Effect of temperature on carbamate stability constants for amines

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Introduction

The absorption of CO_2 in aqueous solution of alkanoalamine couples physical absorption with chemical reactions where both kinetics and thermodynamic equilibrium may play important roles in determining the ultimate gas loading. The chemical reactions usually lead to the formation of carbonates, bicarbonates and carbamates depending on the type of amine being used. The overall reactions that occur are normally complex in nature, but it is agreed that similar reaction steps are involved for all types of amine including the protonation of amine as well as the ionization of different species in the solution. However, an additional step, which is the formation of carbamate ion, has been proposed for systems involving primary and secondary amines. The mechanism for these reactions has been proposed by a number of investigators and is available in the literature[1].

Very little experimental data on carbamate equilibrium constants may be found in the literature. NMR is often used for measurements but the method is very expensive and time consuming. In this work carbamate constants for different amines are measured by wet chemical method.

Reaction mechanism

CO_2 reacts with water to form carbonic acid:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \tag{1}$$

and carbonic acid is involved in two protonation equilibria. The reaction includes two reversible pathways: the reversible interaction of CO_2 with water to form carbonic acid and with hydroxide to form bicarbonate[2]:

$$\begin{aligned} H_2CO_3 &\leftrightarrow HCO_3^- + H^+ \\ RNH_2 + H^+ &\leftrightarrow RNH_3^+ \end{aligned} \tag{2}$$

The other important reaction is the formation of carbamic acid which at relevant pH is deprotonated to the carbamate. The mostused mechanism involves the formation of a zwitterion form of the carbamate followed by a slow proton exchange reaction with a base. This mechanism was originally proposed by Caplow[3] and has been used in many instances since then:

$$\begin{aligned} CO_2 + RNH_2 &\leftrightarrow RNH_2^+CO_2^- \\ RNH_2^+CO_2^- + B &\leftrightarrow RNHCO_2^- + BH^+ \end{aligned} \tag{3}$$

However, a direct mechanism can just as well explain all experimental data available[4].

Experimental set up and procedure

The equilibrium constants are measured using a potentiometric titrator G20 from Mettler Toledo (Figure 1). The system includes a titrator with pH-electrode DSC-115 and temperature sensor DT100. Temperature in a jacketed glass vessel (100 ml) is controlled using Julabo M4 heating circulator. Dow 10 cSt silicone oil is used as a heat transfer media.

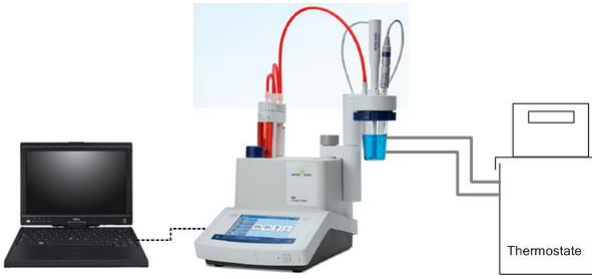

Figure 1. Set-up for potentiometric titration

Two slightly different techniques described in the literature are tested. According to the first method[5-6], a mixture of amine and potassium or sodium carbonate-bicarbonate is prepared and allowed to reach equilibrium at constant temperature. An aliquot sample is then drawn off and mixed rapidly with $BaCl_2$ which precipitates carbonate and bicarbonate but leaves carbamate in solution. The solution is filtrated and clear liquid containing amine, carbamate and hydroxyl ions is titrated with dilute HCl. The equilibrium constant for the hydrolysis of carbamate is then determined:

$$R_2NCOO^- + H_2O \leftrightarrow R_2NH + HCO_3^- \quad (4)$$

According to the second method[7], the equilibrium experiments are carried out by adding a predetermined amount of $NaHCO_3$ to the amine solution. Experiments may be performed at different ratios of sodium bicarbonate/amine. A neutral salt may be added to the solution in order to study the effect of the ionic strength on the equilibrium constant. The system is left to equilibrate at constant temperature. When an aqueous solution is reacted with bicarbonate, the carbamate is formed according to the reaction:

$$R_2NH + HCO_3^- \leftrightarrow R_2NCOO^- + H_2O \quad (5)$$

The carbamate is then titrated with NaOH solution. The apparent equilibrium constant, K_c, for this reaction is given by:

$$K_c = \frac{\left[R_2NCOO^-\right]}{\left[HCO_3^-\right] R_2NH} \quad (6)$$

Conclusion

The effects of temperature and ionic strength on the equilibrium constant for the formation of carbamate from different amines are studied in this work and the results will be presented at the conference. Two titration technique are used to estimate the equilibrium constant for carbamate formation.

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