Low pressure equilibrium between $\text{H}_2\text{S}$ and $\text{CO}_2$ over aqueous alkanolamine solution

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The simultaneous absorption of $\text{H}_2\text{S}$ and $\text{CO}_2$ in aqueous alkanolamine solution is of considerable commercial importance. The reversible nature of reactions always results in equilibrium partial pressure of $\text{CO}_2$ and $\text{H}_2\text{S}$ over amine solution. A simple method is presented to determine the equilibrium partial pressure having very low loading of $\text{H}_2\text{S}$ and $\text{CO}_2$ with the select-ion electrode. The entire equilibrium is divided into two parts, namely first equilibrium and the final equilibrium. A ($\text{H}_2\text{S} + \text{CO}_2$)-aqueous alkanolamine system is highly non-ideal. Therefore, an attempt has been made to correlate data by using "final equilibrium" expression based on ideal behaviour and then introducing a lumped correction factor ($\beta$) to predict observed data between $\text{H}_2\text{S}$-$\text{CO}_2$ and diethanolamine solution. This methodology being process engineering friendly can be extended to other systems also.

The simultaneous absorption of $\text{H}_2\text{S}$ and $\text{CO}_2$ is of considerable importance in sweetening of natural gas, associated gas and biogas. For instance, transportation of natural gas or associated gas needs almost total removal of $\text{H}_2\text{S}$ (say <1 ppm) and to some extent removal of $\text{CO}_2$ to overcome corrosion related problems in pipelines. Bio-gas from fermentation units, anaerobic digester is often used to generate power by firing the same as fuel in gas engines. Though $\text{CO}_2$ along with $\text{CH}_4$ is acceptable, $\text{H}_2\text{S}$ levels are desired to be as low as possible to avoid corrosion related problems.

By and large aqueous solutions of alkanolamines are used for the simultaneous absorption of $\text{H}_2\text{S}$ and $\text{CO}_2$. The reaction between $\text{H}_2\text{S}$, $\text{CO}_2$ and alkanolamine is reversible in nature. Therefore, in the top section of the absorber, the knowledge of equilibrium partial pressure of $\text{H}_2\text{S}$ and $\text{CO}_2$ over partially regenerated amine solution is desirable for the process design of the absorber. The extent of sweetening of gas stream (removal of $\text{H}_2\text{S}$ and $\text{CO}_2$) depends upon the equilibrium consideration in the top section of the countercurrently operated absorption column.

The equilibrium in $\text{CO}_2$-$\text{H}_2\text{S}$-alkanolamine system has been well analysed by Asterita et al.\textsuperscript{2}. Kent and Eisenberg\textsuperscript{3} and Deshmukh and Mather\textsuperscript{4}. The models of Kent-Eisenberg and Deshmukh-mather are briefly reviewed in the following:

Kent and Eisenberg assumed activity coefficient of all species to be unity. Further they used all the published information on the various equilibrium constants at infinite dilution and correlated them with temperature in the polynomial exponential form. In order to fit the experimental data they forced values of $K_a$ and $K_{aa}$ to obtain the best fit. Thus the $K_a$ and $K_{aq}$ were derived. No wonder their model could well predict behaviour of single solute system $\text{CO}_2$ and $\text{H}_2\text{S}$. However, when the mixture is present, their model could not predict the observed values well.

Deshmukh and Mather\textsuperscript{4} proposed the thermodynamic model for the solubility of $\text{CO}_2$ and $\text{H}_2\text{S}$ in alkanolamine solution. They accounted for variation in activity coefficients through modified form of Debye-Huckel expression. The model by Deshmukh and Mather is rather complex to use for it requires the knowledge of various interaction parameters. Their model fails to predict acceptable partial pressures of $\text{H}_2\text{S}$ and $\text{CO}_2$ at higher loading of solutions. The need for reliable information on carbamate hydrolysis equilibrium constants was highlighted by these researchers.

Very scanty information is available in the published literature on very low-pressure equilibrium data. Lal et al.\textsuperscript{5} have published some data on low pressure equilibrium of $\text{H}_2\text{S}$ and $\text{CO}_2$ over aqueous diethanolamine solution. Here, a novel and simpler method of measuring equilibrium pressure of $\text{H}_2\text{S}$ and $\text{CO}_2$ with the help of ion-selective electrodes is pre-
sented here. In addition, a unified approach is also presented to analyze data based on the various equilibrium constants at infinitely dilute solutions along with a lumped correction factor taking into consideration highly non-ideal aqueous system containing various ionic species such as amines, protonated amine, carbamate, bicarbonate, hydroxyl ions etc.

**Experimental Procedure**

**Materials**—Diethanolamine (DEA), sodium carbonate (Na$_2$CO$_3$) and sodium sulphide (Na$_2$S) used were of analytical grade with 99.5% purity and obtained from S.D. Fine Chem. Ind., Mumbai (India). H$_2$S gas was generated in Kipp’s apparatus. CO$_2$ gas is supplied in cylinder obtained from Maharashtra gas Company which is of 99% purity. Sulphuric acid was used to generate H$_2$S from iron sulphide so that contamination due to HCl and water is avoided. Also sufficient quantity of gas is generated and purged out so that air contamination in H$_2$S is eliminated.

**Experimental set-up**—The experimental set-up consisted of a gas bubbler with magnetic stirrer to enhance equilibrium process. The equilibrium cell is fitted with a conductivity probe. The exit of the cell is connected to a glass reservoir. The gas-circulating blower takes gas from reservoir and passes into the equilibrium cell. The pressure maintained in this system is practically near atmosphere. The entire assembly, except gas-circulating blower, is placed into a constant temperature bath maintained at 30°C. The heat losses to the surrounding can safely be neglected at the ambient temperature close to 30°C. Fig. 1 shows the entire set-up schematically.

**Experimental procedure**—A known quantity of alkanolamine solution was taken in an equilibrium cell. H$_2$S and CO$_2$ gases were injected into reservoir to get desired partial pressure. The gas-circulating blower was then started. Some H$_2$S and CO$_2$ would get absorbed into alkanolamine solution. To compensate this, additional quantity of H$_2$S and CO$_2$ gases were injected, so that the system is near atmospheric pressure. The approach to equilibrium is monitored with the help of a conductivity probe. Since the reaction of H$_2$S and CO$_2$ with aqueous alkanolamine solution is ionic in nature, the concentration of ionic species remains constant after reaching equilibrium. The constant reading of conductivity probe over a two-three days means the equilibrium was achieved. At this stage, the gas composition was identical in the cell as well as in the reservoir. The reservoir was then isolated from the system with the help of valves. A known quantity of caustic, which was in far excess than required, was added to the reservoir with the help of liquid syringe. It was then well mixed by shaking and left for about 48 h so that the entire amount of H$_2$S and CO$_2$ gases are absorbed into aqueous NaOH solution. A sample was taken from the solution with the help of a gas-tight syringe and introduced into caustic solution to convert it into corresponding Na$_2$S and Na$_2$CO$_3$. With the help of sulphide and CO$_2$ ion-selective electrodes, both samples were analyzed for sulphide and carbonate content and hence corresponding H$_2$S and CO$_2$ content was back calculated both in the gas phase and in the liquid phase.

The sulphide and CO$_2$ ion selective electrodes ORION (USA) make, were calibrated before the reading with the help of standard aqueous solutions of Na$_2$S and Na$_2$CO$_3$, respectively. It was ensured that all readings were obtained in linear behaviour of the electrodes.

**Results and Discussion**

During the simultaneous removal of H$_2$S and CO$_2$ the following equilibria are established between H$_2$S and CO$_2$ and alkanolamine.

**Reaction of amine with H$_2$S**

\[
\text{H}_2\text{S} + \text{AmH} \rightleftharpoons \text{HS}^- + \text{AmH}_2^+ \quad \ldots \quad (1a)
\]

\[
K_s = \frac{(\text{AmH}_2^+).\text{(HS}^-)}{(\text{H}_2\text{S}).(\text{AmH})} \quad \ldots \quad (1b)
\]
Reaction of amine with CO₂

\[ \text{CO}_2 + 2\text{AmH} \rightleftharpoons \text{AmH}_2^+ + \text{AmCOO}^- \quad \cdots \quad (2a) \]

\[ K_c = \frac{[\text{AmH}_2^+][\text{AmCOO}^-]}{[\text{CO}_2][\text{AmH}]^2} \quad \cdots \quad (2b) \]

Dissociation of H₂S

\[ \text{H}_2\text{S} \rightleftharpoons \text{HS}^- + \text{H}^+ \quad \cdots \quad (3a) \]

\[ K_{H_2S} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} \quad \cdots \quad (3b) \]

Protonation of amine

\[ \text{(AmH)} + \text{H}^+ \rightleftharpoons \text{(AmH}_2^+ \quad \cdots \quad (4a) \]

\[ K_a = \frac{[\text{H}^+][\text{AmH}]}{[\text{AmH}_2^+]} \quad \cdots \quad (4b) \]

Hydrolysis of carbamate

\[ \text{AmCOO}^- + \text{H}_2\text{O} \rightleftharpoons \text{(AmH)} + \text{HCO}_3^- \quad \cdots \quad (5a) \]

\[ K_{eq} = \frac{[\text{HCO}_3^-][\text{AmH}]}{[\text{AmCOO}^-]} \quad \cdots \quad (5b) \]

Hydration of CO₂

\[ \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \quad \cdots \quad (6a) \]

\[ K_f = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \quad \cdots \quad (6b) \]

Amine dissociation in water

\[ \text{(AmH)} + \text{H}_2\text{O} \rightleftharpoons \text{(AmH}_2^+ + \text{OH}^- \quad \cdots \quad (7a) \]

\[ K_b = \frac{[\text{AmH}_2^+][\text{OH}^-]}{[\text{AmH}]} \quad \cdots \quad (7b) \]

Dissociation of water

\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \quad \cdots \quad (8a) \]

\[ K_w = [\text{H}^+][\text{OH}^-] \quad \cdots \quad (8b) \]

Dissociation of bicarbonate

\[ \text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \quad \cdots \quad (9a) \]

\[ K_2 = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} \quad \cdots \quad (9b) \]

Equilibrium pressure of \( \text{H}_2\text{S} \)

\[ P^*_{\text{H}_2\text{S}} = \frac{[\text{H}_2\text{S}]}{[\text{H}_2\text{S}]} \quad \cdots \quad (10) \]

Equilibrium pressure of \( \text{CO}_2 \)

\[ P^*_{\text{CO}_2} = \frac{[\text{CO}_2]}{[\text{CO}_2]} \quad \cdots \quad (11) \]

The absorption of \( \text{H}_2\text{S} \) and \( \text{CO}_2 \) in aqueous solution at the microscopic level consists of the reaction of dissolved \( \text{H}_2\text{S} \) and \( \text{CO}_2 \) with amine and \( \text{OH}^- \) present in the diffusion films [Eqs (1a) and (2a)]. The carbamate formed during the chemical reaction between \( \text{CO}_2 \) and amine undergoes hydrolysis (partial hydrolysis may occur in the gas liquid diffusion film in the liquid phase also) into the bulk of the liquid to regenerate amine [Eq.(5a)]. The regenerated amine is then available for absorption of \( \text{CO}_2 \) and \( \text{H}_2\text{S} \).

If \( K_{eq} \) (Eq. 5b) is very high, there is a distinct possibility of hydrolysis of carbamate, (forward reaction in Eq. 5a) in the film. However the hydrolysis of carbamate in the bulk of liquid would be completed over a larger contact time. The contact time in diffusion film being very low, it is generally considered that the hydrolysis of carbamate takes place entirely in the bulk. When equilibrium experiments are performed as in the case explained below, there is enough contact time for hydrolysis of carbamate to take place. Therefore, for equilibrium data correlation, carbamate hydrolysis to amine (Eqs 5a & b) be considered. Mahajan\(^6\) has analysed such a situation and shown that during \( \text{CO}_2 \) absorption, carbamate hydrolysis is not predominant at the top of the absorption column.

Thus there are two equilibria in the diffusion film, namely, one in the diffusion film known as the ‘First Equilibrium’ and the other due to the hydrolysis of carbamate known as the ‘Final Equilibrium’.

First Equilibrium

The chemical reaction between \( \text{H}_2\text{S}-\text{CO}_2 \) and amine is reversible in nature, an equilibrium exists between all reacting species, as represented by Eqs (1b) and (2b). Simultaneously all the other equilibria, except for carbamate hydrolysis (Eq. 5b) are established. As the basicity of diethanolamine is such that concentration of \( \text{OH}^- \) can safely be neglected, hence the reaction between \( \text{H}_2\text{S} \) and \( \text{CO}_2 \) with \( \text{OH}^- \) can be neglected.
Table 1—H₂S-CO₂ aqueous diethanolamine (DEA) equilibrium data at 313 K by actual experimental technique

<table>
<thead>
<tr>
<th>System</th>
<th>Partial pressure of CO₂ (kPa)</th>
<th>Carbonation ratio (α₁)</th>
<th>Partial pressure of H₂S (kPa)</th>
<th>Sulphidation ratio (α₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S-CO₂-DEA (2M)</td>
<td>0.143</td>
<td>0.143</td>
<td>0.058</td>
<td>0.020</td>
</tr>
<tr>
<td></td>
<td>0.070</td>
<td>0.150</td>
<td>0.074</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td>0.064</td>
<td>0.101</td>
<td>0.130</td>
<td>0.062</td>
</tr>
<tr>
<td></td>
<td>0.78</td>
<td>0.131</td>
<td>0.170</td>
<td>0.075</td>
</tr>
</tbody>
</table>

Let the degree of carbonation α₁ and degree of sulphidation α₂, may be defined as

\[ α₁ = \text{kmols CO}_2 \text{absorbed} / \text{kmols of amine} \]
\[ α₂ = \text{kmols of H}_2\text{S absorbed} / \text{kmols of amine} \]

The amine balance equation is

\[ (\text{AmH}) = (1-2α₁ - α₂) (\text{AmH})_0 \] ... (12)
\[ (\text{AmH}_2^+) = (α₁ + α₂) (\text{AmH})_0 \] ... (13)
\[ (\text{AmCOO}^-) = α₁ (\text{AmH})_0 \] ... (14)
\[ (\text{HS}^-) = α₂ (\text{AmH})_0 \] ... (15)

Eqs (1b), (3b) and (4b), give,

\[ K_S = \frac{K_{\text{HS}}}{K_a} = \frac{(\text{HS}^-) (\text{AmH}_2^+)}{(\text{H}_2\text{S}) (\text{AmH})} \] ... (16)

Substituting the relevant values in Eq. (15) one gets,

\[ K_{\text{HS}} = \frac{α₁ (\text{AmH})_0 (α₁ + α₂) (\text{AmH})_0}{(\text{H}_2\text{S}) (1-2α₁ - α₂) (\text{AmH})_0} \] ... (17)
\[ (\text{H}_2\text{S}) = \frac{K_a}{K_{\text{HS}}} \frac{α₂ (α₁ + α₂) (\text{AmH})_0}{(1-2α₁ - α₂)} \] ... (18)

From Eq. (10), the equilibrium partial pressure of H₂S over amine solution is given by

\[ P * \text{H}_2\text{S} = \frac{K_a}{K_{\text{H}_2\text{S}}} \frac{1}{\text{H}_2\text{S}} \frac{α₁ (α₁ + α₂) (\text{AmH})_0}{(1-2α₁ - α₂)} \] ... (19)

Similarly, substituting for \((\text{AmCOO}^-), (\text{AmH})\) and \((\text{AmH}_2^+)\) in Eq. (2b) from Eqs (12), (13) and (14), it was found that

\[ K_C = \frac{\text{CO}_2 (1-2α₁ - α₂) (\text{AmH})^2}{(α₁ + α₂) (\text{AmH})_0 α₂ (\text{AmH})_0} \] ... (20)
\[ \text{CO}_2 = K_C \frac{α₁ (α₁ + α₂)}{(1-2α₁ - α₂)} \] ... (21)

Eqs (2b), (4b), (5b) and (6b) give,

\[ K_C = \frac{K_{eq} K_a}{K_1} \] ... (22)

Thus, from Eq. (9), the equilibrium partial pressure of CO₂ over amine solution is given by

\[ P * \text{CO}_2 = \frac{K_{eq} K_a}{K_1} \frac{1}{\text{H}_2\text{CO}_2} \frac{α₁ (α₁ + α₂)}{(1-2α₁ - α₂)} \] ... (23)

The Eqs (19) and (23) could be used to correlate the data when the First Equilibrium exists. When vapour-liquid-equilibrium data are generated, there is enough contact time so that carbamate gets hydrolyzed and final or total equilibrium is established. Therefore, it is suggested that the equilibrium pressure measurement data should be analyzed considering only Final Equilibrium (carbamate hydrolysis).

Here a methodology is presented to compute the partial pressures of H₂S and CO₂ considering Final Equilibrium.

**Final Equilibrium**

Final equilibrium is said to be established when carbamate hydrolysis takes place (Eq. 5a). The procedure followed to obtain final equilibrium is:

In the whole solution which is in equilibrium, one has:

**Amine balance equation**

\[ (\text{AmH})_0 = (\text{AmH}) + (\text{AmH}_2^+) + (\text{AmCOO}^-) \] ... (24)

**Carbon dioxide balance yields**

\[ α₁ (\text{AmH})_0 = (\text{AmCOO}^-) + (\text{HCO}_3^-) \] ... (25)

and \(\text{H}_2\text{S} \text{ balance gives}\)

\[ α₂ (\text{AmH})_0 = (\text{HS}^-) \] ... (26)
Table 2—Various equilibria as a function of temperature

1. DEA (diethanolamine)
   \[ pK_a = \alpha(T)^\beta, \quad K_a = (\text{kmol. m}^{-3}) \]
   \[ \alpha = 1111.406 \text{ and } \beta = -0.8477 \]
   \[ 298 < T < 323 \text{ (based on the data by Perrin)} \]

2. First dissociation constant for H\textsubscript{2}S in water
   \[ pK_{H_2S} = -106.67 + 6045.2 / T + 37.744 \log T, \quad K_{H_2S} \equiv (\text{kmol. m}^{-3}) \]

3. Solubility of H\textsubscript{2}S in water
   \[ \log H_{H_2S} = 651.2 / T - 8.206, \quad H_{H_2S} \equiv (\text{kmol. m}^{-3} \text{ Pa}^{-1}) \]

4. Solubility of CO\textsubscript{2} in water
   \[ H_{CO_2} = 3.54 \times 10^4 \exp (2044 / T), \quad (\text{kmol. m}^{-3} \text{ Pa}^{-1}) \]

5. Carbamate hydrolysis Equilibrium Constant
   \[ K_{eq} = a \sqrt{\frac{a}{T}} \quad \text{where, } a = 3.12055 \times 10^{-24} \quad b = -10.88718 \]
   \[ 298 < T < 323 \text{ (kmol. m}^{-3} \text{ Pa}^{-1}) \]
   (From the data given by Blauhoff, we have derived the above correlation)

6. Equilibrium constant for CO\textsubscript{2} hydration
   \[ \log_{10} K_1 = -3404.7 / T + 14.843 - 0.03279 T, \quad (\text{kmol. m}^{-3}) \]

The electroneutrality equation results in

\[ (\text{AmH}_2^+) = (\text{AmCOO}^-)+(\text{HCO}_3^-)+(\text{HS}^-) \quad \ldots (27) \]

from Eqs (25) and (26), gives

\[ (\text{AmH}_2^+) = (\alpha_1 + \alpha_2) (\text{AmH})_0 \quad \ldots (28) \]

substituting above values of (AmH\textsubscript{2}+) and (AmCOO\textsuperscript{-}) in Eq. (24), one gets

\[ (\text{AmH})_0 = (\text{AmH}) + (\text{AmH}_2^+) + (\text{AmCOO}^-) \quad \ldots (29) \]

\[ = (\text{AmH}) + (\alpha_1 + \alpha_2) (\text{AmH})_0 + \alpha_4 (\text{AmH})_0 - (\text{HCO}_3^-) \quad \ldots (30) \]

From Eq. (5b)

\[ (\text{HCO}_3^-) = \frac{K_{eq}(\text{AmCOO}^-)}{(\text{AmH})} \quad \ldots (31) \]

Therefore from, Eqs. (30) and (31)

\[ (\text{AmH})_0^2 + \left[ K_{eq} + (2\alpha_1 + \alpha_2 - 1) (\text{AmH})_0 \right] (\text{AmH}) - K_{eq} [1 - (\alpha_1 + \alpha_2)] (\text{AmH})_0 = 0 \quad \ldots (32) \]

Substituting the values of (HS\textsuperscript{-}) and (AmH\textsubscript{2}+) from Eqs (26) and (27) in Eq. (16), one gets

\[ \hat{P} \ast H_2S = \frac{K_a}{K_{H_2S}} \frac{1}{\text{H}_2S} \frac{\alpha_2 (\alpha_1 + \alpha_2) (\text{AmH})_0^2}{(\text{AmH})} \quad \ldots (34) \]

Similarly, the partial pressure of CO\textsubscript{2} could be obtained from Eq. (2b) as

\[ K_C = \frac{(\text{CO}_2)(\text{AmH})_0^2}{(\text{AmH}_2^+) (\text{AmCOO}^-)} \quad \ldots (35) \]

Now,

\[ (\text{AmH}_2^+) = (\alpha_1 + \alpha_2) (\text{AmH})_0 \quad \ldots (36) \]
Table 3a—Comparison of computed equilibrium partial pressures of CO₂ from the model with the actual experimental value

<table>
<thead>
<tr>
<th>Carbonation ratio (α₁)</th>
<th>Experimental equilibrium partial pressure of CO₂ (P*CO₂) (kPa)</th>
<th>Predicted equilibrium partial pressure of CO₂ (P*CO₂) (kPa)</th>
<th>Computed equilibrium partial pressure of CO₂ (P*CO₂) (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(β₁)</td>
<td>β₁ (kPa)</td>
</tr>
<tr>
<td>0.182</td>
<td>0.143</td>
<td>0.708</td>
<td>0.174</td>
</tr>
<tr>
<td>0.150</td>
<td>0.070</td>
<td>0.495</td>
<td>0.183</td>
</tr>
<tr>
<td>0.101</td>
<td>0.064</td>
<td>0.250</td>
<td>0.212</td>
</tr>
<tr>
<td>0.131</td>
<td>0.078</td>
<td>0.478</td>
<td>0.174</td>
</tr>
</tbody>
</table>

For CO₂

\[ β₁ = \left\{ \exp(-a₁ \sqrt{α₁ - a₂ \sqrt{α₂}}) \right\} \]
\[ a₁ = 3.520 \quad a₂ = 1.727 \]

Table 3b—Comparison of computed equilibrium partial pressures of H₂S from the model with the actual experimental value

<table>
<thead>
<tr>
<th>Sulfidation ratio (α₂)</th>
<th>Experimental equilibrium partial pressure of H₂S (P*H₂S) (kPa)</th>
<th>Predicted equilibrium partial pressure of H₂S (P*H₂S) (kPa)</th>
<th>Computed equilibrium partial pressure of H₂S (P*H₂S) (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(β₂)</td>
<td>β₂ (kPa)</td>
</tr>
<tr>
<td>0.020</td>
<td>0.058</td>
<td>0.337</td>
<td>0.157</td>
</tr>
<tr>
<td>0.038</td>
<td>0.074</td>
<td>0.566</td>
<td>0.154</td>
</tr>
<tr>
<td>0.062</td>
<td>0.130</td>
<td>0.736</td>
<td>0.168</td>
</tr>
<tr>
<td>0.075</td>
<td>0.170</td>
<td>1.230</td>
<td>0.135</td>
</tr>
</tbody>
</table>

For H₂S

\[ β₂ = \left\{ \exp(-b₁ \sqrt{α₁ - b₂ \sqrt{α₂}}) \right\} \]
\[ b₁ = 3.408 \quad b₂ = 2.815 \]

\[(\text{AmCOO}^-) = (1 - α₁ - α₂)(\text{AmH})_0 - (\text{AmH}) \] \quad (37)

Therefore substitution of \((\text{AmH}_2^+), (\text{AmCOO}^-), P_\text{CO₂}\) and \(K_C\) in Eq. (35) gives,

\[ \hat{P} * \text{CO}_2 = \frac{K_{eq} K_2}{K_1} \frac{1}{\text{H}_2\text{CO}_3} \]

\[ \left\{ [(1 - α₁ - α₂)(\text{AmH})_0 - (\text{AmH})][α₁ + α₂](\text{AmH})_0 \right\} \]

\[ \left(\text{AmH}\right)^2 \]

\[ \] \quad (38)

Eqs (34) and (38) can now be used to obtain partial pressures of H₂S and CO₂ over aqueous alkanolamine solution.

The aqueous solution of alkanolamine is a non-ideal solution. At any given time, it contains various ionic species. These species do exert their influence on various equilibria explained above. Instead of quantifying effect of various ionic species on individual equilibrium constant, a process engineer friendly approach is being recommended wherein this effect is lumped together in a single parameter say \( β \), which would then be correlated to the system characteristic such as carbonation ratio α₁ and sulphidation ratio α₂.

Thus,

\[ \hat{P} * \text{CO}_2 = \hat{P} * \text{CO}_2 \beta₁ \]

\[ \hat{P} * \text{CO}_2 = \hat{P} * \text{CO}_2 \left\{ \exp\left(-a₁ \sqrt{α₁ - a₂ \sqrt{α₂}}\right) \right\} \]

where \( \hat{P} * \text{H}_2\text{S} = \hat{P} * \text{H}_2\text{S} \beta₂ \)

... (39)
\[ P \ast H_2S = \hat{P} \ast H_2S \left\{ \exp\left(-b_1 \sqrt{\alpha_1} - b_2 \sqrt{\alpha_2}\right) \right\} \quad \cdots (41) \]

where \( \beta_2 = \left\{ \exp\left(-b_1 \sqrt{\alpha_1} - b_2 \sqrt{\alpha_2}\right) \right\} \quad \cdots (42) \)

In the \( \beta \)'s, the effect of ionic strength on all equilibrium constants and solubility parameters lumped together, has been taken into consideration.

(The particular form of the Eqs. (39) and (41) are chosen as the activity coefficients because they are related to ionic strength in a similar manner, i.e. \( \gamma \approx \sqrt{I} \).)

Table 1 presents data obtained by actual experimental technique. This agrees reasonably well with that reported by Lal et al.\(^5\)

Various equilibria used to compute equilibrium pressure have been presented in Table 2. The computed values of equilibrium partial pressure of \( CO_2 \) and \( H_2S \) are compared with the actual experimental values in Table 3a and 3b respectively, and constants \( a_1, a_2, b_1 \) and \( b_2 \) of Eqs (39) and (41) are also presented. More data points are required to test this model universally. However, in present work, the aim is to demonstrate the approach. The above process engineer friendly approach would help design engineers.

**Conclusion**

A simplified approach to correlate equilibrium partial pressures of \( H_2S \) and \( CO_2 \) over aqueous amine solution is demonstrated based on the equilibrium aspect. Based on the carbonation ratio, sulphi dation ratio and nature of amine, two factors namely \( \beta_1 \) and \( \beta_2 \) were introduced by using ‘final equilibrium’ expression to predict the observed data.

**Nomenclature**

\( (\text{AmH}) \) = concentration of amine, \((\text{kmlol.m}^{-3})\)
\( (\text{AmH})_0 \) = original concentration of amine, \((\text{kmlol.m}^{-3})\)
\( (\text{AmH}_2) \) = concentration of protonated amine \((\text{kmlol.m}^{-3})\)
\( (\text{Am}COO^-) \) = concentration of carbamate \((\text{kmlol.m}^{-3})\)
\( CO_2 \) = concentration of \( CO_2 \) \((\text{kmlol.m}^{-3})\)
\( H_2S \) = concentration of \( H_2S \) \((\text{kmlol.m}^{-3})\)
\( H_2S \) = solubility of \( H_2S \), \((\text{kmlol.m}^{-3}.\text{Pa}^{-1})\)
\( K_a, (pK_a) \) = equilibrium constant in Eq. (4b), \((\text{kmlol.m}^{-3})\)
\( K_b, (pK_b) \) = equilibrium constant in Eq. (7b), \((\text{kmlol.m}^{-3})\)
\( K_C \) = equilibrium constant for \( CO_2\)-amine reaction in Eq. (2b), \((\text{kmlol.m}^{-3})\)
\( K_{eq} \) = carbamate hydrolysis equilibrium constant in Eq. (5b), \((\text{kmlol.m}^{-3})\)
\( K_{eq} \) = equilibrium constant for reaction of amine with \( H_2S \) in Eq. (3b), \((\text{kmlol.m}^{-3})\)
\( K_1 \) = equilibrium constant for \( CO_2 \) hydration in Eq. (6b), \((\text{kmlol.m}^{-3})\)
\( K_2 \) = equilibrium constant for dissociation of bicarbonate in Eq. (9b), \((\text{kmlol.m}^{-3})\)
\( P \ast CO_2 \) = experimental equilibrium partial pressure of \( CO_2 \), \((\text{kPa})\)
\( P \ast H_2S \) = experimental equilibrium partial pressure of \( H_2S \), \((\text{kPa})\)
\( \hat{P} \ast CO_2 \) = predicted equilibrium partial pressure of \( CO_2 \) in the bulk of gas phase, \((\text{kPa})\)
\( \hat{P} \ast H_2S \) = predicted equilibrium partial pressure of \( H_2S \) in the bulk of gas phase, \((\text{kPa})\)
\( P \ast CO_2 \) = computed equilibrium partial pressure of \( CO_2 \) in the bulk of gas phase, \((\text{kPa})\)
\( P \ast H_2S \) = computed equilibrium partial pressure of \( H_2S \) in the bulk of gas phase, \((\text{kPa})\)
\( a_1 \) = carbonation ratio, kmols \( CO_2 \) absorbed / kmols of amine
\( a_2 \) = sulphi dation ratio, kmols of \( H_2S \) absorbed / kmols of amine
\( \beta_1 \) = correction factor defined by Eq. (39)
\( \beta_2 \) = correction factor defined by Eq. (41)

**References**

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