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Solubility of Hydrogen in Aqueous Solutions of Sodium and Potassium Bicarbonate from 293 to 333 K

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An experimental study is presented of the hydrogen solubility in aqueous salt solutions containing sodium and potassium bicarbonate from 293 to 333 K. For this purpose, gas consumption measurements have been performed by determining the ultimate pressure decrease in an intensively stirred, high pressure autoclave. Experiments were carried out at salt concentrations up to 1.0 mol kg⁻¹. At higher salt molalities, the hydrogen solubility was too low to be measured reliably. It was demonstrated that the hydrogen solubility followed the well-known Sechenov salt concentration dependence. At 298 K, the Sechenov or salting-out parameters were equal to 0.41 and 0.32 kg mol⁻¹ for sodium and potassium bicarbonate, respectively. Fairly good agreement was obtained with the salting-out parameters predicted by a recently developed empirical estimation method. The concentration ratio of the bicarbonate and carbonate ions showed only a minor influence on the hydrogen solubility. Furthermore, the Sechenov parameter was found to be a weak function of temperature. Virtually the same, linear temperature dependence was observed for both bicarbonate salts studied, i.e. −0.0023 and −0.0024 kg mol⁻¹ K⁻¹ for sodium and potassium bicarbonate, respectively.

Description of the Hydrogen Solubility

Method. The hydrogen solubility was determined by measuring the molar gas consumption, which appeared after applying a pressure difference (≤2 MPa H₂) with respect to an initial state of equilibrium, usually at atmospheric pressure. The gas−liquid system was stirred vigorously, and a batchwise operation with respect to both phases was employed. Experiments were carried out at temperatures ranging from 293 to 333 K. The salt concentration was kept below 1.0 mol kg⁻¹, because the solubility limit of NaHCO₃ in pure water at 293 K is equal to 1.1 mol kg⁻¹ (Timmermans, 1960; Linke and Seidell, 1958, 1965; Stephen and Stephen, 1963). Moreover, at higher molalities, the hydrogen solubility is generally too low to result in an acceptable experimental accuracy. In order to establish the influence of a partial bicarbonate dissociation on the salting-out effect, a few additional experiments were conducted with aqueous solutions of the corresponding carbonate salts.

Activity Coefficient. For a certain combination of temperature and partial pressure, the activity of a solute in pure water is identical to that occurring in an aqueous solution of arbitrary composition at the state of equilibrium. In the case of a hydrogen gas phase at temperatures ranging from about 293 to 333 K, ideal gas phase behavior can be assumed for partial pressures below about 2 MPa. Then, Henry’s law is applicable for the aqueous solutions used:

\[ \gamma_{mH}(m_{H})/m_{H} = (\gamma_{mH}(m_{H} = 0)/m_{H})_{m_{H} = 0} = \frac{p_{H}}{k_{mH}(m_{S} = 0)} \]  

(1)

If the molal activity coefficient of hydrogen in pure water, \( \gamma_{mH}(m_{S} = 0) \), is assumed to be equal to 1, rearrangement of eq 1 results in:

\[ \gamma_{mH}(m_{S}) = \frac{m_{H}(m_{S} = 0)}{m_{S}(m_{S} = 0)} \]  

(2)

Owing to the salting-out effect, the molal activity coefficient of hydrogen in an aqueous salt solution, \( \gamma_{mH}(m_{S}) \), exceeds the value of unity by definition.

Correlation Methods. In an attempt to empirically describe the salting-out effect for the solubility of a sparingly soluble gas, i.e. in a salt solution, \( c_{s}(sat.,c_{S}) \), as compared to that in pure water, \( c_{s}(sat.,c_{S} = 0) \), Sechenov (1889) proposed the following relationship:
Using the Pitzer equation, the solubility of a salt can be calculated:
\[ c_{\text{(sat., } c_j=0)} \] 
\[ c_{\text{(sat., } c_j)} \]  
\[ \ln \left( \frac{c_{\text{(sat., } c_j=0)}}{c_{\text{(sat., } c_j)}} \right) = k_S c_S \] (3)

Up to moderate salt concentrations, an analogous relationship will apply for a molality basis:
\[ \ln \gamma_{m_i}(m_S) = \ln \left( \frac{m_{\text{(sat., } m_j=0)}}{m_{\text{(sat., } m_j)}} \right) = k_m m_S \] (4)

Apparently, the molal activity coefficient of the dissolved gas, \( \gamma_{m_i}(m_S) \), shows an exponential dependence on the electrolyte concentration. The proportionality of the Sechenov parameter, \( k_S \), is specific to the gas and salt and is usually only a weak function of temperature. If the degree of dissociation of the aqueous salt is hardly concentration dependent, as is generally the case for strong electrolytes, eq 3 may be valid up to electrolyte concentrations as high as 8 mol m\(^{-3}\) (Schumpe, 1993; Weisenberger and Schumpe, 1995; Hermann et al., 1995). Experimentally determined values of the Sechenov parameter \( k_S \), for a great number of aqueous gas–solutions in various handbooks (see, e.g., Young, 1981; Zemaitis et al., 1986; Pitzer, 1991) or publications (see, e.g., Sada et al., 1974; Hikita et al., 1974; Khomutov and Konnik, 1974; Yasaki, 1977; Schumpe et al., 1978; Yasaki and Yoshida, 1979; Ueyama and Hatanaka, 1982; Clever, 1983). If no experimental gas solubility data are available for the specific electrolyte–gas combination, a number of models offer the possibility to estimate the Sechenov parameters. These models have either a purely theoretical basis (see, for instance, Shoor and Gubbins, 1969; Tiegel and Gubbins, 1973; Masterson, 1975) or are based on a semi-empirical approach and thus have to be considered merely as a correlation method (van Krevelen and Hoftijzer, 1950; Schumpe et al., 1978, 1982; Pawlikowski and Prausnitz, 1983; Schumpe, 1993; Weisenberger and Schumpe, 1995).

However, the theoretically based models often require more parameters and, as far as mixed solutions of various aqueous electrolytes are concerned, the agreement with the experimental data is generally poor. Despite the fact that the semi-empirical treatment tends to overestimate the salting-out effect at high electrolyte concentrations (Schumpe, 1993), i.e. the predicted solubility is too low, this estimation method is widely applied. Therefore, only the correlation methods that have a semi-empirical basis will be considered here.

Following van Krevelen and Hoftijzer (1950), who originally developed an equation for the description of the salting-out effect in solutions containing a single electrolyte, Danckwerts (1970) and Onda et al. (1970a, 1970b) extended the obtained result to mixed solutions of various salts, denoted by the index j:
\[ \ln \left( \frac{c_{\text{(sat., } c_j=0)}}{c_{\text{(sat., } c_j)}} \right) = \sum_j (h_+ + h_- + h_i) l_{c_j} \] (5)

However, Schumpe et al. (1978, 1982) pointed out that this equation is inconsistent for mixed electrolyte solutions, as multiplying the cation and anion specific parameters, \( h_+ \) and \( h_- \), by the ionic strength of the salt, \( l_{c_j} \), makes the salting-out effect of a certain ion depend on the valency of the counterion. In other words, the obtained solubility estimate depends on the choice of combining the various ions into salts, whereas this choice should logically be arbitrary. On the basis of these considerations, Schumpe (1993) and Weisenberger and Schumpe (1995) recently suggested the use of an empirical model in which, apart from the gas-specific constant, \( h_+ \) and \( h_- \), the individual salting-out effects of the ions, \( h_i \), are incorporated separately:
\[ \ln \left( \frac{c_{\text{(sat., } c_j=0)}}{c_{\text{(sat., } c_j)}} \right) = \sum_B (h_c + h_i) c_B \] (6)

The gas-specific constant was assumed to be a linear function of the temperature:
\[ h_i = h_{i1} + h_{i2}(T - T^0) \] (7)

Contrary to eq 5 it reveals that eq 6 is consistent in its application to mixed electrolyte solutions. At this point it may be interesting to note that eq 6 is very similar to the result obtained using the semi-empirical, extended Pitzer equation (Clegg and Brimblecombe, 1990). According to these authors, for interactions involving molecules, the Pitzer equation reduces to
\[ \ln \gamma_{m_i}(m_S) = 2 \sum_{B=1}^W m_B l_{w-B} \] (8)

Although the summation in eq 8 includes the molecule–molecule interactions (apart from those pertaining to water, \( w \)), Long and McDevit (1952) stated that the nonelectrolyte self-interaction term could safely be ignored when its solubility was relatively low, as, e.g., in the case of hydrogen. Therefore, usually only the ion–molecule interactions are taken into account. Due to this feature, combining eqs 4 and 8 offers the possibility to relate the molality-based Sechenov parameter to the Pitzer ion–molecule interaction parameters. For hydrogen dissolved in an aqueous solution of an alkali metal bicarbonate salt MHCO\(_3\), it can be written
\[ k_{m,S}(H_2,MHCO_3) = 2(\lambda_{H_2-M+} + \lambda_{H_2-HCO_3}) \] (9)

**Parameter Estimation.** On the basis of eqs 6 and 7 it is possible to provide an estimate of the hydrogen solubility in aqueous sodium and potassium bicarbonate solutions as a function of temperature. Table 1 lists the recommended parameter values for hydrogen and the various aqueous ions, as proposed by Weisenberger and Schumpe (1995) and Hermann et al. (1995). As aqueous bicarbonate solutions can be considered as a mixture of bicarbonate and carbonate salts with a common cation, the parameters of the aqueous carbonate ion are presented as well. Calculation of the approximate Sechenov parameters with eqs 6 and 7 resulted in values of 0.39, 0.70, 0.34, and 0.61 kg mol\(^{-1}\) for NaHCO\(_3\), Na\(_2\)CO\(_3\), KHC0\(_3\), and K\(_2\)CO\(_3\), respectively. However, in a mixture of the corresponding carbonate and bicarbonate salt, the condition of electroneutrality requires that
\[ m_{M+} = 2m_{CO_3^2-} + m_{HCO_3^-} \] (10)

if the hydroxyl and hydrogen ion concentrations are negligible. As a consequence, the evaluated Sechenov parameter must be compared on the basis of the same

<table>
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<tr>
<th>Ion B</th>
<th>( h_B/m^3) kmol(^{-1})</th>
<th>gas i</th>
<th>( h_i/m^3) kmol(^{-1})</th>
<th>( h_i^*/m^3) kmol(^{-1}) K(^{-1})</th>
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<tr>
<td>Na(^+)</td>
<td>0.2632</td>
<td>H(_2)</td>
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<td>-0.000688</td>
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<tr>
<td>K(^+)</td>
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<tr>
<td>HCO(_3^-)</td>
<td>0.2227</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>CO(_3^{2-})</td>
<td>0.3277</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Recommended Ion- and Gas-Specific Parameter Values for Use in Eqs 6 and 7 [Data from Weisenberger and Schumpe (1995) and Hermann et al. (1995) (Converted to ln Scale)]
cation concentration rather than on their identical salt concentration. This means that the Sechenov parameters as determined for the carbonate salts should be divided by a factor of 2. Then, a much smaller difference between the Sechenov parameter of the bicarbonate and the corresponding carbonate salt is noticed. Therefore, a small change in the solution composition toward a higher carbonate concentration is not expected to have a marked influence on the hydrogen solubility in aqueous bicarbonate solutions.

**Experimental Section**

**Equipment.** The solubility measurements were carried out in two separate, high-pressure autoclaves, that have been operated batchwise with respect to both the gas and liquid phases. Except for the difference in total volume, the experimental setups were largely identical. The autoclave pressures were monitored digitally with an accuracy of 1 kPa. The value of the gas and liquid temperatures could be measured with an uncertainty of about 0.2 K. The solubility data for the sodium bicarbonate and sodium carbonate solutions were obtained in setup I (913 mL), whereas for the corresponding potassium salts setup II (549 mL) was applied. A more detailed description of both setups has been given elsewhere (Snijder et al., 1993).

**Operating Procedure.** First, the reactor was filled with known amounts of demineralized water and alkali metal salt. Subsequently, the liquid phase was heated to the desired temperature. Then, the reactor was flushed several times with nitrogen and hydrogen successively. The hydrogen gas–liquid equilibrium was established at atmospheric pressure, whereafter the system was further pressurized with hydrogen up to a maximum value of about 2 MPa. Intensive agitation of the solution was accomplished until no further pressure change could be observed (depending on the agitation speed, usually after a few minutes). At the end of an experiment, the total electrolyte concentration was verified titrimetrically within 0.001 mol kg⁻¹. In order to obtain a reliable experimental result at a certain combination of temperature and salt concentration, the solubility measurement was repeated at least twice. High-purity hydrogen (≥ 99.999%) was supplied by Hoekloos. The bicarbonate and carbonate salts (analytical grade, > 99.5%) were purchased from Merck and used without further purification.

**Determination of the Hydrogen Solubility.** \(P_{H,1}\) is the initial hydrogen pressure in equilibrium with the electrolyte solution, and \(P_{H,3}\) is the final hydrogen pressure prior to equilibration. Equilibration of the gas phase and the electrolyte solution will finally yield a saturation pressure \(P_{H,3}\). If the ideal gas law at constant temperature is used, the difference in hydrogen solubility at the respective equilibrium pressures \(P_{H,1}\) and \(P_{H,3}\) can be calculated from the molar balance between the gas and liquid phase:

\[
\Delta m_{H}(\text{sat}) = m_{H,3}(\text{sat}) - m_{H,1}(\text{sat}) = \frac{(P_{H,2} - P_{H,3})V_G}{n_wM_wRT} \tag{11}
\]

By insertion of this result into eq 1, the hydrogen activity coefficient can be calculated according to

\[
\gamma_{m,H}(m) = \frac{n_wM_wRT}{V_Gk_{m,H}(m, T, m = 0)} \frac{P_{H,3} - P_{H,1}}{P_{H,2} - P_{H,3}} \tag{12}
\]

where \(n_wM_w\) denotes the total mass of water present in the salt solution and \(V_G\) represents the volume occupied by the gas phase.

![Figure 1. Salt concentration dependence of the hydrogen activity coefficient in aqueous NaHCO₃ at 298 K (●) and at 333 K (○).](image1)

![Figure 2. Molal Sechenov parameter \(k_{m,S}\) as a function of temperature in aqueous NaHCO₃ (●) and KHCO₃ (○).](image2)

The estimated experimental accuracy of the measured hydrogen solubilities amounted to ±0.002 mol kg⁻¹. The relative experimental accuracy of the determined activity coefficients, \(\gamma_{m,H}(m)\), and the salting-out parameters, \(k_{m,S}\), is estimated at 2% and 4%, respectively.

**Results and Discussion**

In order to test the validity of eq 4 for application in the current gas–electrolyte system, Figure 1 presents the hydrogen activity coefficient in an aqueous solution of sodium bicarbonate at 298 and 333 K. As can be noticed, a linear relationship occurs at both temperatures. The slope of the straight line can thus be interpreted as the molality-based Sechenov parameter \(k_{m,S}\) at the experimental temperature for the specific gas–electrolyte combination. Within a range of 293–333 K, the temperature dependence of \(k_{m,S}\) is shown in Figure 2. Clearly, a virtually identical temperature dependence is observed for both bicarbonate salts studied. The solubility of hydrogen in the potassium salt appears to be somewhat higher; witness its lower Sechenov parameter. On the basis of the obtained experimental results, the Sechenov parameter can be represented by a linear function of temperature:

\[
k_{m,S} = k_{m,S}^0 + k_{m,S}^1(T - T^0) \tag{13}
\]

which is analogous to the empirical model proposed by Schumpe (1993); see eq 7.

For the bicarbonate salts studied, the currently determined activity coefficients and salting-out parameters of hydrogen are given in Tables 2 and 3, respectively. At increasing salt concentrations, it appears that at higher
temperatures the smaller salting-out effect is accompanied with a lower solubility in pure water. The partial compensation of these effects implies that the hydrogen solubility becomes nearly temperature independent at high salt concentrations. Table 4 represents the parameter values which can be used in eq 13 to calculate \( k_{m,5} \) for sodium and potassium bicarbonate at temperatures from 293 to 333 K.

Referring to the possibility of a decomposition of the aqueous bicarbonate into carbonate, carbon dioxide, and water; some additional solubility measurements have been performed with aqueous solutions of the corresponding alkali metal carbonates. Table 5 lists relevant results regarding these experiments. It can be concluded that the influence of the carbonate/bicarbonate equilibrium on the salting-out effect is negligible. At this point, it has to be remarked that the agreement between the measured and calculated salting-out parameters is very satisfactory. Moreover, the experimental, molality-based Sechenov parameters reported here are in reasonable agreement with the early measurements of Steiner (1894), being 0.66 kg mol\(^{-1}\) for sodium carbonate and 0.63 kg mol\(^{-1}\) for potassium carbonate, respectively.

Conclusions

The frequently employed Sechenov approach to account for the salting-out effect of nonpolar gases in electrolyte solutions can suitably be used to describe the hydrogen solubility in aqueous solutions of pure sodium and potassium bicarbonate. The determined Sechenov parameter for sodium bicarbonate at 298 K (0.41 kg mol\(^{-1}\)) was somewhat higher than the one evaluated for the corresponding potassium salt at the same temperature (0.32 kg mol\(^{-1}\)).

A weak temperature dependence was observed for both parameters and the respective temperature constants were virtually equal, viz. \(-0.0023\) kg mol\(^{-1}\) K\(^{-1}\) and \(-0.0024\) kg mol\(^{-1}\) K\(^{-1}\) for NaHCO\(_3\) and KHCO\(_3\), respectively.

It was confirmed experimentally that the observed salting-out effect was similar if the bicarbonate salt was substituted by the corresponding carbonate salt, provided that the comparison was based on an equal concentration of the alkali metal cation. At high electrolyte concentrations, the hydrogen solubility appeared to be nearly temperature independent, which was due to a partial compensation of temperature effects on the Henry coefficient and the Sechenov parameter. Finally, a fairly good agreement was shown between the Sechenov parameters calculated using a recently developed correlation method (Schumpe, 1993, and Weisenberger and Schumpe, 1995) and those determined in the present study.

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