the effect of a dissolved gas on the solubility of a salt in water, using experimental information for the water-gas and water-salt binary systems. Solubility data for the gas in the aqueous salt solution are also necessary for the thermodynamic-consistency analysis proposed here.

The validity of our predictions is confirmed by our measurements of salt solubility in water for the system $\text{H}_2\text{O}-\text{CO}_2-\text{Na}_2\text{SO}_4$ at 50 and 75 °C, and for the system $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ at 50 °C.

As a result of a dissolved-gas effect, when solubility is plotted versus pressure, the systems studied here exhibit a solubility minimum. For these systems, this minimum is only a few percent below the salt solubility in water in the absence of dissolved gas. However, the effect of gas solubility on salt solubility is likely to be larger for highly soluble gases such as NH_3 and H_2S .

The reduction of salt solubility in water created by a dissolved gas should be taken into consideration for the design of boilers and heat exchangers where gases are present. For salts that are only moderately soluble in water, such as CaSO_4 , this reduction could be significant.

We must bear in mind that all the systems studied here exhibit a negative dissolved-gas concentration effect. However, for some salts, such as LiCl , the dissolved-gas effect can be positive; i.e. it can give rise to a solubility in water that is higher when dissolved gas is present.

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Appendix: Activity Coefficient γ_2 as a Function of m_2 . Pitzer's Equation.

In this work, the mean activity coefficient of the electrolyte, γ_2 , is calculated from Pitzer's equation:

$$\ln \gamma_2 = -|Z_M Z_X| A_\phi \left[\frac{I^{1/2}}{1 + 1.2 I^{1/2}} + \frac{2}{1.2} \ln (1 + 1.2 I^{1/2}) \right] + \left(\frac{2\nu_M \nu_X}{\nu} \right) m_2 B_{MX} + \left(\frac{3(\nu_M \nu_X)^{3/2}}{\nu} \right) m^2 C_{MX},$$

where

$$B_{MX} = 2\beta^{(0)}_{MX} + \frac{2\beta^{(1)}_{MX}}{\alpha^2 I} \left[1 - (1 + \alpha I^{1/2}) - \frac{\alpha^2 I}{2} \exp(-\alpha I^{1/2}) \right].$$

Here α is a constant set equal to 2.0; I is ionic strength; ν is the total number of ions formed from dissociation of salt MX ($\nu = \nu_M + \nu_X$); Z_M and Z_X are the charges on ions M and X .

Parameters $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$ and $C_{MX}\phi$ are temperature dependent. Tables for these parameters, as well as for the Debye-Hückel slope A_ϕ , can be found in references [22] and [25] for $NaCl$ and for Na_2SO_4 , respectively.

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TABLE I - Properties of Binary Systems

CO_2-H_2O			
$T (^{\circ}C)$	$\bar{v}_1 (cm^3 mol^{-1})$	$H_1^{\infty} (bar)$	
50	35	2912	
75	35	4020	
$Na_2SO_4-H_2O$			
$T (^{\circ}C)$	$\bar{v}_2 (cm^3 mol^{-1})$	$\ln \gamma_2 (sat)$	$(\partial \ln \gamma_2 / \partial m_2)_{sat}$ ($kgmol^{-1}$)
50	43.7	0.143	-0.0389
75	44.5	0.137	-0.0763

TABLE II - Measured Densities, Gas Solubilities and Salt
Solubilities for the System $H_2O-CO_2(1)-Na_2SO_4(2)$ at 50 and 75 ° C

T ° C	P(bar)	$\rho(gcm^{-3})$	$m_1 (molkg^{-1})$	$m_2(molkg^{-1})$	$m_2^o (molkg^{-1})$
50	1.0	1.306	0	3.254	3.254
50	16.4	1.306	0.038	3.248	3.261
50	35.7	1.306	0.095	3.237	3.270
50	57.6	1.306	0.139	3.220	3.280
50	121.6	1.308	0.215	3.237	3.308
50	160.0	1.312	0.230	3.251	3.325
75	1.0	1.273	0	3.066	3.066
75	19.0	1.273	0.052	3.046	3.074
75	33.8	1.273	0.097	-	3.080
75	43.8	1.273	0.123	3.014	3.084
75	50.7	1.273	0.169	3.011	3.087
75	72.0	1.273	0.176	3.000	3.096
75	86.7	1.273	0.196	-	3.102
75	102.0	1.274	0.228	2.991	3.108
75	120.3	1.275	0.226	2.976	3.116
75	148.9	1.278	0.241	2.993	3.128
75	175.7	1.280	0.265	3.024	3.139
75	197.3	1.282	0.273	3.059	3.148

Table III- Measured Solubility of CO_2 in Aqueous Solutions
of Na_2SO_4 at 50 and 75 ° C

T ° C	P (bar)	m_2 (mol kg ⁻¹)	$x_1 10^3$
50	95.6	1.95	5.99
50	145.1	1.98	6.27
50	76.6	2.71	3.47
50	137.6	2.72	4.62
75	37.9	0.95	4.48
75	75.8	0.96	7.87
75	97.9	0.97	9.33
75	43.1	1.97	2.59
75	72.1	1.91	4.28
75	132.7	2.01	6.54

TABLE IV- Thermodynamic Properties of the System
 $H_2O-CO_2(1)-Na_2SO_4(2)$ at 50 and 75 ° C Calculated
from Data in Table III

T ° C	$\frac{\partial \ln \gamma_1}{\partial m_2}$ (kg mol ⁻¹)	k_{21} (kg mol ⁻¹)
50	0.27 ± 0.04	0.110 ± 0.010
75	0.40 ± 0.02	0.174 ± 0.009

TABLE V- Solubility Properties for the System $H_2O-CO_2(1)-NaCl(2)$
Calculated from Published Data

T ° C	$m_2(P^s, T, 0)$ (mol kg ⁻¹)	$\frac{\partial \ln \gamma_2}{\partial m_2}$ (kg mol ⁻¹)	$\frac{\partial m_2}{\partial P}$ (mol (kg bar) ⁻¹)	$\frac{\partial \ln \gamma_1}{\partial m_2}$ (kg mol ⁻¹)	k_{21} (kg mol ⁻¹)
50	6.275	0.1269	1.94	0.20	0.056
100	6.680	0.0929	1.85	0.14	0.042
150	7.198	0.0562	1.89	0.21	0.075
250	8.989	-0.0046	3.23	0.26	0.136

FIGURE 1

Experimental apparatus. (1) Feed pump. (2) Recirculation pump, bottom phase. (3) Recirculation pump, upper phase. (4) 15- μ m filter to prevent solids from reaching the sampling valve. (5) Cartridge filled with solid salt to ensure saturation. (6) Six-port sampling valve.

FIGURE 2

Sampling section. After taking a sample, the amount of gas is measured by liquid displacement. The remaining solution is flushed out with water and collected for analysis.

FIGURE 3

Effect of dissolved gas on salt solubility. Depending on the signs of the pressure coefficient and the solubility coefficient, four different types of behavior can arise. Here, Δm_2^P and Δm_2^C are given by

$$\Delta m_2^P = \frac{m_2(P, T, 0)}{m_2(P^s, T, 0)}$$

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

Δm_2^P denotes the change in electrolyte solubility, relative to a state at the same temperature but at the vapor pressure of the saturated electrolyte solution (in the absence of dissolved gas), as a result of pressure. Δm_2^C denotes the change in electrolyte solubility as a result of a dissolved-gas effect, relative to a state at the same temperature and the same pressure but in the absence of dissolved gas.

FIGURE 4

Effect of Na_2SO_4 concentration on $\ln \gamma_{1x}$ at 50 and 75 ° C, respectively. The curves shown here are calculated from the data in Table III. Subscript 1x indicates that $\ln \gamma_{1x}$ is calculated from Equation (9) and is therefore based on a molar scale.

FIGURES 5a and 5b

Effect of dissolved CO_2 on the solubility of Na_2SO_4 at 50 (Figure 5a) and 75 ° C (Figure 5b). The upper curve shows the effect of pressure. The bottom curve shows the effect of dissolved gas. The joint effect of pressure and dissolved gas is shown by the shaded region between the dashed curves. The solid line shows the smoothed experimental solubility.

FIGURE 6

Estimated solubility of $NaCl$ in water as a function of CO_2 partial pressure. These curves were calculated from data in Table V.

FIGURE 7

Effect of pressure and dissolved CO_2 on the solubility of $NaCl$ in water. Δm_2^P and Δm_2^C are defined in Figure 3.

FIGURE 8

Experimental and predicted solubility of $NaCl$ as a function of CO_2 concentration at $50^\circ C$.

FIGURE 9

Effect of dissolved CH_4 on the solubility of $NaCl$ in water. Δm_2^P and Δm_2^C are defined in Figure 3. Note that Δm_2^C is almost identical for the three temperatures shown in this figure). Δm_2 denotes the joint effect of pressure and gas concentration; it is defined by

$$\Delta m_2 = \frac{m_2(P, T, m_1)}{m_2(P', T, 0)}$$

Therefore, Δm_2 indicates the change in salt solubility due to changes in pressure and gas concentration relative to that for a solution at the same temperature T and pressure P' in the absence of dissolved gas.

Figure 1

Figure 2 : Sampling section

FIGURE 3

FIGURE 4

FIGURE 5a

FIGURE 5b

FIGURE 6

FIGURE 7

FIGURE 8

FIGURE 9

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