ENTHALPIES OF ABSORPTION OF CARBON DIOXIDE IN AQUEOUS SODIUM GLYCINATE SOLUTIONS

V. Salazar, Y. Sánchez-Vicente, A. Cabañas, J.A.R. Renuncio and C. Pando*

Dpto de Química Física I, Universidad Complutense, E-28040 Madrid, Spain

pando@quim.ucm.es

Abstract

The enthalpies of absorption ($\Delta_r H$) of carbon dioxide in aqueous 10 mass % sodium glycinate (SG) solutions were determined at 313.15 and 323.15 K and 12.00 MPa using an isothermal high-pressure flow calorimeter. Very exothermic absorption enthalpies are obtained at the two temperatures studied. $\Delta_r H$ values expressed in J per g of sodium glycinate decrease very fast as CO_2 loading increases until saturation is reached; from this point, a slowly decreasing value is obtained for the absorption enthalpy. CO_2 loading is expressed as mol CO_2/mol amine (α). The calorimetric data provides a means to determine the saturated loading point of CO_2 in the solution; values of 0.90 and 0.86 mol CO_2/mol SG were estimated for this magnitude at at 313.15 and 323.15 K, respectively. Absorption enthalpies expressed in kJ per mol of CO_2 were also calculated. These enthalpies become more exothermic as α decreases until a limit value characteristic of each amine is observed for low CO_2 loading. This value can be regarded as the enthalpy of solution at infinite dilution. Limit values of -72.5 and -59.5 kJ/mol CO_2 are obtained for 10 mass % SG solutions at 313.15 and 323.15 K, respectively.

1. Introduction

Carbon dioxide absorption in amine solutions is a combination of chemical reactions and physical dissolution that has been the subject of numerous thermodynamics and kinetic investigations. The overall reaction of carbon dioxide in aqueous primary and secondary amine solutions consists of several steps: (i) carbamate formation, (ii) amine protonation, (iii) bicarbonate formation, and (iv) carbonic acid formation. Because of the similar functional groups, a solution of an alkaline salt of aminoacid is expected to react in a similar way to that of a primary amine through a zwiterionic mechanism[1]. The overall reaction may be written as

$$CO_2 + 2\ RNH_2 \leftrightarrow RHNCOO^- + RHNH_2^+ \tag{1}$$

The exothermic reaction starts when carbon dioxide is mixed with the solution; CO_2 is absorbed until saturation is reached for a given condition of temperature, pressure and amine concentration. CO_2 loading (α) is expressed as mol CO_2/mol amine. The reaction may reversed by heating; CO_2 may be also considered as an agent to protect the primary amine in the form of ammonium carbamate. Monoethanolamine, diethanolamine, *N*-methyldiethanolamine and diglycolamine are examples of amines used in this reaction. Inconveniences such degradation through oxidation of the amine, low reaction rates or high enthalpies of reaction that increase the energy required for amine regeneration have led to the investigation of other absorbents. Amino acid salts have the advantages of a high surface tension, nonvolatile nature, good absorption and resistance to degradation. Sodium glycinate (SG) has been recently proposed as an alternative and the physicochemical properties of SG aqueous solutions and the kinetics of CO_2 absorption in these solutions have been investigated[1-4]. In this study, the enthalpies of absorption ($\Delta_r H$) of carbon dioxide in aqueous 10 mass % sodium glycinate (SG) solutions were determined at 313.15 and 323.15 K and 12.00 MPa.

2. Experimental

The materials employed were CO_2 (Air Liquide 99.98 mol % pure) and sodium glycinate (Sigma-Aldrich > 99 mol % pure). Commercial materials were used without further purification. Solutions were prepared gravimetrically using deionized distilled water and preventing contamination by atmospheric CO_2. The 10 mass % sodium glycinate concentration was chosen taken into account previous solubility studies[3] showing that CO_2 loading capacity decreased as SG concentration

increased from 10 to 20 or 30 mass %. The value of the pressure was chosen to avoid the difficulties of measuring the enthalpy of absorption of a gas in an aqueous solution.

Fig. 1 is a schematic diagram of the isothermal high-pressure flow calorimeter (Hart Scientific model 7501) used to perform the enthalpy of absorption measurements. More details about the calorimeter and the procedure used in the measurements are described elsewhere[5]. The reactants were pumped into the calorimetric cell by two thermostated pumps (ISCO, model LC-2600) at constant flow rates. Temperature of the pumps was controlled with ±0.02 K. All runs were made in the steady-state fixed composition mode. Measurements were carried out at total volume flow rates of 0.0028 and 0.0056 cm^3s^{-1}. Flow rates were selected to cover the concentration range until saturation is reached and approximately constant values are obtained for $\Delta_r H$. The volume flow rates were converted to molar flow rates using the densities and molar masses of CO_2[6] and SG aqueous solutions[2]. Mole fraction and CO_2 loading precision were estimated to be ± 0.001. The calorimetric cell was located into a silicon bath in which temperature was controlled within $\pm$ 0.001 K. A Peltier cooling device and a pulsed heater kept the cell under isothermal conditions. A back-pressure regulator situated outside the calorimeter kept the pressure within ±0.01 MPa. The error of $\Delta_r H$ measurements was estimated to be $\pm(1 + 0.01\ \Delta_r H)$ J mol^{-1}.
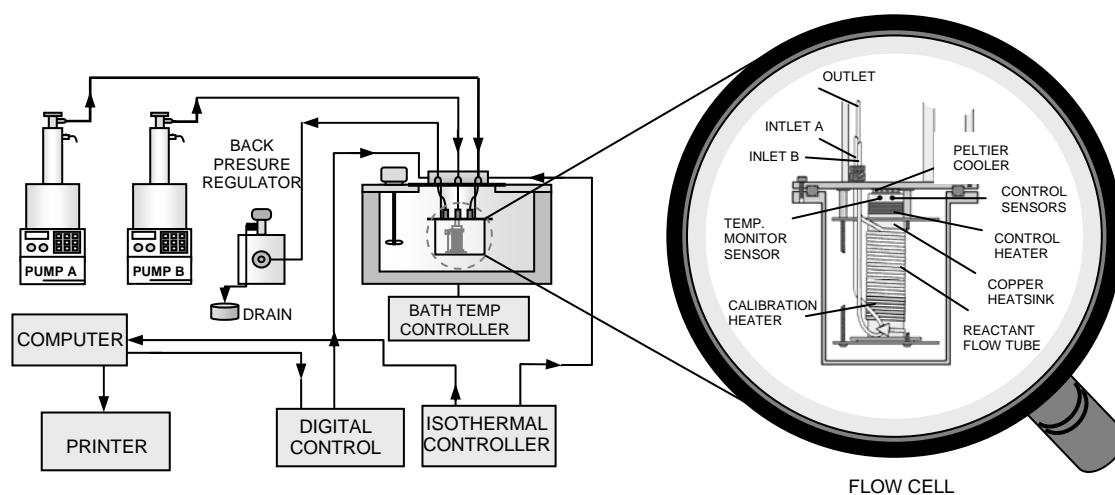

Fig. 1. Schematic diagram of the isothermal flow calorimeter used to perform the enthalpy of absorption measurements.

3. Results and discussion

Very exothermic absorption enthalpies are obtained at the two temperatures studied. Fig. 2 shows the $\Delta_r H$ expressed in J per g of SG vs α plots at the two temperatures studied. $\Delta_r H$ values decrease very fast as CO_2 loading increases until saturation is reached; from this point, a fairly constant or slowly decreasing value is obtained for the absorption enthalpy. This behavior is similar to that reported previously for the absorption of CO_2 in primary and secondary amine solutions[7-11].

The calorimetric data provides a means to determine the saturated loading point of CO_2 in the solution. $\Delta_r H$ data for low α values were adjusted to an exponential curve; data for high α values were adjusted to a first degree polynomial in α. From the intersection of both functions, values of 0.90 and 0.86 mol CO_2/mol SG were estimated for this magnitude at 313.15 and 323.15 K, respectively.
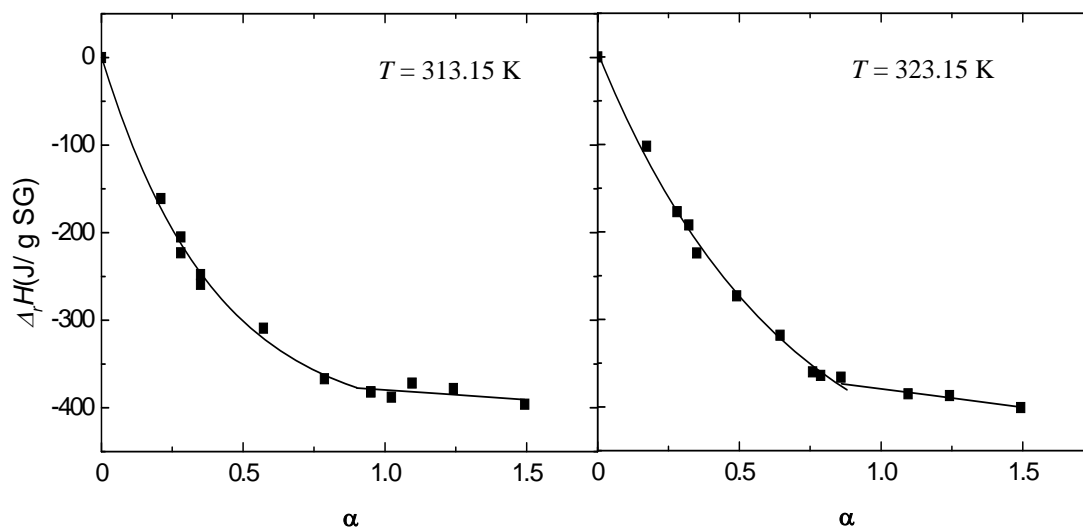
Fig. 2. Carbon dioxide absorption enthalpies, $\Delta_r H$, in aqueous 10 mass % sodium glycinate solutions vs. CO_2 loading expressed as mol CO_2/mol amine, α, at 313.15 and 323.15 K.

Absorption enthalpies expressed in kJ per mol of CO_2 were also calculated. These enthalpies become more exothermic as α decreases until a limit value characteristic of each amine is observed for low CO_2 loading. The region where the enthalpy is independent of CO_2 loading is limited to α lower than 0.4. For a given amine, this limit value changes appreciably with temperature and very slightly with the amine concentration in the aqueous solution. Limit values of −72.5 and −59.5 kJ/mol CO_2 are obtained for 10 mass % SG solutions at 313.15 and 323.15 K, respectively. These values can be regarded as the enthalpy of solution at infinite dilution and are compared in Table 1 to those previously reported[7-10] for solutions of other amines at the same or similar amine concentration and temperature. It may observed that SG absorption enthalpies are less exothermic than those of monoethanolamine or diglycolamine and of similar magnitude than those of diethanolamine, 2-amino-2-methyl-1-propanol or N-methyldiethanolamine. These values imply a moderate energetic cost to reverse reaction (1) and represent an advantage to be added to those mentioned in the introduction section for sodium glicinate solutions as a good absorbent alternative.

Table 1

Absorption enthalpies, $\Delta_r H$, of carbon dioxide in aqueous amine solutions

Amine	$-\Delta_r H$ (kJ/ mol CO_2)	T (K)	Amine mass fraction	Source
Monoethanolamine	81.0	298.15	0.10	10
Diethanolamine	68.8	299.82	0.10	10
	69.1	299.82	0.20	9
	74.7	349.82	0.20	
N-methyldiethanolamine	50.3	298.15	0.10	10
	49.1	313.15	0.10	8
	50.3	323.15	0.10	
Diglycolamine	82.7	288.71 – 422.04	0.10	7
2-Amino-2-methyl-1-propanol	70.4 – 75.1	322.5	0.15	11
Sodium glicinate	72.5	313.15	0.10	This paper
	59.5	323.15	0.10	This paper

Acknowledgements

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