The pH Monitoring of the non-steady CO₂ Absorption Process in Aqueous Sodium Carbonate Solutions

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The paper presents the possibilities to monitor the non-steady carbon dioxide absorption processes in aqueous sodium carbonate solutions through a method based on associating the pH measurement of the solution with a mathematical model of the equilibrium state, developed to calculate the concentration of the present chemical species. The deprotonation constants necessary to solve the model, have been experimentally determined for aqueous sodium carbonate-bicarbonate solutions with ionic strength in the 0.45-2 mol L⁻¹ range. The dependence of the Kᵢ constants on the ionic strength was modelled according to the specific ionic interactions theory (SIT), taking into account the influence of the sodium ions. The developed model permits the use of the monitoring system based on measuring of the the hydrogen ions activity and the total sodium concentration, in a range of ionic strenght up to 2 mol L⁻¹, with a standard uncertainty of the pKᵢ values of 0.015 units. The monitoring method was validated by applying it in two semi-continuous absorption processes and comparing the results with the ones that we got by sampling and by the determination of the carbonate, bicarbonate and CO₂ dissolved contents, through classical analysis methods. The method based on pH-metric measurement associated with the mathematical model of the equilibrium state can be applied for determining the concentration of the carbonate and bicarbonate ions. The results are in accordance with those of the chemical determinations considered as reference. The deviations do not exceed 5%. In the non-steady absorption processes in aqueous carbonate solutions with concentrations in the 2-5% range and a volumetric rate of CO₂ to absorbing solution of 0.15 min⁻¹, the equilibrium state model cannot be used for the monitoring of the CO₂ dissolved concentration because the equilibrium state between the dissolved carbon dioxide and the bicarbonate ions is not achieved.

Keywords: carbon dioxide sequestration, CO₂ absorption monitoring, equilibrium model, protonation of carbonate, dependence on ionic strength, specific ion interaction theory (SIT), ion pair formation model

The first phase of the sequestration process of the carbon dioxide from the atmosphere or from the burning gases is represented by the absorption through various methods, in synthetical or natural media. Among these processes is the absorption in alkaline solutions. The control of the absorption process implies the monitoring of the chemical species in the solution and sometimes in gaseous phase.

This paper presents a monitoring procedure of the semi-continuous absorption processes of the CO₂ in aqueous sodium carbonate solutions, which are based on the association of the pH measurement of the solution with the mathematical model of the equilibrium state of the system.

By bubbling of a CO₂ flow or inert gas that contains CO₂ through a Na₂CO₃ aqueous solution, the following equilibrium reactions take place:

\[ \text{CO}_2 + H_2O \rightleftharpoons K_1 H^+ + HCO_3^- \]  
\[ \text{HCO}_3^- \rightarrow K_2 H^+ + CO_3^{2-} \]  
\[ \text{H}_2O \rightleftharpoons K_w H^+ + OH^- \]

The application of the equilibrium state model in order to monitor the non-steady absorption process is based on the following hypotheses:

- the rates of the acid-basic reactions in aqueous solutions are very high, so that pseudo-equilibria are established between the present species.
- the response of the pH electrode is fast enough, so that the information about the system is transmitted in real time.

The current paper presents the results of the study undertaken to check these assumptions.

In monitoring the carbonate species, based on measuring the hydrogen ion activity is necessary to know deprotonation constants on the mixed scale where the carbonate species are represented in molar concentrations and the protons in molar activities: \( K_1 = [\text{HCO}_3^-]a_H / [\text{CO}_2]_{aq} \) and \( K_2 = [\text{CO}_3^{2-}]a_H / [\text{HCO}_3^-] \).

It is also necessary to know the dependence of these deprotonation constants on the ionic strength of the medium.

In the monitoring process using the model of the equilibrium status, the uncertainties associated with the equilibrium constants and the calculation models of the equilibrium constants and the activity coefficients of the chemical species in specific media are significant, but frequently they are not mentioned. The literature in the field provides accurate values for the equilibrium constants at infinite dilution. At 25°C these values are [1,2]:

\[ \lg K_0^1 = -6.355 \]
\[ \lg K_0^2 = -10.336 \]
\[ \lg K_0^w = -14.006 \]

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The determination of the thermodynamical parameters of the carbon dioxide systems has been extensively investigated in natural waters, especially in sea water in order to identify the relation between the CO₂ gas – aqueous solution equilibrium and the global climate changes. Simultaneously with these studies in the field, databases have been created and programs to calculate the activity coefficients of the ions and the equilibrium constants in various media and various models of calculation [3,6].

The literature reports deprotonation constants of the carbonate species in NaCl, KNO₃, and NaClO₄ media, many of them without taking into consideration the possible interaction of the carbonate and bicarbonate with the supporting electrolyte cation.

With respect to the protonation equilibrium of the carbonate species in concentrated carbonate and bicarbonate solutions, the few data reported have not been included in the databases created with rigorous selection.

For the sodium carbonate-bicarbonate system, Vas Bhat and his collaborators present calculation formulas of the equilibrium constants depending on the sodium ion concentration [7]. The Vas Bhat model does not make the difference between the solutions that have the same total sodium concentration and different reports of the carbonate and bicarbonate concentrations.

In the absence of some reliable data, expressed on the appropriate scale of the monitoring necessities, the values of the acidity constants of the $K_2$ bicarbonate in their own ionic medium, have been experimentally determined using the pH-metric method for ionic strength range 0.45-2 mol L⁻¹. The obtained data was modeled based on the specific ion interaction theory (SIT) and have been compared with the values obtained by applying the Vas Bhat model. The differences between the models are interpreted by reporting them to different scales and by ion associations forming weak complexes.

**Experimental part**

The measurement equipment is a Mettler-Toledo portable pH-meter 1140 model, equipped with a combined glass electrode, provided with temperature sensor InPro 3253/120/Pt 1000 type. The hydrogen ion activity scale has been used ($pH=-\log a_H$).

For the determination of the acidity constants a glass measurement cell, with thermostated jacket, at 25±1°C was used.

At the monitoring of the CO₂ absorption the pH-meter was connected to a computer that uses a specialized software and receives, saves and graphically presents the data of the original measurements as functions of time.

For the purpose of determination of the equilibrium constants a series of 13 standard carbonate-bicarbonate solutions have been prepared, having a sodium concentration between 0.37 and 1.6 mol L⁻¹ and apparent ionic strength between 0.45-2 mol L⁻¹ and their pH was determined at 25 ± 0.1°C.

The composition of the standard solutions and the pH values used for the determination of the equilibrium constants are presented in table 1.

**Table 1**

<table>
<thead>
<tr>
<th>Standard solution</th>
<th>NaHCO₃ molL⁻¹</th>
<th>Na₂CO₃ molL⁻¹</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.225</td>
<td>0.075</td>
<td>9.43</td>
</tr>
<tr>
<td>2</td>
<td>0.187</td>
<td>0.094</td>
<td>9.61</td>
</tr>
<tr>
<td>3</td>
<td>0.150</td>
<td>0.113</td>
<td>9.76</td>
</tr>
<tr>
<td>4</td>
<td>0.075</td>
<td>0.151</td>
<td>10.16</td>
</tr>
<tr>
<td>5</td>
<td>0.921</td>
<td>0.027</td>
<td>8.21</td>
</tr>
<tr>
<td>6</td>
<td>0.875</td>
<td>0.049</td>
<td>8.48</td>
</tr>
<tr>
<td>7</td>
<td>0.779</td>
<td>0.098</td>
<td>8.79</td>
</tr>
<tr>
<td>8</td>
<td>0.537</td>
<td>0.222</td>
<td>9.27</td>
</tr>
<tr>
<td>9</td>
<td>0.475</td>
<td>0.043</td>
<td>10.57</td>
</tr>
<tr>
<td>10</td>
<td>1.207</td>
<td>0.151</td>
<td>8.73</td>
</tr>
<tr>
<td>11</td>
<td>0.905</td>
<td>0.303</td>
<td>9.13</td>
</tr>
<tr>
<td>12</td>
<td>0.603</td>
<td>0.453</td>
<td>9.49</td>
</tr>
<tr>
<td>13</td>
<td>0.308</td>
<td>0.598</td>
<td>9.88</td>
</tr>
</tbody>
</table>

**Fig. 1. Photobioreactor**

http://www.revistadechimie.ro
where \( cc \) and \( cb \) represent the total carbonate and bicarbonate concentration.

The apparent ionic strength is calculated based on the total ion concentration, without taking into account the association with weak complex formation between sodium ions and carbonate ions.

The standard uncertainties of the determined \( pK_2 = -\log_{10} K_2 \) values are 0.012.

In table 3 are presented both the experimentally determined \( pK_2 \) constants and the ones calculated with the V as Bhat formula:

\[
\frac{K_{2a}}{K_{2e}} = 0.03194\sqrt{[Na^+]_m} + 0.000125[Na^+]
\]  

In this relation, the sodium concentration is expressed in mol m\(^{-3}\).

A strict comparison with the V as Bhat model cannot be made because of the different \( pH \) calculation scale, but the differences can be attributed to the simplification introduced by replacing the ionic strength with the sodium ion concentration.

The SIT model applicable to the \( pK_2 \) data expressed on a mixed scale has the general form:

\[
\log\left(\frac{K_{2a}}{K_{2e}}\right) = \frac{0.5093\sqrt{I_a}}{1 + 1.5\sqrt{I_a}} + L(I_a)
\]  

Results and discussions

The modeling of the \( K_2 \) dependence constants on the ionic strength

In figure 3, for apparent ionic strength \( (I_a) \) within the 0.45-2 mol L\(^{-1}\) range, are presented the \( K_2 \) equilibrium constants calculated based on table 1 with the formula:

\[
pK_2 = pH - \log_{10}\left(\frac{cc}{cb}\right) + \frac{0.0928}{x_2} - 0.4166 + 10.054
\]

where \( c_c \) and \( c_b \) represent the total carbonate and bicarbonate concentration.

The apparent ionic strength is calculated based on the total ion concentration, without taking into account the association with weak complex formation between sodium ions and carbonate ions.

The standard uncertainties of the determined \( pK_2 = -\log_{10} K_2 \) values are 0.012.

In table 3 are presented both the experimentally determined \( pK_2 \) constants and the ones calculated with the V as Bhat formula:

\[
\log\left(\frac{K_{2a}}{K_{2e}}\right) = \frac{0.03194\sqrt{[Na^+]_m} + 0.000125[Na^+]}{1 + 0.0416\sqrt{[Na^+]_m}}
\]

In this relation, the sodium concentration is expressed in mol m\(^{-3}\).

A strict comparison with the V as Bhat model cannot be made because of the different \( pH \) calculation scale, but the differences can be attributed to the simplification introduced by replacing the ionic strength with the sodium ion concentration.

The SIT model applicable to the \( pK_2 \) data expressed on a mixed scale has the general form:

\[
\log\left(\frac{K_{2a}}{K_{2e}}\right) = \frac{0.5093\sqrt{I_a}}{1 + 1.5\sqrt{I_a}} + L(I_a)
\]  

<table>
<thead>
<tr>
<th>Standard</th>
<th>Ionic strength mol L(^{-1})</th>
<th>Sodium concentration mol L(^{-1})</th>
<th>Experimental ( pK_2 )</th>
<th>Vas Bhat modeled ( pK_2 )</th>
<th>SIT model ( pK_2 )</th>
<th>L(I(_a))/I(_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.450</td>
<td>0.375</td>
<td>9.905</td>
<td>9.939</td>
<td>9.903</td>
<td>0.575</td>
</tr>
<tr>
<td>2</td>
<td>0.469</td>
<td>0.375</td>
<td>9.909</td>
<td>9.939</td>
<td>9.939</td>
<td>0.579</td>
</tr>
<tr>
<td>3</td>
<td>0.491</td>
<td>0.377</td>
<td>9.883</td>
<td>9.940</td>
<td>9.877</td>
<td>0.565</td>
</tr>
<tr>
<td>4</td>
<td>0.528</td>
<td>0.377</td>
<td>9.856</td>
<td>9.940</td>
<td>9.852</td>
<td>0.570</td>
</tr>
<tr>
<td>5</td>
<td>1.002</td>
<td>0.975</td>
<td>9.744</td>
<td>9.769</td>
<td>9.723</td>
<td>0.386</td>
</tr>
<tr>
<td>6</td>
<td>1.022</td>
<td>0.973</td>
<td>9.732</td>
<td>9.770</td>
<td>9.711</td>
<td>0.389</td>
</tr>
<tr>
<td>7</td>
<td>1.074</td>
<td>0.976</td>
<td>9.689</td>
<td>9.771</td>
<td>9.689</td>
<td>0.408</td>
</tr>
<tr>
<td>8</td>
<td>1.204</td>
<td>0.981</td>
<td>9.653</td>
<td>9.771</td>
<td>9.633</td>
<td>0.391</td>
</tr>
<tr>
<td>9</td>
<td>1.467</td>
<td>0.992</td>
<td>9.527</td>
<td>9.770</td>
<td>9.523</td>
<td>0.401</td>
</tr>
<tr>
<td>10</td>
<td>1.660</td>
<td>1.509</td>
<td>9.632</td>
<td>9.662</td>
<td>9.683</td>
<td>0.288</td>
</tr>
<tr>
<td>11</td>
<td>1.813</td>
<td>1.510</td>
<td>9.661</td>
<td>9.661</td>
<td>9.641</td>
<td>0.277</td>
</tr>
<tr>
<td>12</td>
<td>1.962</td>
<td>1.509</td>
<td>9.664</td>
<td>9.662</td>
<td>9.599</td>
<td>0.250</td>
</tr>
<tr>
<td>13</td>
<td>2.103</td>
<td>1.505</td>
<td>9.591</td>
<td>9.662</td>
<td>9.558</td>
<td>0.245</td>
</tr>
</tbody>
</table>
In table 2 are presented the experimental values of the adjustable parameter $L(\Sigma)/\Sigma_I$. It can be noticed the existence of a reverse proportionality of this parameter with the sodium ion concentration, described by the equation:

$$L(\Sigma)/\Sigma_I = -0.2829[Na] + 0.6843, \ r^2 = 0.9957 \quad (7)$$

The relation (7) permits a data fitting on a wide field of concentration, with low uncertainties.

On a total concentration scale, the SIT model applicable for the monitoring of the $CO_2$ absorption is the following:

$$\log \left( \frac{K_{Na}}{K_{Na}^0} \right) = -\frac{\sqrt{I_a}}{1 + 1.5\sqrt{I_a}} + 0.658I_a - 0.2634I_a[Na] \quad (8)$$

The residual uncertainty of the $pK_2$ values calculated with the equation (8), expressed as standard deviation is 0.0064 units.

The influence of the sodium ion concentration can be evaluated using a model that takes into consideration the formation of ion pairs.

The researchers published values of the associating constants of sodium ions with carbonate and bicarbonate ions in tetraethylammonium iodide medium, where the association with the support electrolyte ions is supposed to be minimal [9]. These values, valid at ion strengths lower than 1mol L$^{-1}$ are:

$$\log K_{Na}^2(Na^++L_2^- = NaL) = 0.95 \pm 0.15$$

$$\log K_{Na}^1(Na^++HL^- = NaHL) = 0.15 \pm 0.15$$

We have used these constants to determine the concentration of the free ions by solving the model represented by the equations:

$$K_{Na}^0K_{Na}^2(Na^+)[Na^+] + (K_{Na}^1 + K_{Na}^2 + K_{Na}^0K_{Na}^2)c_s +$$

$$+ (1 + K_{Na}^1c_s + K_{Na}^2c_s)[Na^+] = c_s + 2c_s$$

$$[HCO_3^-] = \frac{c_s}{1 + K_{Na}^2[Na^+]} \quad (10)$$

$$[CO_3^{2-}] = \frac{c_s}{1 + K_{Na}^0[Na^+]} \quad (11)$$

$$[NaHCO_3] = \frac{c_sK_{Na}^0}{1 + K_{Na}^2[Na^+]} \quad (12)$$

In table 3 are presented the concentrations of the free and associated carbonate species and the ionic strength determined on their basis.

The data has been used to determine the experimental acidity constants based on the concentration of free ions, $K_i'$:

$$pK_i' = pH - \log \left[ \frac{[CO_3^{2-}]}{[HCO_3^-]} \right] \quad (14)$$

The influence of the ion pair formation on the ionic strength is manifested by a drastic decrease of this comparing it to the apparent ionic strength.

The dependence of the $K_{Na}$ constant on the ionic strength, represented in figure 4, for the declared reliable range of the association constants, is a linear function of ionic strength and its value extrapolated to zero ionic strength is 10.332. The accurate reproduction of the $K_{Na}$ value (of 10.334) existing in the databases and confirmed by the latest published papers in the field, proves the consistency of the determined $K_{Na}$ values in this experiment and accuracy of the $K_{Na}$ constants used by us in the ion pair formation model.

The $K_i'$ acidity constants have been modeled according to the SIT model. The modeled values and the adjustable parameters $L(\Sigma)/\Sigma_I$ are presented in table 3.

![Fig. 4. Dependence of the $pK_i'$ on real ionic strength, on free ion concentration scale](image-url)
According to the SIT theory, \( L(I)/I \) is defined as:

\[
L(I)/I = \Delta\varepsilon = \varepsilon_{CO_3^2-} - \varepsilon_{HCO_3^-} \quad (15)
\]

In the range of ionic strength lower than 1 mol L\(^{-1}\), the average value of the \( L(I)/I \) SIT parameter is -0.082. The value is in good accordance with the corresponding \( \Delta\varepsilon = -0.08 \) in NaClO\(_4\) medium, calculated with data from IUPAC database \([6]\).

The validation of the monitoring method

The equilibrium state of the carbonate species in the solution is modeled by the following system of equations:

\[
\begin{align*}
K_1 &= \frac{[H^+][HCO_3^-]}{[CO_3^{2-}]_{aq}} \quad (16) \\
K_2 &= \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (17) \\
K_{w} &= [H^+][OH^-] \quad (18) \\
[Na^+] &= [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \quad (19)
\end{align*}
\]

where the square brackets represent the concentrations and the round brackets, the molar activities of the corresponding species.

Figure 5 presents the concentration of the dissolved carbon dioxide \([CO_2(\text{aq})]\) experimentally determined and the ones calculated with the 16-19 equation system for the experiment of absorption in 5% carbonate solution.

There are significant differences in the equilibrium state described by the model and the measured concentrations, which consist of an initial accumulation of carbon dioxide in the solution, over the saturation concentration, which is consumed during the experiment. In the case of absorption in 2% sodium carbonate solution, the accumulation of carbon dioxide is kept at approximately 0.028 mol L\(^{-1}\), a value that is approximately 100 times higher than the equilibrium concentration.

The partial pressures of the carbon dioxide in gaseous phase, calculated with the 16-19 model have been compared with the ones of the equilibrium state calculated with the following equation \([10,11]\):

\[
P_r = \frac{f^2 N^{129}}{9.875(1-f)(185-t)} \quad (20)
\]

where: 
- \( f \) is the sodium ion molar fraction corresponding to the bicarbonate; 
- \( N \) - the normal concentration of the sodium 
- \( S \) - \( CO_2 \) solubility in water 
- \( t \) - temperature in °C.

The differences between the two sets of values strengthen the conclusion that during the experiment, the reaction (1) does not reach the equilibrium state because the carbon dioxide desorption step is slow.

The concentrations of the carbonate and bicarbonate ions, determined by solving the model for the momentary values of the \( pH \), using the acidity constants determined by the equation (8) are in accordance with the values determined by the chemical analysis for both experiments. Figure 6 exemplifies the comparative data for the absorption experiment in 5% Na\(_2\)CO\(_3\) solution. A similar result was obtained by the absorption experiment in 2% Na\(_2\)CO\(_3\).

For the reaction described by equation (2), both the representations confirm the formulated hypotheses at the foundation of the procedures: the quick protonation-deprotonation reaction of ionic carbonate species reaches successive stages of pseudo-equilibrium and the glass electrode transmits the information in real time allowing us to monitor the process.

The registered deviation of the concentrations compared to the reference values are presented in figure 7 as relative values reported to the total molar concentration of the carbonate species in the solution.

The deviations do not exceed 5%. Great values are registered when the concentration of the analyte are low and they can be attributed to the analysis methods. The
extended uncertainties of the analysis applied methods are 1% for the determination of the bicarbonate and 1.5% for the determination of the carbonate. The pH is determined with a 0.02 unit uncertainty.

Conclusions

The experiments made for the validation of the pH – metrical procedure to monitor the absorption process of the carbon dioxide in aqueous sodium carbonate solutions with concentration between 2-5% and a rate of CO₂ to absorbing solution of 0.15 min⁻¹ has demonstrated that the process that uses the equilibrium state model cannot be applied for the determination of the dissolved carbon dioxide because reaction (1) does not reach the equilibrium state.

The procedure can be applied to determine the concentration of the carbonate and bicarbonate ionic species. The rate of the protonation-deprotonation reactions being high the second reaction (2) reaches successive pseudo-equilibrium stages. The method based on pH-metrical measurement associated with the mathematical equilibrium model is in accordance with the results of the chemical determinations considered as reference. The deviation does not exceed 5%. The model of the equilibrium state applicable to monitor the non-steady CO₂ absorption processes is the (17) (18) and (19) equation system.

The uncertainties of the carbonate and bicarbonate ions determinations are significantly influenced by the uncertainty of the $K_a$ acidity constant and of $K_b$ dependence model on the ion strength of the medium.

The established model based on the experimental determination of the $K_a$ values (8) extends the maximum application level of the classic SIT model to ion strength from approximately 1mol L⁻¹ up to 2 mol L⁻¹, taking into account the influence of the sodium ions. For ion strengths lower than 2 mol L⁻¹, the equation (8) permits the use of the mathematical model, with a standard uncertainty of the $pK_a$ of 0.015 units, when the activity of the hydrogen ion and the total sodium concentration are known.

References

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