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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 Na₂SO₄ in aqueous CO₂ 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 CO₂ or CH₄, using available data for gas solubility in the respective binary electrolyte solutions. The predicted decrease of NaCl solubility with rising CO₂ 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 CaCl₂, and gases such as N₂, CO₂ and CH₄, 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 $\text{CO}_2$ concentration. Because the solubility of $\text{CO}_2$ in aqueous $\text{Na}_2\text{SO}_4$ 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 $\text{H}_2\text{O}-\text{CO}_2-\text{Na}_2\text{SO}_4$. This particular system was chosen first, because the solubility of $\text{CO}_2$ in aqueous solutions is higher than that of other non-polar gases and second, because $\text{Na}_2\text{SO}_4$ produces a relatively large salting-out effect for aqueous $\text{CO}_2$ solutions.

Finally, we present estimates of the effect of dissolved $\text{CO}_2$ or $\text{CH}_4$ 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 CO₂ 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 valve is switched, the contents of the loop are flashed to atmospheric pressure. The amount of CO₂ is measured by displacement of a CO₂-saturated aqueous solution. CO₂ volumes are measured with an accuracy of about 1%.

Having evacuated the CO₂ 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 °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 cm³; 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, \( \rho \), is related to the period, \( \tau \), 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 CO₂, water, ethylene glycol and saturated electrolyte solutions to calibrate the densimeter. Densities are measured with an accuracy of 0.0001 g cm⁻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 $\mu_1$ and $\mu_2$ are related by

$$\left(\frac{\partial \mu_1}{\partial n_2}\right)_{T,P,m_1,m_0} = \left(\frac{\partial \mu_2}{\partial n_1}\right)_{T,P,m_2,m_0}, \tag{1a}$$

which can be rewritten in the form

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

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

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

and

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

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

$$\ln \frac{m_1^0}{m_1} = k_{12} m_2, \tag{3}$$

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

$$k_{12} = \frac{\left(\frac{\partial \mu_1}{\partial m_2}\right)_{m_1} m_1}{\left(\frac{\partial \mu_1}{\partial m_1}\right)_{m_0} m_2}, \tag{4a}$$
For the solutes, mean activity coefficients \( \gamma \) are related to \( \mu \) by

\[
\mu_1 = \mu_1^\infty (T) + RT \ln m_1 \gamma_1
\]

\[
\mu_2 = \mu_2^\infty (T) + \nu RT \ln m_2 \gamma_2
\]

where standard-state chemical potentials \( \mu_1^\infty \) and \( \mu_2^\infty \) depend only on temperature, and \( \nu \) 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

\[
\left( \frac{\partial \mu_1}{\partial m_1} \right)_{m_2} = RT \left( \frac{\partial \ln \gamma_1}{\partial m_1} \right)_{m_2}
\]

and

\[
\left( \frac{\partial \mu_2}{\partial m_1} \right)_{m_2} = \nu RT \left( \frac{\partial \ln \gamma_2}{\partial m_1} \right)_{m_2}
\]

It then follows that

\[
\left( \frac{\partial \mu_1}{\partial m_2} \right)_{m_1} = RT k_{12} \left( 1 + m_1 \left( \frac{\partial \ln \gamma_1}{\partial m_1} \right)_{m_2} \right)
\]

\[
\left( \frac{\partial \mu_2}{\partial m_1} \right)_{m_2} = \nu RT k_{21} \left( 1 + m_2 \left( \frac{\partial \ln \gamma_2}{\partial m_2} \right)_{m_1} \right)
\]

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

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

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 Krichhevsky-Ilinskaya equation [7]

\[
\ln \gamma_{1x} = \ln \left( \frac{y_1 \phi_1 P}{x_1 H_1^{\infty}} \right) - \int_{P^o}^P \frac{\nu_1^{\infty}}{RT} \, dP,
\]

where \( \gamma_1 \) is the mole fraction and \( \phi_1 \) is the fugacity coefficient of component 1 in the vapor phase; \( x_1 \) is the mole fraction of component 1 in the liquid phase, \( H_1^{\infty} \) is Henry’s constant for component 1 in the salt-free solvent, \( P^o \) is the vapor pressure of the solvent at temperature \( T \), and \( \nu_1^{\infty} \) is the partial molar volume of component 1 in solution at infinite dilution.

We use the notation \( \gamma_{1x} \) 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

\[
\left( \frac{\partial m_2}{\partial P} \right)_T = \frac{\nu_2 - \nu_1^s}{\nu RT \left( 1 + \frac{\partial \ln \gamma_2}{\partial m_2} \right)}
\]

where \( \nu_2 \) is the partial molar volume of the salt in aqueous solution and \( \nu_1^s \) 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

$$m_2(P, T, m_1=0) = m_2(P', T, m_1=0) + \left( \frac{\partial m_2}{\partial P} \right)_{T} (P-P')$$

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

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

where $m_2(P, T, 0)$ 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), $m_2(P, T, 0)$, 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 $v_2 - v_2'$ (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 $v_2$, $\gamma_2$ and $\partial ln\gamma_2/\partial m_2$, and that the pressure effect on $v_2$ 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~ 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 $NaCl-CO_2-H_2O$ 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 $\frac{\partial \ln \gamma_2}{\partial m_2}$. 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 $\frac{\partial m_2}{\partial P}$ 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 $NaCl-CO_2-H_2O$ 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 NaCl–CH₄–H₂O were also performed using data for CH₄ solubility in aqueous NaCl solutions [23]. Henry's constants for the binary system CH₄–H₂O were reported by Gillespie et al [13].

The predicted results are shown in Figure 9. It is important to note that the effect of CH₄ concentration is one order of magnitude lower than that of CO₂; 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 CH₄. However, highly soluble gases such as NH₃ and H₂S 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 H₂O–CO₂–Na₂SO₄ at 50 and 75 °C, and for the system H₂O–CO₂–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 NH₃ and H₂S.

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 CaSO₄, 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.
Acknowledgements

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Appendix: Activity Coefficient $\gamma_2$ as a Function of $m_2$. Pitzer's Equation.

In this work, the mean activity coefficient of the electrolyte, $\gamma_2$, is calculated from Pitzer's equation:

$$\ln \gamma_2 = -1Z_MZ_X A_\phi \left[ \frac{I^{1/2}}{1 + 1.2 I^{1/2}} + \frac{2}{1.2} \ln \left( 1 + 1.2 I^{1/2} \right) \right] + \frac{2v_Mv_X}{v} m_2 B_{MX^2} + \frac{3(v_Mv_X)^{3/2}}{v} m_2^2 C_{MX^2},$$

where

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

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

Parameters $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$ and $C_{MX^2}$ are temperature dependent. Tables for these parameters, as well as for the Debye-Hückel slope $A_\phi$, can be found in references [22] and [25] for NaCl and for Na$_2$SO$_4$, respectively.
References


### TABLE I - Properties of Binary Systems

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<th>( \bar{v}_1 , (cm^3 , mol^{-1}) )</th>
<th>( H_1^\infty , (bar) )</th>
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<td>1.273</td>
<td>0</td>
</tr>
<tr>
<td>75</td>
<td>19.0</td>
<td>1.273</td>
<td>0.052</td>
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<tr>
<td>75</td>
<td>33.8</td>
<td>1.273</td>
<td>0.097</td>
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<tr>
<td>75</td>
<td>43.8</td>
<td>1.273</td>
<td>0.123</td>
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<td>50.7</td>
<td>1.273</td>
<td>0.169</td>
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<td>72.0</td>
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<td>0.176</td>
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<td>86.7</td>
<td>1.273</td>
<td>0.196</td>
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<tr>
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<td>102.0</td>
<td>1.274</td>
<td>0.228</td>
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<td>120.3</td>
<td>1.275</td>
<td>0.226</td>
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<td>148.9</td>
<td>1.278</td>
<td>0.241</td>
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<tr>
<td>75</td>
<td>175.7</td>
<td>1.280</td>
<td>0.265</td>
</tr>
<tr>
<td>75</td>
<td>197.3</td>
<td>1.282</td>
<td>0.273</td>
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</table>
Table III - Measured Solubility of CO₂ in Aqueous Solutions of Na₂SO₄ at 50 and 75 °C

<table>
<thead>
<tr>
<th>T °C</th>
<th>P (bar)</th>
<th>m₂ (mol kg⁻¹)</th>
<th>x₁ 10³</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>95.6</td>
<td>1.95</td>
<td>5.99</td>
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<tr>
<td>50</td>
<td>145.1</td>
<td>1.98</td>
<td>6.27</td>
</tr>
<tr>
<td>50</td>
<td>76.6</td>
<td>2.71</td>
<td>3.47</td>
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<tr>
<td>50</td>
<td>137.6</td>
<td>2.72</td>
<td>4.62</td>
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<tr>
<td>75</td>
<td>37.9</td>
<td>0.95</td>
<td>4.48</td>
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<tr>
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<td>75.8</td>
<td>0.96</td>
<td>7.87</td>
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<tr>
<td>75</td>
<td>97.9</td>
<td>0.97</td>
<td>9.33</td>
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<tr>
<td>75</td>
<td>43.1</td>
<td>1.97</td>
<td>2.59</td>
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<tr>
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<td>72.1</td>
<td>1.91</td>
<td>4.28</td>
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<td>75</td>
<td>132.7</td>
<td>2.01</td>
<td>6.54</td>
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</table>

TABLE IV - Thermodynamic Properties of the System H₂O-CO₂(l)-Na₂SO₄(2) at 50 and 75 °C Calculated from Data in Table III

<table>
<thead>
<tr>
<th>T °C</th>
<th>∂lnγ₁/∂m₂ (kgmol⁻¹)</th>
<th>k₂₁ (kgmol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.27 ± 0.04</td>
<td>0.110 ± 0.010</td>
</tr>
<tr>
<td>75</td>
<td>0.40 ± 0.02</td>
<td>0.174 ± 0.009</td>
</tr>
</tbody>
</table>

TABLE V - Solubility Properties for the System H₂O-CO₂(l)-NaCl(2) Calculated from Published Data

<table>
<thead>
<tr>
<th>T °C</th>
<th>m₂(P,T,0) (mol kg⁻¹)</th>
<th>∂lnγ₂/∂m₂ (kgmol⁻¹)</th>
<th>∂m₂/∂P (mol (kg bar)⁻¹)</th>
<th>∂lnγ₁/∂m₂ (kgmol⁻¹)</th>
<th>k₂₁ (kgmol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>6.275</td>
<td>0.1269</td>
<td>1.94</td>
<td>0.20</td>
<td>0.056</td>
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<td>100</td>
<td>6.680</td>
<td>0.0929</td>
<td>1.85</td>
<td>0.14</td>
<td>0.042</td>
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<tr>
<td>150</td>
<td>7.198</td>
<td>0.0562</td>
<td>1.89</td>
<td>0.21</td>
<td>0.075</td>
</tr>
<tr>
<td>250</td>
<td>8.989</td>
<td>-0.0046</td>
<td>3.23</td>
<td>0.26</td>
<td>0.136</td>
</tr>
</tbody>
</table>
FIGURE 1
Experimental apparatus. (1) Feed pump. (2) Recirculation pump, bottom phase. (3) Recirculation pump, upper phase. (4) 15-μm 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, $\Delta m_2^P$ and $\Delta m_2^C$ are given by

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

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

$\Delta m_2^P$ 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. $\Delta m_2^C$ 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. $\Delta m_2^p$ and $\Delta m_2^c$ are defined in Figure 3.

FIGURE 8
Experimental and predicted solubility of NaCl as a function of CO$_2$ concentration at 50 °C.

FIGURE 9
Effect of dissolved CH$_4$ on the solubility of NaCl in water. $\Delta m_2^p$ and $\Delta m_2^c$ are defined in Figure 3. Note that $\Delta m_2^c$ is almost identical for the three temperatures shown in this figure. $\Delta m_2$ 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, $\Delta m_2$ 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

equilibrium cell

delonized water

sampling loop

nitrogen

saturated water

solution collection

burette
\[ \frac{\partial m_2}{\partial P} > 0 \]

\[ k_{21} > 0 \]

\[ \frac{\partial m_2}{\partial P} < 0 \]

\[ k_{21} > 0 \]

\[ \Delta m_2^P \]

\[ \Delta m_2^C \]

---

Pressure Effect

Concentration Effect

FIGURE 3
This Work

FIGURE 4

\[ \ln \gamma_{1x} \]

\[ m_2 \text{ (mol/kg)} \]

50 °C

75
FIGURE 5a

Effect of Pressure

Effect of Dissolved Gas
Effect of Pressure

Effect of Dissolved Gas

FIGURE 5b
\[ m_2 \text{(mol/kg)} \]

\[ P_{CO_2} \text{(bar)} \]

\[ 250 ^\circ C \]

\[ 9.00 \]

\[ 8.00 \]

\[ 7.00 \]

\[ 6.00 \]

\[ 0 \]

\[ 100 \]

\[ 300 \]

\[ 500 \]

\[ 150 \]

\[ 100 \]

\[ 50 \]

FIGURE 6
FIGURE 7
$m_2 (mol/kg)$

- Measured (This Work)
- Predicted

FIGURE 8
FIGURE 9