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ENTHALPIES OF ABSORPTION AND SOLUBILITY OF CARBON DIOXIDE IN AQUEOUS POLYAMINE SOLUTIONS

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Abstract

The enthalpies of absorption and solubility at T=298.15 K of carbon dioxide in aqueous solutions of bis-(3-dimethylaminopropyl)amine (CAS RN: [6711-48-4]) are reported in this paper. It was observed that the saturation loading of the CO_2 is α=2.9 mol CO_2/mol TMBPA, which is close to the theoretical value, α_0=3 mol CO_2/mol TMBPA. The molar heat of absorption of CO_2 is independent of the polyamine concentration of the solutions and the amount of CO_2 absorbed and was calculated to be $\Delta_{abs}H_m=-44$ (±2) kJ mol^{-1} CO_2.

Keywords: absorption, carbon dioxide, enthalpy, polyamine, solubility

Introduction

Some industrial processes such as the purification of natural, synthesis and combustion gases require the removal of acid gases. Aqueous amine solutions are widely used for the removal of carbon dioxide from gas streams. The knowledge of the enthalpies of absorption of the gas in the solvent is useful for the design of equipment used for gas separation. The physical and chemical solubility of CO_2 in aqueous solutions of alkanolamines, modified amines and polyamines and the enthalpy of absorption have been studied by several authors. Merkley, Christensen and Izatt [1] reported that the partial pressure of CO_2 has virtually no effect on the value of heat of absorption of CO_2 in aqueous methyldiethanolamine (MDEA) solutions at loadings below the saturation point. Oscarson, Van Dam, Christensen and Izatt [2] have found that the enthalpy of absorption of CO_2 in aqueous diethanolamine (DEA) solutions is independent of pressure and DEA concentration. Mathonat, Majer, Mather and Grolier [3] have pointed out that calorimetric data can serve for indirect determination of the saturation point of CO_2 in the solution: $\Delta_{abs}H_m$ is independent of the CO_2 concentration after the saturation loading point.

The enthalpies of absorption and solubility of carbon dioxide at T=298.15 K and at different partial pressure (0.003–3 bar) in aqueous solutions of various concentrations ([5–30% (m/m)] of bis-(3-dimethylaminopropyl)amine) CAS RN: [6711-48-4],

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common name: tetramethyl-imino-bis-propyl amine, abbreviated TMBPA, structural formula: Fig. 1) are given in this paper.

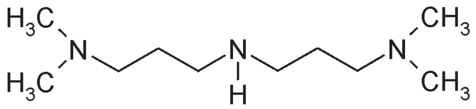

Fig. 1 The structural formula of bis-(3-dimethylaminopropyl)amine

Experimental

The polyamine solutions were prepared from TMBPA [99.16% (m/m) pure] supplied by Nitroil Co. Ltd. (Pétfürdő, Hungary), and doubly distilled water. The carbon dioxide and nitrogen were obtained from Messer Griesheim Ltd. (Krefeld, Germany), and had a purity of 99.995 and 99.999% (*v/v*), respectively. All materials were used without further purification.

The calorimetric measurements were carried out in a Setaram C80 D computer-controlled mixing and reaction calorimeter using high-pressure gas circulation vessels. Both measuring and reference cells are made from Hastelloy C. Each gas circulation vessel is in the form of a 74 mm high vertical cylinder with 16.9 mm outside and 13.8 mm inside diameter with a liaison consisting of two coaxial pipes to enable the continuous and intermittent circulation of gas on the liquid sample. The calorimeter was calibrated electrically using the Joule-effect by means of a special cell with calibrated heaters as recommended by IUPAC. Prior to preparation the aqueous TMBPA solutions, the water was boiled for 30 min to drive out any dissolved CO_2 and was cooled under nitrogen atmosphere. Solutions were prepared under nitrogen atmosphere by injection the components through fine teflon tubings into airtight screw-capped vessels and compositions were determined by mass. All of the aqueous solutions were degassed in an ultrasonic bath from Branson (Hayes, Middx, UK; model 5200). The samples were pressed without contact with air into the measuring cell of the calorimeter filled with nitrogen and weighed by an analytical balance from Sartorius (Göttingen, Germany, model 2474) with a precision of ±0.00001 g. The measuring and reference cells were placed inside a metallic block of the Calvet-type calorimeter. The temperature was measured by means of a 100 Ω platinum resistance thermometer located between the two vessels, and was held constant to within ±0.05 K during each measurement. The working temperature was fixed and when thermal equilibrium was reached carbon dioxide was then added to an amount determined by observation heat-flux signal and/or of the pressure change in the vessel. The pressure was only a control parameter, and its increase, i.e. the partial pressure of carbon dioxide, was measured by a digital differential pressure gauge from Heise (Bassweiler, Germany; model 710B) with a precision of ±1 mbar. The differential heat-flux was then recorded and integrated as a function of time to give the heat changes during absorption. After the absorption process the measuring cell was closed and reweighed with gas phase correction to determine the quantity of CO_2 absorbed.

Results and discussion

The measured exothermic enthalpy changes during the absorption are given in Fig. 2, where ΔH_{abs} values expressed as of kJ g^{-1} solution is plotted *vs.* the amount of CO_2 absorbed, $m_{abs}(CO_2)$ in g CO_2/g solution. Figure 2 reveals that the specific heat of absorption of CO_2 in kJ g^{-1} CO_2 is independent of the TMBPA concentration of the solutions and the amount of CO_2 absorbed. Its value can be determined from the slop of the function between ΔH_{abs} values and $m_{abs}CO_2$: $\Delta_{abs}H=(\partial\Delta H_{abs}/\partial m_{abs}CO_2)=1.0$ kJ g^{-1} CO_2. The corresponding molar heat of absorption of CO_2 is $\Delta_{abs}H_m=-44$ (±3) kJ mol^{-1} CO_2 at 298.15 K.

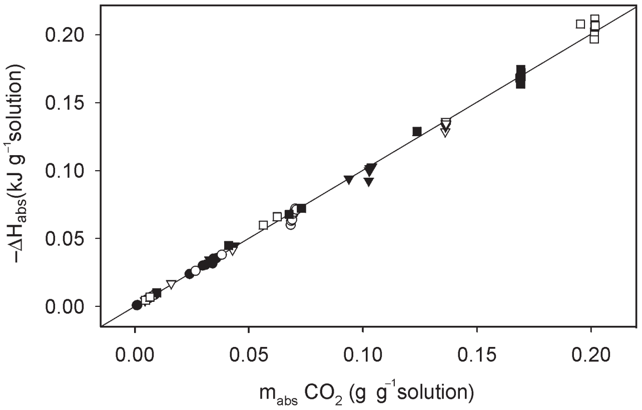

Fig. 2 Enthalpies of absorption of carbon dioxide in aqueous solution of TMBPA as a function of the amount of CO_2 absorbed at various TMBPA concentrations
● – 5% (m/m); o – 10% (m/m); ▼ – 15% (m/m); ∇ – 20% (m/m);
■ – 25% (m/m); □ – 30% (m/m)

The partial pressure of CO_2 ranging from 0.003 to 3 bar was found to have small effect on the values of enthalpies of adsorption and solubility of carbon dioxide in aqueous solution of TMBPA for a given TMBPA concentration. However, the observed heats of absorption and loading are linearly dependent on the concentration of TMBPA in aqueous solutions.

This behavior is very specific for absorption processes controlled by chemical reaction in the solution and corresponds to the chemical solubility of the carbon dioxide as the aqueous solution of TMBPA is saturated and only small amount additional CO_2 is absorbed physically [1, 4]. Below the saturation point the partial pressure of CO_2 was less than 0.003 bar.

We have not been able to find measurements reported in the literature for the enthalpy of absorption of TMBPA. However, the value proposed in this work is comparable to the values given by Mathonat *et al.* [3]: $\Delta_{abs}H_m = -49$ (±4) kJ mol^{-1} CO$_2$ at 313.15 K and reported by Merkley *et al.* [1]: $\Delta_{abs}H_m = -47$ (±5) kJ mol^{-1} CO$_2$ at 288.75 K for enthalpies of absorption of CO_2 in aqueous solution of MDEA.

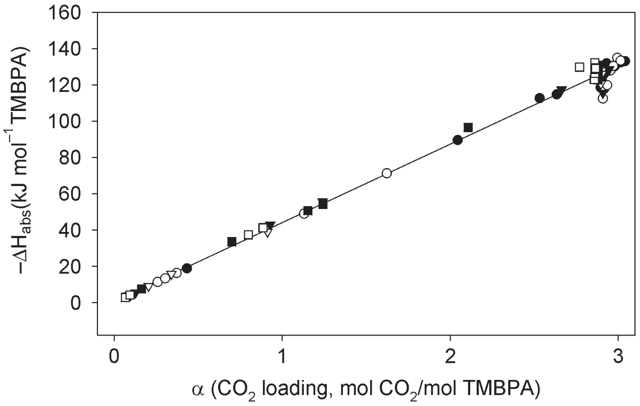

Fig. 3 Enthalpies of absorption of carbon dioxide in aqueous solution of TMBPA as a function of CO_2 loading, symbols as in Fig. 2

The calorimetric data are useful tools to determine the saturation point of CO_2 absorption in aqueous TMBPA solutions too. Figure 3 shows the experimental $\Delta_{abs}H$ values in units of J mol^{-1} TMBPA plotted *vs.* CO_2 loading (mol CO$_2$/mol TMBPA). Apparently $\Delta_{abs}H$ become independent of the CO_2 loading in the region of the saturation point, at $\alpha=2.9$ mol CO$_2$/mol TMBPA, which is close to the theoretical value $\alpha_0=3$ mol CO$_2$/mol TMBPA.

On the basis of the calorimetric results and taken into account the suggestions of Mathonet *et al.* [3], Bishnoi and Rochelle [4] and Posey and Rochelle [5] and we can present a simple thermodynamic model for the TMBPA | CO_2 | H_2O system:

$$\text{TMBPA}+3\,\text{H}_3\text{O}^+ \leftrightarrow [\text{TMBPA(H)}_3]^{3+}+3\text{H}_2\text{O}$$

$$\text{TMBPA}+3\text{CO}_2 \leftrightarrow [\text{TMBPA}]^{3+}(\text{COO}^-)_3$$

$$[\text{TMBPA}]^{3+}(\text{COO}^-)_3+3\text{H}_2\text{O} \leftrightarrow [\text{TMBPA(H)}_3]^{3+}+3\text{HCO}_3^-$$

$$\text{CO}_2+2\text{H}_2\text{O} \leftrightarrow \text{HCO}_3^-+\text{H}_3\text{O}^+$$

$$\text{HCO}_3^-+\text{H}_2\text{O} \leftrightarrow \text{CO}_3^{2-}+\text{H}_3\text{O}^+$$

$$2\text{H}_2\text{O} \leftrightarrow \text{OH}^-+\text{H}_3\text{O}^+$$

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