Enthalpies of protonation of amines at elevated temperatures

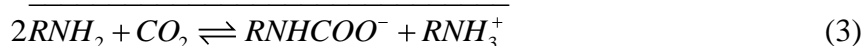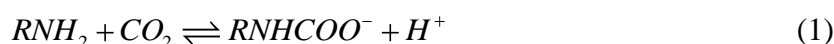Inna Kim[1*], Christian M. Jens[2], Hallvard F. Svendsen[2]

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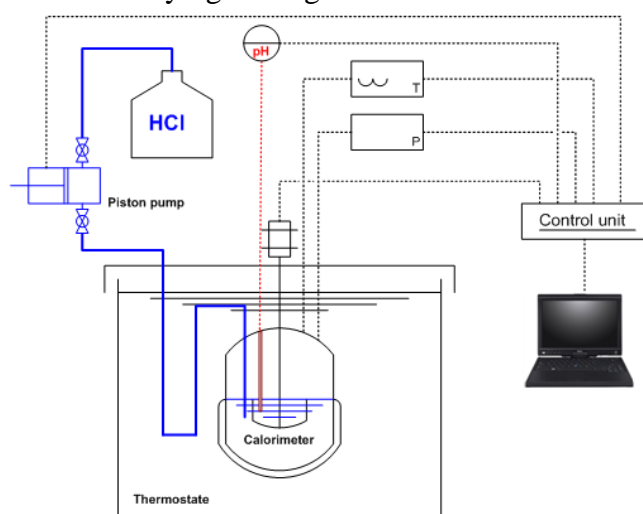
Introduction

Aqueous solutions of amines absorb CO_2 primarily by chemical reactions. The reactions between amines and CO_2 are quite complex. However, the overall reactions can be represented as follows[1]:

$$RNH_2 + CO_2 \rightleftharpoons RNHCOO^- + H^+ \tag{1}$$

$$RNH_2 + H^+ \rightleftharpoons RNH_3^+ \tag{2}$$

$$\overline{2RNH_2 + CO_2 \rightleftharpoons RNHCOO^- + RNH_3^+} \tag{3}$$

Where equation (1) is the carbamate formation reaction and equation (2) is the amine protonation reaction. The equilibrium of the overall reaction (3) is pushed all the way to the right even under conditions of low CO_2 partial pressures at low temperatures (typically < 40 ^{o}C). The equilibrium shifts dramatically to the left under high temperature conditions. Thus CO_2 can be absorbed under low partial pressure, typically 3-15 kPa, at low temperature conditions and the CO_2 loaded solvent can be regenerated at relatively high CO_2 partial pressure, 1-2 bars, at high temperature in a stripping column. Thus, understanding temperature dependence of the equilibrium of reactions (1) and (2) is of crucial importance.

Experimental

In this work enthalpies of protonation, ΔH_p, were measured in a reaction calorimeter, CPA202 (Chemisens), over a range of temperatures for five different amines used in CO_2 capture - MDEA, MEA, AMP, AEEA and piperazine. In addition, the effect of ionic strength of the solutions on the protonation of MDEA was studied using NaCl as background salt (0 to 5 mol/L). The scheme of the experimental set-up is presented in Figure 1. It consisted of a mechanically agitated glass reactor of 250 ml volume suitable for operation at temperatures up to 200 ^{o}C and pressures up to 10 bar, immersed into a thermostatted bath, and a piston pump having a capacity of (0.005 to 5) mL/min. The system continuously measured temperature, pressure, pH and heat flow during addition of hydrochloric acid (1 mol/L) to the amine solution (0.1 mol/L) in the reactor. Chemicals used in this work were of minimum 99 % purity and were used without further treatment. Hydrochloric acid (HCl) solution used for titration was prepared from Merck Titrisol ampoules. Distilled de-ionized water was used in all experiments.

Figure 1. The set-up for enthalpy measurements

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Results and discussion

Effect of ionic strength

Dependence of equilibrium constants and enthalpies of protonation on ionic strength was reported by different authors[2,3] Use of background salt allows maintaining constant ionic strength in during titration while amine concentration can be kept low enough to assume the activity coefficient of amine to be constant. The measured protonation constants in this work showed a very weak dependency on ionic strength and could be extrapolated to zero ionic strength. As also the amine concentrations were low (0.1 mol/L), it could be assumed that enthalpies of protonation measured were equal to those at infinite dilution.

Effect of temperature

Heats of protonation of amines were measured by titrating 0.1 mol/L (MDEA, MEA and AMP) or 0.05 mol/L (AEEA and Pz) solutions with 1 mol/L HCl. Only a few experimental data points were found in the literature for these amines, almost all of them at 25 °C. As an example, the first and the second enthalpies of protonation for piperazine are compared with data from the literature[4] in Figure 2.
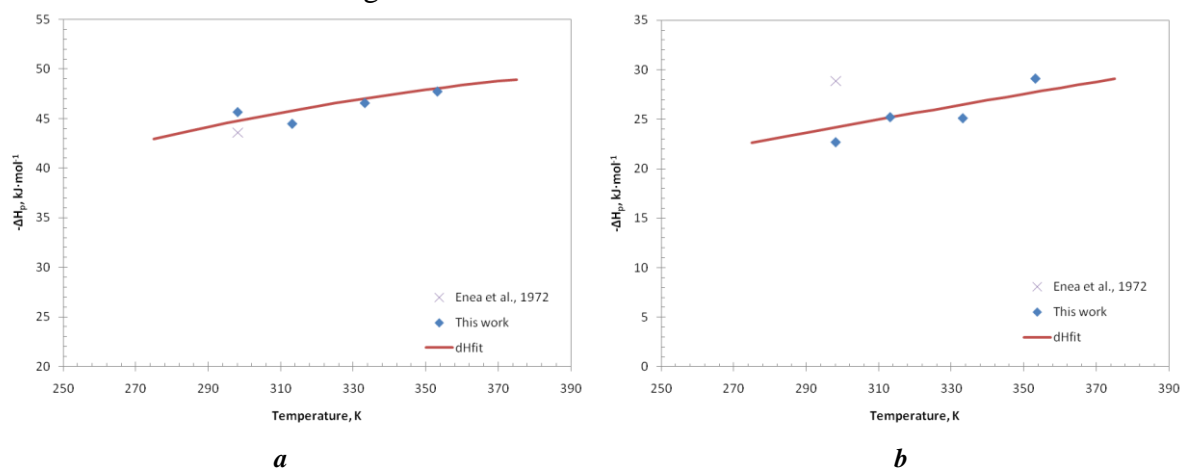

a   *b*

Figure 2. The first (*a*) second (*b*) enthalpies of protonation for piperazine.

Conclusions

Enthalpies of protonation, ΔH_p, were measured in a reaction calorimeter at temperatures from (298.15 to 393.15) K for MDEA, MEA and AMP and from (298.15 to 353.15) for AEEA and Pz. In addition, the effect of the ionic strength of the solutions on the protonation of MDEA was studied using NaCl as background salt (0 to 5 mol/ℓ). The experimental dissociation constants and enthalpies of protonation were used for fitting reaction equilibrium constants, and thus derived correlations are thermodynamically consistent. The results from this work may be used for thermodynamic modelling of CO_2 capture processes using amines.

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