J. Chem. Eng. Data **2010,** *55,* 1215–1218

Enthalpies of Absorption of Carbon Dioxide in Aqueous Sodium Glycinate Solutions at Temperatures of (313.15 and 323.15) K

Verónica Salazar, Yolanda Sánchez-Vicente, Concepción Pando,* Juan A. R. Renuncio, and Albertina Cabañas

Departamento de Química Física I, Facultad CC. Químicas, Universidad Complutense, E-28040 Madrid, Spain

The enthalpies of absorption ($\Delta_r H$) of carbon dioxide in aqueous sodium glycinate (SG) solutions of 0.10 in mass fraction were determined at temperatures of (313.15 and 323.15) K and a pressure of 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 $\text{kJ}\cdot\text{mol}^{-1}$ of SG decrease very quickly 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 provide 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 temperatures of (313.15 and 323.15) K, respectively. Enthalpies of solution 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) $\text{kJ}\cdot\text{mol}^{-1}$ are obtained for SG solutions of 0.10 in mass fraction at temperatures of (313.15 and 323.15) K, respectively. In spite of the complex zwitterionic mechanism involved in the reaction between glycinate and carbon dioxide, SG enthalpies of solution at infinite dilution and SG saturated loading points are of similar magnitude than those previously reported for other primary and secondary amines at the same or similar amine molal concentration and temperature.

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 kinetics investigations. Alkanolamines have been extensively used during the last decade for the removal of CO_2 from gas streams in the chemical industry. Recently, the need to reduce CO_2 emissions has led to an increasing interest in the design of efficient amine-based absorbents. 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 amino acid is expected to react in a similar way to that of a primary amine through a zwitterionic mechanism involving various steps. A detailed description of this mechanism is given by Kumar et al.[1] and Lee et al.[2] The overall reaction may be written as

$$CO_2 + 2RNH_2 \leftrightarrow RHNCOO^- + RHNH_2^+ \qquad (1)$$

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 be reversed by heating; CO_2 may be also considered as an agent to protect the primary amine in the form of ammonium carbamate. Several factors must be considered for the selection of an efficient CO_2 absorbent: the rate of reaction, the absorption capacity, heat of reaction, solution regeneration energy, durability, thermal stability, and corrosion. The solution regeneration energy is a key factor. Since reaction 1 is highly exothermic, as much as (50 to 80) % of the total process energy is used to reverse this reaction, recovering the amine and separating CO_2 from the solution. Data for the absorption enthalpies of carbon dioxide in aqueous solutions of amines required to estimate the regeneration energy are relatively scarce; several types of calorimeters: isothermal displacement, reaction, and mostly flow calorimeters were used for these measurements.[3−13] Usually, the gas solubility data as a function of temperature and CO_2 partial pressure are available in the literature for the amines currently used, and very often these data are used to estimate absorption enthalpies.[14,15]

Monoethanolamine, diethanolamine, *N*-methyldiethanolamine, and diglycolamine are examples of amines frequently used in this reaction. Inconveniences such as 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.[2,16−18] In this study, the enthalpies of absorption ($\Delta_r H$) of carbon dioxide in aqueous SG solutions of 0.10 mass fraction were determined at temperatures of (313.15 and 323.15) K and a pressure of 12.00 MPa using an isothermal high-pressure flow calorimeter. The temperatures chosen are typical for these processes. The concentration of 0.10 mass fraction for SG solutions was chosen taken into account previous solubility studies[17] showing that the CO_2 loading capacity at temperatures of (313.15 and 323.15) K decreased as the SG

---

* Corresponding author. Phone: +34 91394 4304. Fax: +34 91394 4135. E-mail: pando@quim.ucm.es.

10.1021/je9005954 © 2010 American Chemical Society
Published on Web 10/16/2009

Table 1. Experimental Enthalpies of Absorption of Carbon Dioxide in Aqueous Sodium Glycinate Solutions at Temperatures of (313.15 and 323.15) K

T/K = 313.15		T/K = 323.15	
α	Δ_rH/kJ·mol^{-1}	α	Δ_rH/kJ·mol^{-1}
0.210	−15.6	0.173	−9.9
0.280	−21.6	0.280	−17.2
0.280	−19.9	0.322	−18.6
0.350	−25.1	0.350	−21.7
0.350	−24.1	0.491	−26.5
0.572	−30.0	0.644	−30.9
0.787	−35.6	0.759	−34.9
0.950	−37.1	0.787	−35.3
1.023	−37.7	0.859	−35.5
1.096	−36.1	1.096	−37.4
1.242	−36.7	1.242	−37.6
1.493	−38.4	1.493	−38.9

mass fraction increased from 0.10 to 0.20 or 0.30. In most previous experimental determinations, the enthalpy of absorption for a given amine solution at infinite dilution has been shown to change appreciably with temperature and very slightly with amine concentration or pressure. For instance, Mathonat et al.[6,7] used a flow calorimeter to measure Δ_rH for methyldiethanolamine and monoethanolamine solutions of 0.30 mass fraction at temperatures of (313.15, 353.15, and 393.15) K and pressures of (2.0, 5.0, and 10.0) MPa and found coincident values at a given temperature within the experimental errors. In this study, a value for the pressure similar to those used by Mathonat et al. was chosen.

Experimental Section

The materials employed were CO_2 (Air Liquide, 0.9998 purity in mole fraction) and SG (Sigma-Aldrich, purity > 0.99 in mole fraction). Commercial materials were used without further purification. SG solutions of 0.10 in mass fraction were prepared gravimetrically using deionized distilled water and preventing contamination by atmospheric CO_2. To this end, the previously deionized distilled water was boiled for 20 min in a flask connected to a reflux refrigerant and a CO_2-absorbing solution. After boiling, the flask was sealed using a septum under nitrogen atmosphere. Water was then transferred using a needle to a 1 L bottle containing the required amount of SG under nitrogen atmosphere. The solution was kept in the sealed bottle and was transferred to the pump used in the calorimetric measurements without exposure to the surroundings.

Figure 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.[19] The reactants were pumped into the calorimetric cell by two thermostatted pumps (ISCO, model LC-2600) at constant flow rates. The temperature of the pumps was controlled within ± 0.02 K. All runs were made in the steady-state fixed composition mode. The volume flow rates were converted to molar flow rates using the densities and molar masses of CO_2[20] and SG aqueous solutions.[16] The mole fraction and CO_2 loading (α) values were derived from the molar flow rate values of each pump. Measurements were carried out at total volume flow rates of (0.0028 and 0.0056) cm^3·s^{-1}. The CO_2 loading range is covered by combining adequate values for the flow rates of the two pumps at these total volume flow rates. Also, the coincidence within the experimental error of results obtained using different total flow rates is an indication of equilibrium conditions in the calorimeter. Measurements at different α values were carried out until saturation is reached, and approximately constant values are obtained for Δ_rH. The calorimetric cell was located into a silicon bath in which temperature was controlled to within ± 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 to within ± 0.01 MPa. A constant pressure of 12.00 MPa was maintained during the experiment. Since densities are affected by temperature and pressure changes, the error in molar flow rates was derived taking into account contributions from variations in volume flow rates, pressure, and pump temperature. The mole fraction and CO_2 loading precision are based on the error in molar flow rates and were estimated to be better than ± 0.001. The error in Δ_rH in previous heat of mixing measurements using this calorimeter was obtained taking into account contributions from molar flow rates, pulse energy, and frequency and was estimated to be ± 1 % or at least ± 1 J·mol^{-1}. The estimation of errors is described in detail by Cabañas.[21] Following a similar procedure, the error in Δ_rH of present measurements was calculated for each experimental point, and a value of at least ± 0.3 kJ·mol^{-1} was obtained; the mean relative error was ± 3 %.

Results and Discussion

Very exothermic absorption enthalpies are obtained at the two temperatures studied. Table 1 lists the α and Δ_rH values obtained. Figures 2 and 3 show the Δ_rH values versus α plots at temperatures of (313.15 and 323.15) K, respectively. Δ_rH 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 previously reported for the absorption of CO_2 in primary and secondary amine solutions.[3−13]

The calorimetric data provide a means to determine the saturated loading point of CO_2 in the solution. Δ_rH 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 temperatures of (313.15 and 323.15) K, respectively. The decrease in α values with temperature has been already observed for other amine solutions.[6,7] On the other hand, these α values are lower than those previously reported by Song et al.[17] from direct solubility measurements at the same temperatures and lower pressures. Values for the saturated loading point of CO_2 in the solution are compared in Table 2 to those previously obtained by a calorimetric procedure for solutions of other amines at the same or similar amine molal concentration and temperature. Table 2 lists mass fraction values since this is the usual unit to express the amine concentration. The saturated loading point of CO_2 for SG solutions adopts values similar to those observed for other amine solutions. Only those reported by Arcis et al. for *N*-methyldiethanolamine[12] and for 2-amino-2-methyl-1-propanol[9] are significantly larger.

The enthalpies of solution 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 and in most cases does not depend on pressure. Limit values of (−72.5 and −59.5) kJ·mol^{-1} are obtained for SG solutions of 0.10 in mass fraction at temperatures of (313.15 and 323.15) K, respectively. The limit values can be regarded as the enthalpy

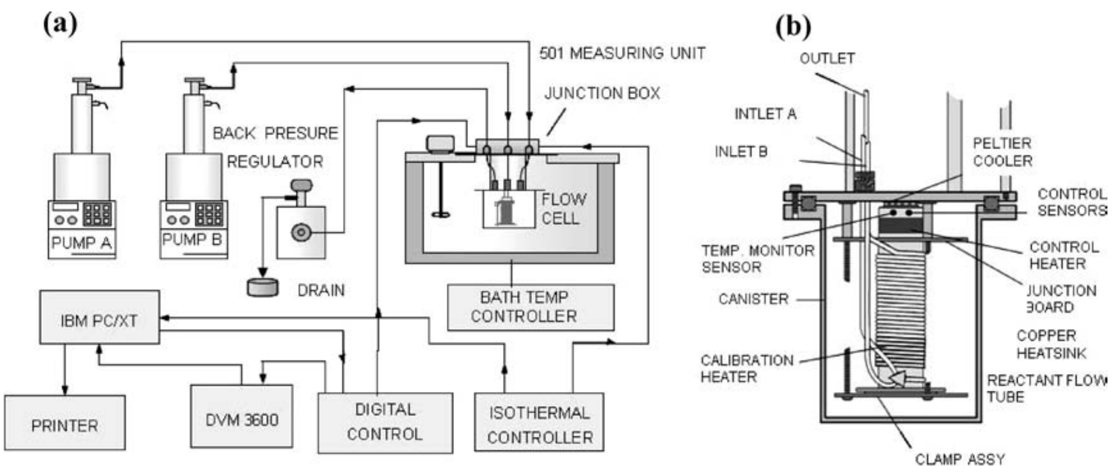

Figure 1. Schematic diagrams of (a) the isothermal flow calorimeter and (b) the flow cell used to perform the enthalpy of absorption measurements.

Table 2. Comparison of Enthalpies of Solution, Δ_rH, at Infinite Dilution and the Saturated Loading Point, α, of Carbon Dioxide in Aqueous Amine Solutions Obtained in This Study with Those from the Literature[a]

amine	$-\Delta_rH$ kJ·mol^{-1}	$10^2\cdot\delta$	α	T K	amine mass fraction	source
monoethanolamine	81.0	0.8		298.15	0.10	8
diethanolamine	68.8	0.6		299.82	0.10	8
	69.1	5	0.87	299.82	0.20	5
	74.7	5		349.82	0.20	5
N-methyldiethanolamine	50.3	0.6		298.15	0.10	8
	49.1	5		313.15	0.10	4
	50.3	5	1.0[b]	323.15	0.10	4
	50.3	2.6	1.07	313.15	0.10	11
	55.7	2.9	0.95	333.15	0.10	11
	49.6[c]	2.8	1.26	322.5	0.15	12
diglycolamine	82.7	3		288.71, 333.15	0.10	3
2-amino-2-methyl-1-propanol	70.4[d]	1.3	1.32[d]	322.5	0.15	9
SG	72.5	4	0.90	313.15	0.10	this paper
	59.5	4	0.86	323.15	0.10	this paper

[a] δ is the estimated relative uncertainty for Δ_rH. [b] The α value was taken at a temperature of 333.15 K. [c] Value obtained at pressure of 5.17 MPa. [d] Value obtained at pressure of 5.20 MPa. The Δ_rH at infinite dilution and α values reported in refs 9 and 12 exhibit a slight pressure dependence.

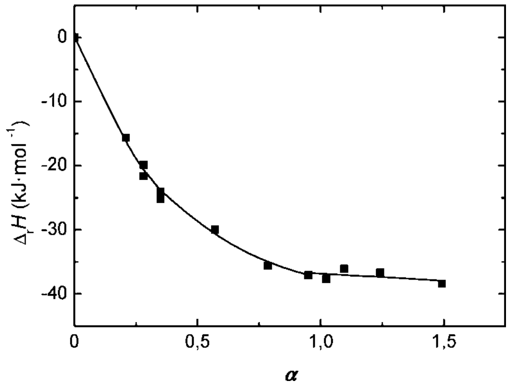

Figure 2. Carbon dioxide absorption enthalpies, Δ_rH, in aqueous SG solutions of 0.10 in mass fraction vs CO_2 loading expressed as mol CO_2/mol amine, α, at a temperature of 313.15 K.

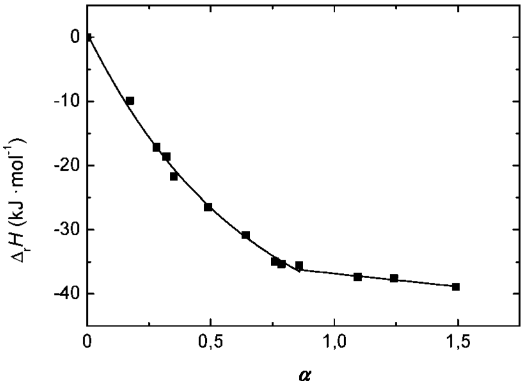

Figure 3. Carbon dioxide absorption enthalpies, Δ_rH, in aqueous SG solutions of 0.10 in mass fraction vs CO_2 loading expressed as mol CO_2/mol amine, α, at a temperature of 323.15 K.

of solution at infinite dilution. The relative uncertainty δ for these extrapolated values is estimated to be ± 4 %. Table 2 includes a comparison of the enthalpy of solution at infinite dilution values obtained in this paper and those previously reported for solutions of other amines at the same or similar amine molal concentration and temperature. The estimated relative uncertainty is expressed using one or two digits as reported by the authors. Values for δ range from less than 1 % for the measurements of Carson et al.[8] made by isothermal displacement calorimetry to 5 % for some flow calorimetry measurements.[4,5] It may be observed that both SG solution enthalpies at infinite dilution and SG saturated loading points are of similar magnitude than those of other amines. This implies a moderate energetic cost to reverse reaction 1 and makes SG solutions a good absorbent alternative. On the other hand, the similarity of solution enthalpy values also indicates that the reaction 1 energetics is not affected by the presence of the zwitterion. In spite of the complex mechanism involved in this reaction, the acid−base interaction of carbon dioxide and the glycinate is essentially similar to that of carbon dioxide and a primary amine.

Literature Cited

(1) Kumar, P. S.; Hogendoorne, J. A.; Versteeg, G. F.; Feron, P. H. M. Kinetics of the reaction of CO_2 with aqueous potassium salt of taurine and glycine. *AIChE J.* **2003**, *49*, 203–213.

(2) Lee, S.; Song, H. J.; Maken, S.; Park, J. W. Kinetics of CO_2 absorption in aqueous sodium glycinate solutions. *Ind. Eng. Chem. Res.* **2007**, *46*, 1578–1583.

(3) Christensen, S. P.; Christensen, J. J.; Izatt, R. M. Enthalpy of solution of carbon dioxide in aqueous diglycolamine solutions. *Thermochim. Acta* **1986**, *106*, 241–251.

(4) Merkley, K. E.; Christensen, J. J.; Izatt, R. M. Enthalpies of absorption of carbon dioxide in aqueous methyldiethanolamine solutions. *Thermochim. Acta* **1987**, *121*, 437–446.

(5) Oscarson, J. L.; Van Dam, R. H.; Christensen, J. J.; Izatt, R. M. Enthalpies of absorption of carbon dioxide in aqueous diethanolamine solutions. *Thermochim. Acta* **1989**, *146*, 107–114.

(6) Mathonat, C.; Majer, V.; Mather, A. E.; Grolier, J.-P. E. Enthalpy of absorption and solubility of CO_2 in aqueous solutions of methyldiethanolamine. *Fluid Phase Equilib.* **1997**, *140*, 171–182.

(7) Mathonat, C.; Majer, V.; Mather, A. E.; Grolier, J.-P. E. Use of flow calorimetry for determining enthalpies of absorption and the solubility of CO_2 in aqueous monoethanolamine solutions. *Ind. Eng. Chem. Res.* **1998**, *37*, 4136–4141.

(8) Carson, J. K.; Marsh, K. N.; Mather, A. E. Enthalpy of solution of carbon dioxide in (water + monoethanolamine, diethanolamine, or *N*-methyl diethanolamine) and water + monoethanolamine + *N*-methyl diethanolamine) at 298.15 K. *J. Chem. Thermodyn.* **2000**, *32*, 1285–1296.

(9) Arcis, H.; Rodier, L.; Coxam, J.-Y. Enthalpy of solution of CO_2 in aqueous solutions of 2-amino-2-methyl-1-propanol. *J. Chem. Thermodyn.* **2007**, *39*, 878–887.

(10) Kim, I.; Svendsen, F. H. Heat of absorption of carbon dioxide (CO_2) in monoethanolamine (MEA) and 2-(aminoethyl)ethanolamine (AEEA) solutions. *Ind. Eng. Chem. Res.* **2007**, *46*, 5803–5809.

(11) Kierzkowska-Pawlak, H. Enthalpies of absorption and solubility of CO_2 in aqueous solutions of methyldiethanolamine. *Sep. Sci. Technol.* **2007**, *42*, 2723–2737.

(12) Arcis, H.; Rodier, L.; Ballerat-Busserolles, K.; Coxam, J.-Y. Enthalpy of solution of CO_2 in aqueous solutions of methyldiethanolamine at $T = 322.5$ K and pressures up to 5 MPa. *J. Chem. Thermodyn.* **2008**, *40*, 1022–1029.

(13) Arcis, H.; Rodier, L.; Ballerat-Busserolles, K.; Coxam, J.-Y. Enthalpy of solution of CO_2 in aqueous solutions of methyldiethanolamine at $T = 372.9$ K and pressures up to 5 MPa. *J. Chem. Thermodyn.* **2009**, *41*, 836–841.

(14) McCann, N.; Maeder, M.; Atalla, M. Simulation of enthalpy and capacity of CO_2 absorption by aqueous amine systems. *Ind. Eng. Chem. Res.* **2008**, *47*, 2002–2009.

(15) Song, H. J.; Lee, S.; Park, K.; Lee, J.; Spah, D. C.; Park, J. W.; Filburn, T. P. Simplified estimation of regeneration energy of 30 wt % sodium glycinate solution for carbon dioxide absorption. *Ind. Eng. Chem. Res.* **2008**, *47*, 9925–9930.

(16) Lee, S.; Choi, S. I.; Maken, S.; Song, H. J.; Shin, H. C.; Park, J. W.; Jang, K. R.; Kim, J. H. Physical properties of aqueous sodium glycinate solutions as an absorbent for carbon dioxide removal. *J. Chem. Eng. Data* **2005**, *50*, 1773–1776.

(17) Song, H. J.; Lee, S.; Maken, S.; Park, J. J.; Park, J. W. Solubility of carbon dioxide in aqueous sodium glycinate solutions. *Fluid Phase Equilib.* **2006**, *246*, 1–5.

(18) Lee, S.; Song, H. J.; Maken, S.; Shin, H. C.; Song, H. C.; Park, J. W. Physical solubility and diffusivity of aqueous sodium glycinate solutions. *J. Chem. Eng. Data* **2006**, *51*, 504–509.

(19) Dávila, M. J.; Cabañas, A.; Pando, C. Excess molar enthalpies for binary mixtures related to supercritical antisolvent precipitation: carbon dioxide + *N*-methyl-2-pyrrolidone. *J. Supercrit. Fluids* **2007**, *42*, 172–179.

(20) NIST Standard Reference Database Number 69. http://webbook.nist.gov/chemistry/ (accessed May 2007).

(21) Cabañas, A. Thermodynamic study of mixtures formed by nitrous oxide and hydrocarbons in the critical and supercritical regions. Ph.D. Thesis, Universidad Complutense de Madrid, Spain, 1998.

Received for review July 14, 2009. Accepted October 1, 2009. We gratefully acknowledge the financial support of the Universidad Complutense de Madrid, research project SANTANDER-COMPLUTENSE PR34/07-15789, and the Spanish Ministry of Education and Science (MEC), research project CTQ2006-07172/PPQ. Y.S. thanks MEC for its support through a FPI predoctoral grant.

JE9005954