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Measurement and Modeling of Enthalpy of Solution of Carbon Dioxide in Aqueous Solutions of Diethanolamine at Temperatures of (322.5 and 372.9) K and Pressures up to 3 MPa

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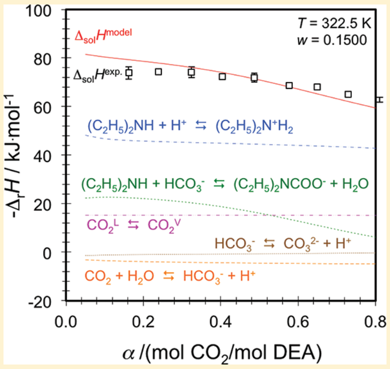
S Supporting Information

ABSTRACT: The enthalpies of solution ($\Delta_{sol}H$) of carbon dioxide (CO_2) in two aqueous solutions (w = 0.1500 and w = 0.3000) of diethanolamine (DEA) have been measured at two temperatures ((322.5 and 372.9) K) and pressures up to 3 MPa. Measurements were carried out by a flow calorimetric technique using a custom-made flow-mixing unit combined with a SETARAM C-80 isothermal differential heat-flux calorimeter. Enthalpies of solution of CO_2 ($\Delta_{sol}H$) have been obtained as function of loading, α (moles CO_2/mol amine). Influences of temperature, pressure, and absorbent composition have been discussed. Solubility data of the gas into the different absorbent (*s*) were derived from the enthalpic data. The experimental enthalpies of solution ($\Delta_{sol}H$) of carbon dioxide (CO_2) in the two aqueous solutions of diethanolamine have been compared with data derived from a rigorous thermodynamic model of phase equilibria based on a $\gamma-\phi$ approach. Interaction parameters were chosen to be adjustable parameters in this model and were fitted to vapor−liquid equilibrium data. Several formulations for the amine protonation and carbamate formation equilibrium constants have been tested. The different contributions to the enthalpy of solution of CO_2 in aqueous solutions of DEA have been analyzed.



1. INTRODUCTION

The capture of carbon dioxide from postcombustion emission is one of the challenges for reducing the release of greenhouse gases into the atmosphere. Aqueous amine solutions are well-known to be efficient chemical solvents for the industrial capture of CO_2. Gas capture combines physical dissolution and subsequent reactions of CO_2 into the absorbent solution. The acid−base reaction between the carbon dioxide and the amine is reversible, making it possible to separate the gas from the absorbent solution in a cyclic process. The purpose of current researches carried on CO_2 capture is the reduction of the energy cost of CO_2 removal in the amine washing process. To design new industrial processes for gas treating operations, the development of better theoretical models describing the {CO_2 + amine + H_2O} systems is required. The existing models[1−9] are based on temperature-dependent liquid vapor equilibria data from which the enthalpy of solution of CO_2 was derived.[4,7−9] Although gas solubility data as a function of temperature, amine composition, and partial pressure of CO_2 are available in the literature,[10−22] only a few experimental enthalpy studies have been published[4,23,24] for the system {CO_2 + DEA + H_2O}. A literature review for both solubility data and enthalpy of solution of CO_2 is reported in Tables 1 and 2. To develop thermodynamic models able to describe the {CO_2 + DEA + H_2O} system we decided to extend the existing enthalpy data.[4,23,24] In addition, the new proposed set of data makes it possible to investigate the pressure effect on the enthalpy of solution on a wider experimental range.

The models mentioned above differ from the approach used to describe the liquid phase and the gas phase. For the liquid phase, authors generally made use of activity coefficient models such as the extended Debye−Hückel model,[1,9] the nonrandom-two liquid (NRTL),[2,7] or equations introduced by Pitzer.[3−6] To describe the gas phase, the most common equations of state (EOS's) employed are the Peng−Robinson,[1,4,7,9] the Redlich−Kwong,[2] the Soave−Redlich−Kwong,[3] and the virial ones.[5,6,8] All of these models provide a good estimation of the CO_2 equilibrium pressure as a function of the temperature and the amine composition. A few studies were focused on testing the ability of such models to predict the enthalpy of solution of CO_2 into different absorbents: monoethanolamine (MEA),[7,9] diethanolamine (DEA),[4,7] methyldiethanolamine (MDEA),[4,7−9] and diglycolamine (DGA).[4] Oscarson et al.[4] included in addition experimental enthalpy when fitting the liquid vapor−equilibria data.

In this paper, we report a new set of experimental data on the enthalpy of solution for the systems {CO_2 + DEA + H_2O}. Measurements were performed for two aqueous amine solutions

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Table 1. Literature Review of Gas Solubility Data for the System $\{CO_2 + DEA + H_2O\}$

		T	p_{CO_2}	p	δ_{max}
source	composition	K	kPa	kPa	%
Lee et al.[10]	0.5−8.0[a]	273−413	0.69−6900		5
Oyevaar et al.[11]	0.984−2.463[a]	298	1.844−14.8		5
Kennard and Meisen[12]	0.100−0.300[b]	373−478	73.1−3746.7	165.5−4137.0	10
Dawodu and Meisen[13]	4.2[a]	373	455−3863		13.5
Lal et al.[14]	2.0[a]	313−373	0.0026−3.336		15
Otto et al.[15]	3.0−4.0[a]	298−403	0.001−5000		
Lawson and Garst[16]	0.250[b]	311−394	1.974−4315.79		9
Mason and Dodge[17]	0.5−8.3[a]	273−348	1.32−100		2
Sidi-Boumedine et al.[18]	0.4178[b]	298−348	2.46 4662.7		2
Seo and Hong[19]	0.300[b]	313−353	4.85−357.3		3
Benamor and Aroua[20]	2.0−4.0[a]	303−323	0.1−104.7		2
Haji-Sulaiman et al.[21]	2.0−4.0[a]	303−323	0.1−104.7		2
Haji-Sulaiman and Aroua[22]	2.0[a]	301−353	5−100.3		12

[a] Molarity in $mol \cdot L^{-1}$. [b] Mass fraction.

Table 2. Literature Review of Enthalpy Data for the System $\{CO_2 + DEA + H_2O\}$

		T	p_{CO_2}	δ_{max}
source	w	K	kPa	%
Oscarson et al.[4]	0.206−0.498	300−450	90−1121	5
Carson et al.[23]	0.100−0.300	298	265	2
Helton et al.[24]	0.300−0.500	300−400	87−1121	5

($w_{DEA} = 0.1500 \pm 0.0001$ and $w_{DEA} = 0.3000 \pm 0.0001$) at temperatures of (322.5 and 372.9) K and pressures from (0.5 to 3) MPa for CO_2 loadings up to the saturation of the absorbent solution. The measurements were carried out using a custom-made mixing cell developed for an isothermal differential heat flux calorimeter, the Setaram C-80.[25] Solubilities of the gas into the different absorbents (s) at the same temperature, pressure, and amine weight fraction were deduced from the experimental enthalpic data.

The experimental enthalpies of solution ($\Delta_{sol}H$) of carbon dioxide in the two aqueous solutions of diethanolamine have been compared with data derived from a rigorous thermodynamic model of phase equilibria based on a $\gamma-\phi$ approach. In the model, a Pitzer equation was used to describe the liquid phase, and only binary interactions were considered. Parameters were adjusted when fitting vapor−liquid equilibrium data. Several formulations for the amine protonation and carbamate formation equilibrium constants have been tested, and results are discussed. The different contributions to the enthalpy of solution of CO_2 in aqueous solutions of DEA have also been analyzed.

2. EXPERIMENTAL SECTION

2.1. Experimental Arrangement. The calorimetric technique was similar to the one used previously to study the dissolution of CO_2 in aqueous solutions of 2-amino-2-methyl-1-propanol (AMP),[26] *N*-methyl-diethanolamine (MDEA),[27,28] and monoethanolamine (MEA).[29] The heat of absorption of CO_2 in an aqueous solution of amine was measured using a custom-made flow-mixing cell adapted to a Setaram C-80 heat conduction differential calorimeter.[25,29] The overall experimental arrangement is depicted in Figure 1. Both fluids, CO_2 and aqueous amine solution, were injected into the mixing cell supplied by two ISCO model 100 DM high-pressure syringe pumps. The syringe pumps were regulated at a constant temperature of 298.15 K, using water baths, to maintain a constant mass flow rate. The system pressure was maintained at a constant pressure to within ± 0.02 MPa using a Circle Seal backpressure regulator placed at the end of the flow line. A buffer volume filled with nitrogen and placed just before the backpressure regulator was used to get a better control of the pressure stability. The pressure was measured by three electronic Keller pressure transducers connected to pressure indicators WEST 8010 with accuracy of 0.25 % of the full scale. The pressure gauges were located at the outlets of the acid gas and aqueous phase pumps and between the mixing cell and the backpressure regulator. The temperature of the injected fluids was adjusted to the working temperature of the calorimeter before entering the mixing cell using four preheaters.[29] The temperature of the calorimeter was set up and controlled within 0.01 K using a Setaram G11 electronic control device.

2.2. Operating Procedure. The experiments were designed to measure the enthalpy of mixing between the two fluids (gas and aqueous solution) at constant temperature and pressure as a function of the CO_2 loadings, α (moles CO_2/moles amine). In our case, this enthalpy of mixing characterized the dissolution of the carbon dioxide into the amine solution and was defined as the enthalpy of solution of CO_2 in the aqueous solution of amine. The loading was determined by the total molar flow-rate of CO_2 $\dot{n}_{CO_2}$ divided by the total molar flow-rate of amine $\dot{n}_{amine}$ (eq 1).

$$\alpha = \frac{\dot{n}_{CO_2}}{\dot{n}_{amine}} \tag{1}$$

Typically the flow rates varied from (0.1 to 2) $mL \cdot min^{-1}$ and (0.04 to 0.4) $mL \cdot min^{-1}$ for CO_2 and the aqueous phase respectively, with a relative uncertainty of 0.3 %. The molar flow rates were calculated from the pump flow rates using the densities, mass composition (for the aqueous amine solution), and molar mass of the fluids. The densities of aqueous DEA solutions were measured at 298.4 K (the regulation temperature of the syringe pump) as a function of the pressure using an Anton Paar densimeter DMA 512 (P model) following Jacquemin's procedure;[30] values are reported in Table 3. The densities of CO_2 were calculated from ALLPROPS software.[31]

The enthalpy was directly obtained from the thermopile signal S (μV) of the calorimeter and the molar flow-rate $\dot{n}$ ($mol \cdot s^{-1}$) of the solution. Before measuring the thermopile signal S_M (μV) during the mixing process, a baseline signal S_{BL} (μV) was recorded with only the aqueous solution flowing through the calorimeter. The baseline signal was kept close to zero by adjusting the thermoregulation of the entering fluid. The signal was recorded for 20 min before the gas injection. The heat effect due to the gas dissolution corresponded to a thermopile signal ($S_M - S_{BL}$) ranging from (4 to 16) mV and typically had a stability better than ± 0.1 mV. This signal was recorded for at

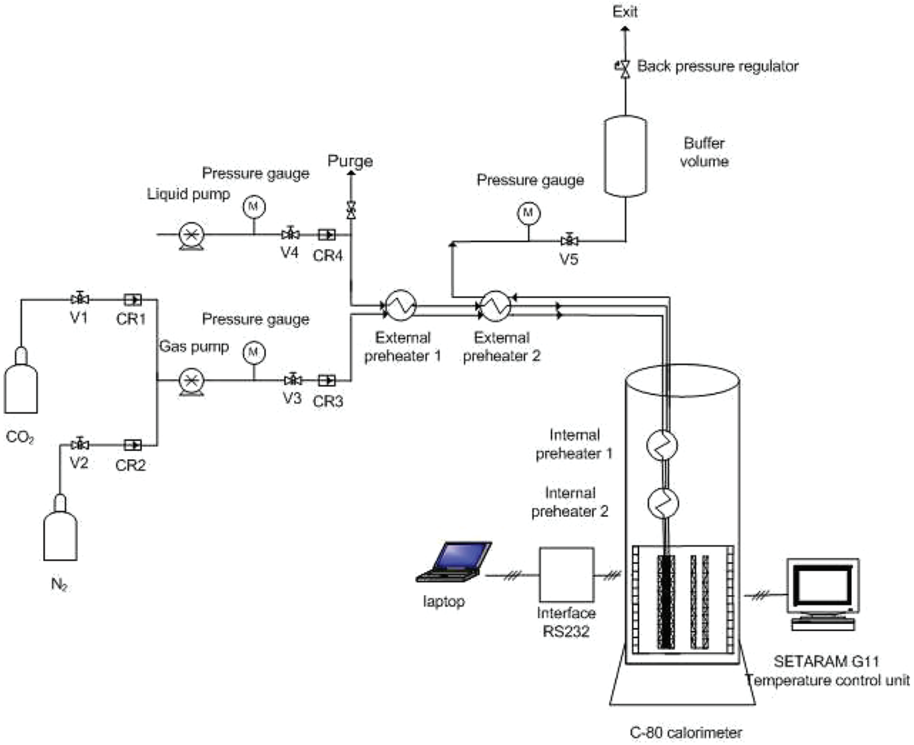

Figure 1. Schematic diagram of the flow-mixing calorimeter.

Table 3. Experimental Density of Aqueous DEA Solutions (w_{DEA} = 0.1500 and 0.3000) Used for Calculating the Molar Flow Rates of the Amine Solutions Used in Equation 1

T	p	ρ	T	p	ρ
K	MPa	kg·m^{-3}	K	MPa	kg·m^{-3}
	w_{DEA} = 0.1500			w_{DEA} = 0.3000	
298.35	0.203	1015.3 ± 0.1	298.38	0.208	1033.2 ± 0.1
298.35	0.502	1015.4 ± 0.1	298.38	0.506	1033.3 ± 0.1
298.35	1.007	1015.6 ± 0.1	298.38	1.006	1033.5 ± 0.1
298.36	2.001	1016.0 ± 0.1	298.39	2.009	1033.9 ± 0.1
298.36	3.004	1016.3 ± 0.1	298.38	2.997	1034.3 ± 0.1
298.35	5.005	1017.0 ± 0.1	298.39	5.000	1035.0 ± 0.1

least 30 min, and then the baseline signal was again recorded for 20 min.

The enthalpies of solution ($\Delta_{sol}H$) expressed as kJ·mol^{-1} of CO_2 or kJ·mol^{-1} of amine were calculated from eq 2 using the molar flow rate of gas ($\Delta_{sol}H$/kJ·mol^{-1} of CO_2) or the molar flow rate of amine (($\Delta_{sol}H$/kJ·mol^{-1} of amine):

$$\Delta_{sol}H = \frac{\Delta \text{signal}}{E \cdot \dot{n}} \qquad (2)$$

where Δsignal represents the difference in the thermopile signal during the mixing process and the baseline (only when the aqueous amine solution was running through the mixing flow calorimeter). The thermopile sensitivity E (μV·mW^{-1}) used to convert the thermopile signal to heat power was given by the constructor as a function of the temperature. Since it could have slightly changed with time, it was recalibrated by measuring the heat of mixing of a binary system whose enthalpy of mixing is well-known. For this purpose we chose the reference {$C_2H_5OH + H_2O$} system, using the enthalpy data provided by Ott et al.[32,33] Calibration constants were adjusted by measuring the enthalpy of mixing of the reference system {$C_2H_5OH + H_2O$} at 323 K and 0.4 MPa and 373 K and 1 MPa, respectively. The difference between the thermopile sensitivity obtained by chemical calibration and the one reported by Setaram was less than 5 %.

2.3. Experimental Uncertainty.

The experimental uncertainty on the enthalpy of solution, $\delta(\Delta_{sol}H)$, was determined as a statistical estimate from the expected error in E, uncertainties on the molar flow rate, and the heat power based on eq 2. The uncertainty on the molar flow rates depended on the uncertainty on the volumic flow rates of the pumps and the accuracy of the fluid densities. For the gas it was estimated to be smaller than 0.3 % at 3 MPa and 3 % at 0.2 MPa, and for the aqueous amine solution it was estimated to be smaller than 1 %. The error on the heat power is related to the accuracy of the thermopile sensitivity E of the calorimeter, estimated to 2 %, and to the fluctuations of the calorimetric signal. The uncertainty in the difference in the thermopile signal during the mixing process and the baseline was between 1 and 3 % and can reach 5 % for the smallest measured heat effects. Calculations for the determination of the experimental uncertainties are described in detail elsewhere.[34]

2.4. Chemicals and Materials.

Diethanolamine was obtained from Fluka Organics with a purity >98 % and was used without further purification. Carbon dioxide (purity of 99.998 %) was obtained from Saga. Water was distilled and degassed before used (resistivity 18.2 MΩ·cm). Aqueous solutions were prepared by mass with an uncertainty in the mass fraction estimated as less than ± 10^{-4} and kept under nitrogen atmosphere. Aqueous solutions were stored in glass bottle in an opaque cabinet to prevent any photodegradation.

Table 4. Experimental Enthalpies of Solution of CO_2 in Aqueous Solutions of DEA (w_{DEA} = 0.1500) at 322.5 K

α	$\delta\alpha$	$-\Delta_{sol}H$	$\delta\Delta_{sol}H$	$-\Delta_{sol}H$	$\delta\Delta_{sol}H$
mol_{CO_2}/mol_{DEA}		$kJ\cdot mol^{-1}$ of DEA		$kJ\cdot mol^{-1}$ of CO_2	
		p = 0.55 MPa			
0.162	0.003	12.0	0.4	73.9	2.6
0.238	0.004	17.7	0.1	74.4	0.5
0.324	0.006	24.0	0.7	74.1	2.2
0.404	0.007	29.3	0.3	72.4	0.6
0.486	0.009	35.0	0.9	71.9	1.8
0.577	0.010	39.7	0.3	68.8	0.6
0.649	0.012	44.1	0.6	68.1	0.9
0.729	0.013	47.4	0.5	65.0	0.7
0.811	0.015	51.0	0.8	62.9	1.0
0.891	0.016	54.0	0.6	60.6	0.7
0.956	0.018	54.8	0.8	57.3	0.8
1.112	0.020	55.0	0.6	49.5	0.6
1.156	0.021	54.1	0.6	46.8	0.5
1.301	0.023	53.2	1.0	40.8	0.8
1.463	0.026	53.4	0.7	36.5	0.5
1.625	0.029	53.1	0.7	32.7	0.4
1.820	0.032	52.9	0.7	29.1	0.4
2.020	0.035	53.3	0.7	26.4	0.4
		p = 1.04 MPa			
0.153	0.003	11.33	0.2	73.8	1.0
0.237	0.003	17.2	0.2	72.3	0.7
0.320	0.004	22.8	0.2	71.4	0.7
0.380	0.005	26.9	0.4	70.7	1.0
0.443	0.005	30.6	0.6	69.1	1.3
0.506	0.006	34.5	0.7	68.1	1.4
0.569	0.007	38.4	0.3	67.4	0.6
0.634	0.008	41.0	0.4	64.6	0.6
0.712	0.009	45.1	0.4	63.4	0.6
0.785	0.009	48.0	0.4	61.2	0.6
0.863	0.010	50.4	0.5	58.4	0.5
0.951	0.011	53.4	0.5	56.2	0.5
1.011	0.012	55.4	0.6	54.8	0.6
1.079	0.013	56.4	0.6	52.3	0.5
1.144	0.014	57.8	0.6	50.5	0.5
1.257	0.015	57.1	0.7	45.4	0.6
1.334	0.016	57.6	0.8	43.2	0.6
1.411	0.017	57.3	0.6	40.6	0.4
1.571	0.019	57.3	0.7	36.5	0.4
1.571	0.019	57.2	0.7	36.4	0.4
1.740	0.021	57.3	0.6	32.9	0.3
		p = 2.07 MPa			
0.176	0.001	11.0	1.0	62.6	5.9
0.200	0.001	12.4	1.3	62.0	6.6
0.204	0.001	13.1	2.4	64.0	11.6
0.244	0.002	15.4	2.8	63.2	11.6
0.309	0.002	19.4	0.4	62.8	1.2
0.323	0.002	20.3	3.5	62.9	11.0
0.409	0.003	26.3	0.3	64.1	0.6
0.460	0.003	28.8	11.3	62.7	24.5
0.492	0.004	31.7	0.5	64.4	1.1
0.534	0.004	33.1	5.7	62.1	10.7
0.632	0.004	38.0	3.6	60.1	5.7
0.658	0.005	37.8	7.1	57.5	10.8
0.745	0.005	44.3	7.1	59.4	9.5
0.866	0.006	48.9	0.6	56.5	0.7
0.968	0.007	53.1	4.3	54.8	4.5
1.027	0.007	54.3	0.5	52.8	0.5
1.126	0.008	55.9	5.7	49.6	5.1
1.126	0.008	54.5	5.0	48.4	4.4
1.187	0.008	57.3	1.0	48.2	0.9
1.240	0.009	59.7	1.3	48.1	1.0
1.278	0.009	60.0	1.3	46.9	1.0
1.315	0.009	58.1	2.9	44.2	2.2
1.349	0.010	59.5	2.9	44.1	2.2
1.350	0.009	58.3	0.6	43.2	0.4
1.511	0.010	58.2	0.8	38.5	0.5
1.664	0.011	58.3	0.5	35.0	0.3
1.813	0.013	57.9	0.6	32.0	0.3
1.820	0.013	61.2	0.9	33.6	0.5
1.960	0.014	58.1	1.0	29.6	0.5
2.494	0.018	60.6	0.5	24.3	0.2
3.219	0.023	60.4	0.5	18.8	0.1

3. EQUATIONS USED FOR CALCULATING THE ENTHALPY OF SOLUTION OF CO_2 IN THE AQUEOUS DEA SOLUTIONS

3.1. Modeling of Phase Equilibria. The thermodynamic model described below is similar to the one used previously to study the dissolution of CO_2 in aqueous solutions of *N*-methyl diethanolamine (MDEA).[8] The modeling of phase equilibria in the system $\{CO_2 + DEA + H_2O\}$ was based on a system of equations related to chemical reactions in the liquid phase, vapor−liquid equilibria, charge, and mass balances. The standard state of the acid gas and the aqueous amine solution were respectively taken as the ideal gas at the temperature of reaction and as the hypothetical one molal solution at infinite dilution on a molality basis.

When considering the dissolution of CO_2 in aqueous DEA solution, chemical reactions E1 to E5 take place in the liquid phase.

$$H_2O \leftrightarrows H^+ + OH^- \tag{E1}$$

$$(C_2H_5)_2NH + H^+ \leftrightarrows (C_2H_5)_2N^+H_2 \tag{E2}$$

$$CO_2(aq) + H_2O \leftrightarrows HCO_3^- + H^+ \tag{E3}$$

$$HCO_3^- \leftrightarrows CO_3^{2-} + H^+ \tag{E4}$$

$$(C_2H_5)_2NH + HCO_3^- \leftrightarrows (C_2H_5)_2NCOO^- + H_2O \tag{E5}$$

Equilibrium constants for the chemical reactions E1 to E5 are expressed by eq 3.

$$K_{m,r_i} = \prod_j a_j^{\upsilon_{j,r_i}} = \prod_j (\gamma_j \cdot m_j)^{\upsilon_{j,r_i}} \qquad i = \text{E1 to E5} \tag{3}$$

where a_j, γ_j, m_i, and ν_j are, respectively the activity, the activity coefficient, the molality, and the stoichiometric coefficient of the species j.

To calculate the different equilibrium constants we used respectively Marshall and Franck's formulation,[35] for water (eq E1), Renon equations,[36] for carbonate (eq E3), and bicarbonate (eq E4), and three different formulations for the amine protonation (eq E2): Oscarson et al.,[4] Benamor and Aroua,[20] and Böttinger et al.[37] Regarding the carbamate formation (eq E5) we also used three different sources: Oscarson et al.,[4] Böttinger et al.,[37]

Table 5. Experimental Enthalpies of Solution of CO_2 in Aqueous Solutions of DEA (w_{DEA} = 0.3000) at 322.5 K

α	$\delta\alpha$	$-\Delta_{sol}H$	$\delta\Delta_{sol}H$	$-\Delta_{sol}H$	$\delta\Delta_{sol}H$
mol_{CO_2}/mol_{DEA}		$kJ\cdot mol^{-1}$ of DEA		$kJ\cdot mol^{-1}$ of CO_2	
		p = 0.54 MPa			
0.077	0.001	6.0	0.1	77.0	0.8
0.116	0.002	9.0	0.1	77.3	1.0
0.152	0.003	11.9	0.2	78.1	1.4
0.191	0.004	14.7	0.2	77.2	0.8
0.229	0.004	17.8	0.2	77.8	1.0
0.321	0.006	25.0	0.2	77.9	0.6
0.361	0.007	27.8	0.2	77.1	0.7
0.401	0.007	30.8	0.3	76.8	0.7
0.433	0.008	33.1	0.3	76.4	0.8
0.473	0.009	35.3	0.4	74.7	0.7
0.536	0.010	40.7	0.5	75.9	1.0
0.591	0.010	42.3	0.7	71.5	1.2
0.650	0.012	44.6	0.9	68.6	1.4
0.727	0.013	49.2	0.5	67.6	0.6
0.800	0.015	51.3	0.7	64.1	0.9
0.905	0.016	52.9	0.5	58.5	0.6
0.957	0.018	52.2	0.6	54.6	0.6
1.076	0.019	52.3	0.7	48.6	0.6
1.115	0.020	52.8	0.6	47.3	0.5
1.324	0.023	52.8	0.6	39.9	0.5
1.514	0.026	53.4	0.6	35.3	0.4
		p = 1.03 MPa			
0.114	0.001	8.9	0.4	78.2	3.7
0.152	0.002	12.0	0.2	79.1	1.2
0.230	0.003	17.9	0.2	77.8	1.0
0.309	0.004	22.8	0.4	73.8	1.4
0.395	0.005	28.6	0.3	72.6	0.7
0.476	0.006	33.9	0.3	71.2	0.6
0.551	0.007	38.2	0.4	69.3	0.7
0.627	0.008	42.3	0.4	67.5	0.6
0.654	0.008	43.5	0.4	66.5	0.6
0.655	0.008	43.8	0.3	66.9	0.5
0.727	0.009	46.4	0.6	63.8	0.8
0.783	0.009	49.8	0.6	63.6	0.9
0.790	0.009	49.4	1.5	62.5	1.9
0.848	0.010	51.5	0.6	60.8	0.7
		p = 1.03 MPa			
0.914	0.011	54.4	0.6	59.5	0.7
0.983	0.012	55.4	0.5	56.4	0.5
1.067	0.013	56.2	0.6	52.7	0.6
1.070	0.013	54.8	0.6	51.2	0.6
1.221	0.015	55.3	0.6	45.3	0.5
1.360	0.017	55.3	0.6	40.6	0.4
1.508	0.019	55.5	0.7	36.8	0.5
		p = 1.97 MPa			
0.197	0.003	14.7	0.2	74.5	1.2
0.224	0.003	16.2	0.9	72.2	4.0
0.308	0.004	22.1	1.1	71.9	3.6
0.308	0.004	21.6	1.3	70.3	4.1
0.370	0.005	26.5	0.4	71.7	1.0
0.453	0.006	31.4	2.1	69.4	4.7
0.455	0.006	33.2	0.3	72.9	0.6
0.515	0.007	36.5	1.1	70.8	2.2
0.586	0.008	39.7	1.0	67.7	1.6
0.638	0.008	43.3	0.6	67.9	0.9
0.684	0.009	44.5	1.1	65.0	1.7
0.734	0.009	46.4	0.4	63.3	0.6
0.785	0.010	47.3	0.5	60.3	0.6
0.836	0.010	50.5	0.5	60.5	0.6
0.879	0.011	51.1	2.1	58.2	2.4
0.881	0.011	53.0	0.5	60.1	0.6
0.916	0.011	53.5	1.4	58.4	1.5
0.955	0.012	54.4	0.5	57.0	0.5
0.962	0.012	55.8	0.5	58.0	0.5
1.041	0.013	55.8	0.7	53.6	0.7
1.118	0.014	54.9	2.8	49.1	2.5
1.224	0.015	55.1	0.6	45.1	0.5
1.226	0.016	56.8	1.0	46.3	0.8
1.312	0.017	55.3	0.7	42.1	0.5
1.512	0.019	54.9	0.5	36.3	0.4
1.636	0.021	54.9	0.6	33.5	0.3
1.792	0.023	54.7	0.6	30.5	0.3

and Aroua et al.[38] Oscarson et al.[4] considered ion paring formation to adjust their model for particular amines. As there is no experimental evidence of ion pairing formation in the $\{CO_2 + DEA + H_2O\}$ system, it was not taken into account in this work. Equilibrium constants for eqs E1 to E5 are given as a function of temperature in the Supporting Information.

The following mass conservation and electroneutrality (eqs 4 to 8) were applied to our system:

$$m_{(C_2H_5)_2NCOO^-} + m_{HCO_3^-} + m_{CO_3^{2-}} + m_{CO_2} = m_{CO_2}^{dis} \tag{4}$$

$$m_{(C_2H_5)_2NCOO^-} + m_{(C_2H_5)_2N^+H_2} + m_{(C_2H_5)_2NH} = m_{(C_2H_5)_2NH}^{0} \tag{5}$$

$$m_{H_2O} = 55.508 - m_{HCO_3^-} - m_{CO_3^{2-}} - m_{OH^-} + m_{(C_2H_5)_2NCOO^-} \tag{6}$$

$$m_{(C_2H_5)_2NCOO^-} + m_{HCO_3^-} + 2m_{CO_3^{2-}} + m_{OH^-} = m_{(C_2H_5)_2N^+H_2} + m_{H^+} \tag{7}$$

$$y_{CO_2} + y_{H_2O} + y_{(C_2H_5)_2NH} = 1 \tag{8}$$

Vapor−liquid equilibria were defined by eqs E6 to E8.

$$(C_2H_5)_2NH^L \leftrightarrows (C_2H_5)_2NH^V \tag{E6}$$

$$H_2O^L \leftrightarrows H_2O^V \tag{E7}$$

$$CO_2{}^L \leftrightarrows CO_2{}^V \tag{E8}$$

DEA was considered as a nonvolatile compound leading to $y_{(C_2H_5)_2NH} = 0$ and to omission of eq E6. Vapor phase is represented by a truncated virial equation[39,40] (see the Supporting Information).

A $\gamma-\phi$ approach was used to describe phase equilibria in the $\{CO_2 + DEA + H_2O\}$ system. The extended Raoult's law was thus used (eq 9) to represent water vapor−liquid

Table 6. Experimental Enthalpies of Solution of CO_2 in Aqueous Solutions of DEA ($w_{DEA} = 0.1500$) at 372.9 K

α	$\delta\alpha$	$-\Delta_{sol}H$	$\delta\Delta_{sol}H$	$-\Delta_{sol}H$	$\delta\Delta_{sol}H$
mol_{CO_2}/mol_{DEA}		$kJ\cdot mol^{-1}$ of DEA		$(kJ\cdot mol^{-1}$ of CO_2	
		$p = 0.55$ MPa			
0.106	0.002	7.9	0.2	73.9	1.5
0.145	0.003	10.6	0.3	73.4	2.4
0.192	0.004	13.8	0.2	72.0	1.2
0.234	0.004	17.5	0.2	74.7	0.9
0.239	0.004	17.4	0.2	72.9	0.9
0.263	0.005	19.1	0.5	72.6	1.9
0.290	0.006	21.3	0.3	73.6	0.9
0.312	0.006	22.8	0.4	72.9	1.2
0.398	0.007	28.1	0.3	70.7	0.7
0.477	0.009	32.7	0.5	68.4	1.0
0.568	0.010	38.0	1.1	66.9	2.0
0.599	0.011	39.0	0.4	65.1	0.6
0.647	0.012	39.0	0.4	60.3	0.6
0.728	0.013	38.2	0.4	52.5	0.6
0.809	0.015	37.1	0.5	45.9	0.6
0.889	0.016	36.5	0.8	41.0	0.9
0.954	0.018	35.5	0.5	37.2	0.5
1.272	0.023	32.3	0.5	25.4	0.4
1.561	0.029	29.1	0.4	18.6	0.3
1.876	0.035	25.2	0.4	13.4	0.2
		$p = 1.04$ MPa			
0.148	0.002	10.7	0.3	72.2	2.3
0.224	0.003	15.3	0.5	68.0	2.1
0.299	0.004	20.4	0.7	68.0	2.3
0.375	0.005	26.2	0.8	69.9	2.2
0.455	0.006	30.9	1.2	67.9	2.6
0.522	0.007	36.1	0.4	69.1	0.8
0.597	0.008	39.9	0.4	66.9	0.6
0.671	0.008	45.6	0.7	67.9	1.0
0.745	0.009	45.6	1.0	61.2	1.3
0.818	0.010	45.7	0.4	55.8	0.5
0.884	0.011	45.2	0.4	51.1	0.5
1.021	0.013	44.0	0.5	43.1	0.5
1.179	0.015	43.3	1.0	36.7	0.9
1.434	0.017	43.2	0.5	30.2	0.4
1.499	0.019	42.8	1.5	28.5	1.0
1.766	0.021	41.7	0.4	23.6	0.2
		$p = 1.04$ MPa			
1.863	0.022	41.1	0.4	22.0	0.2
1.901	0.023	41.7	1.4	22.0	0.7
		$p = 3.08$ MPa			
0.407	0.002	22.8	0.4	56.0	0.9
0.408	0.002	24.1	0.5	59.2	1.3
0.408	0.002	23.5	1.1	57.6	2.7
0.503	0.003	28.0	0.4	55.7	0.8
0.506	0.003	27.3	0.8	54.0	1.6
0.593	0.003	33.0	1.0	55.6	1.7
0.593	0.003	33.6	0.4	56.6	0.7
0.651	0.004	35.6	0.3	54.7	0.4
0.750	0.004	40.8	0.8	54.4	1.0
0.762	0.004	44.2	0.4	58.0	0.5
0.794	0.004	43.1	0.4	54.2	0.6
0.836	0.005	44.6	0.5	53.3	0.6
0.840	0.005	45.2	0.2	53.8	0.2
0.853	0.005	46.7	0.6	54.8	0.7
0.903	0.005	47.0	0.2	52.1	0.2
0.927	0.005	48.2	0.4	52.0	0.5
0.938	0.005	48.9	0.3	52.1	0.3
0.946	0.005	51.3	0.3	54.3	0.4
0.947	0.005	49.8	0.9	52.6	1.0
0.987	0.005	52.2	0.4	52.9	0.4
1.000	0.006	50.3	0.2	50.3	0.2
1.005	0.006	49.2	0.5	49.0	0.5
1.023	0.006	53.0	0.5	51.8	0.5
1.068	0.006	53.5	0.5	50.1	0.5
1.107	0.006	53.6	0.4	48.4	0.4
1.190	0.007	53.8	0.3	45.2	0.3
1.240	0.007	54.3	0.4	43.8	0.4
1.372	0.008	53.6	0.4	39.0	0.3
1.552	0.009	53.4	0.4	34.4	0.3
1.735	0.010	53.3	0.4	30.7	0.2
1.897	0.011	53.5	0.6	28.2	0.3
2.029	0.011	52.8	0.4	26.0	0.2
2.324	0.013	52.0	0.5	22.4	0.2

equilibrium.

$$\phi_w \cdot y_w \cdot p = a_w \cdot \phi_w^s \cdot p_w^s \cdot \exp\left[\frac{v_w(p - p_w^s)}{RT}\right] \tag{9}$$

where ϕ_w, y_w, p_w, and v_w are respectively the fugacity coefficient, gas molar fraction, pressure, and molar volume of water. Superscript s indicates saturation.

For CO_2 phase equilibrium extended Henry's law was used (eq 10).

$$\phi_{CO_2} \cdot y_{CO_2} \cdot p = \gamma_{CO_2} \cdot m_{CO_2} \cdot k_{H,CO_2}(T, p_w^s) \cdot \exp\left[\frac{v_{CO_2}^{\infty}(p - p_w^s)}{RT}\right] \tag{10}$$

where ϕ_{CO_2}, y_{CO_2}, γ_{CO_2}, m_{CO_2}, and $v^{\infty}{}_{CO_2}$ are respectively the fugacity coefficient, gas molar fraction, activity coefficient, molality. and partial molar volume at infinite dilution of carbon dioxide.

Information on the calculation of the different properties (Henry's law constant,[41] partial molar volume of CO_2 in water at infinite dilution,[42] properties of water,[43]) used in this work is given in the Supporting Information. Details on the calculation of the activity and fugacity coefficients[44,45] are also given in the Supporting Information.

Interaction parameters $\beta_{i,j}^0$ and $\beta_{i,j}^1$ (see the Supporting Information) were regressed from Lawson and Garst solubility data.[16] According to Oscarson et al.,[4] binary interaction parameters were divided into four groups: like charged ions, cation−anion, ion−neutral, and neutral−neutral. The regression was performed by using Minuit software,[46] for parameter estimation. The regression method used was a Levenberg−Marquardt minimization with the normalized objective function expressed in eq 11.

$$F = \sum_i^n \left(\frac{p_{i,exp.} - p_{i,calc.}}{\delta p_{i,exp.}}\right)^2 \tag{11}$$

3.2. Modeling of the Enthalpy of Solution.

The enthalpy of solution characterizes the energetic effect resulting from the dissolution of CO_2 into the aqueous amine

Table 7. Experimental Enthalpies of Solution of CO_2 in Aqueous Solutions of DEA ($w_{DEA} = 0.3000$) at 372.9 K

α	$\delta\alpha$	$-\Delta_{sol}H$	$\delta\Delta_{sol}H$	$-\Delta_{sol}H$	$\delta\Delta_{sol}H$
mol_{CO_2}/mol_{DEA}		$kJ\cdot mol^{-1}$ of DEA		$kJ\cdot mol^{-1}$ of CO_2	
		$p = 0.55$ MPa			
0.147	0.003	11.6	0.2	79.1	1.4
0.180	0.004	14.3	0.2	79.3	1.2
0.233	0.004	17.8	0.2	76.2	0.7
0.242	0.005	18.8	0.1	77.7	0.6
0.311	0.006	23.0	0.3	74.0	0.8
0.390	0.007	29.1	0.3	74.8	0.7
0.445	0.008	32.9	0.3	73.8	0.6
0.469	0.009	35.0	1.4	74.5	2.9
0.515	0.010	35.4	0.3	68.7	0.6
0.603	0.011	35.1	0.6	58.2	0.9
0.662	0.013	33.6	0.3	50.8	0.5
0.713	0.013	33.6	2.7	47.2	3.8
0.752	0.014	33.9	0.4	45.1	0.5
0.888	0.016	33.4	0.4	37.6	0.5
0.900	0.017	31.3	0.8	34.8	0.9
1.050	0.019	32.0	0.3	30.4	0.3
1.110	0.020	31.0	0.4	27.9	0.3
1.213	0.022	30.7	0.4	25.3	0.3
1.223	0.023	29.0	0.4	23.7	0.4
1.460	0.026	28.8	0.4	19.7	0.2
		$p = 1.02$ MPa			
0.140	0.002	10.4	0.3	74.5	2.4
0.208	0.003	15.8	0.2	76.1	0.7
0.277	0.004	21.3	0.2	76.8	0.8
0.351	0.005	26.8	0.4	76.4	1.0
0.439	0.006	31.7	0.3	72.2	0.6
0.512	0.006	36.0	0.3	70.3	0.6
0.585	0.007	39.8	0.3	68.0	0.5
0.658	0.008	40.5	0.4	61.6	0.5
		$p = 1.02$ MPa			
0.726	0.009	40.2	0.3	55.4	0.5
0.833	0.011	40.4	0.5	48.5	0.6
1.040	0.013	40.8	0.5	39.2	0.4
1.142	0.015	40.4	0.4	35.3	0.3
1.338	0.017	39.7	0.4	29.6	0.3
1.472	0.019	39.2	0.5	26.6	0.3
		$p = 3.09$ MPa			
0.251	0.002	17.8	0.1	71.2	0.5
0.301	0.003	21.4	0.2	71.0	0.6
0.348	0.003	24.7	0.7	70.9	2.0
0.400	0.003	27.9	0.2	69.8	0.4
0.447	0.004	30.9	0.3	69.1	0.7
0.519	0.004	35.7	0.3	68.8	0.6
0.519	0.004	35.8	0.2	69.1	0.4
0.618	0.005	40.8	0.3	66.1	0.4
0.719	0.006	45.0	0.3	62.7	0.4
0.720	0.006	44.3	0.3	61.6	0.5
0.753	0.006	47.1	0.3	62.6	0.4
0.775	0.006	46.6	1.0	60.2	1.3
0.812	0.007	48.2	0.3	59.4	0.4
0.899	0.008	48.4	0.3	53.8	0.4
0.987	0.008	47.9	0.3	48.5	0.3
1.101	0.009	47.9	0.3	43.5	0.3
1.274	0.010	47.7	0.3	37.5	0.2
1.404	0.012	47.6	0.3	33.9	0.2
1.514	0.013	47.4	0.3	31.3	0.2
1.743	0.015	47.1	0.3	27.0	0.2
1.983	0.017	46.6	0.3	23.5	0.2

solution. It is possible to quantify it as a combination of enthalpies associated to every single reactions occurring at the thermodynamic equilibrium (eqs E1 to E8). Enthalpies of reactions in liquid phase (eqs E1 to E5) were expressed by eq 12:

$$\Delta_{r_i}H = \Delta_{r_i}H^\circ + \sum_j \upsilon_{j,i}H_j^E \qquad i = \text{E1 to E5} \tag{12}$$

where $\upsilon_{j,i}$ are the stoichiometric coefficients of the different reactants and products for eq i, $\Delta_{r_i}H^\circ$, the standard reaction enthalpy and H_j^E, the excess partial molar enthalpy of the species j.

$\Delta_{r_i}H^\circ$ were calculated from van't Hoff equation (eq 13)

$$\left(\frac{\partial \ln K_{m,r_i}}{\partial T}\right)_p = \frac{\Delta_{r_i}H^\circ}{RT^2} \qquad i = \text{E1 to E5} \tag{13}$$

Excess enthalpies H_j^E for species j (eq 14) were obtained by temperature differentiation of activity coefficients:

$$H_j^E = -RT^2\left(\frac{\partial \ln \gamma_j}{\partial T}\right)_p \qquad i = \text{E1 to E5} \tag{14}$$

In the case of pure water (H_2O), the activity coefficient γ_j was replaced by the activity a_w in eq 14.

A heat of absorption Q_i for every single chemical reaction occurring was calculated from eq 15 using the standard enthalpies of reaction $\Delta_{r_i}H^\circ$ and excess partial molar enthalpies H_j^E.

$$Q_i(\text{kJ}) = \xi_i\cdot\Delta_{r_i}H = \xi_i\cdot(\Delta_{r_i}H^\circ + \sum_j \upsilon_{j,i}H_j^E) \qquad i = \text{E1 to E5} \tag{15}$$

where ξ_i is the extent of reaction i.

The enthalpy $\Delta_{r_k}H$ of physical dissolution for CO_2 (eq E8) was calculated using the Gibbs–Helmholtz equation (eq 16).

$$\left(\frac{\partial(\Delta_{r_k}G/T)}{\partial T}\right)_P = -\frac{\Delta_{r_k}H}{T^2} \qquad k = \text{E8} \tag{16}$$

The Gibbs energy of reaction for eq E8 was calculated from eq 17.

$$\Delta_{r_k}G = RT\cdot\ln(k_{H,CO_2}(T, p_w^s)) + RT \cdot\ln\left(\gamma_{CO_2}\cdot m_{CO_2}\cdot\exp\left[\frac{v_{CO_2}^{\infty}(p - p_w^s)}{RT}\right]\right) - RT\cdot\ln(\phi_{CO_2}\cdot y_{CO_2}\cdot p) \qquad k = \text{E8} \tag{17}$$

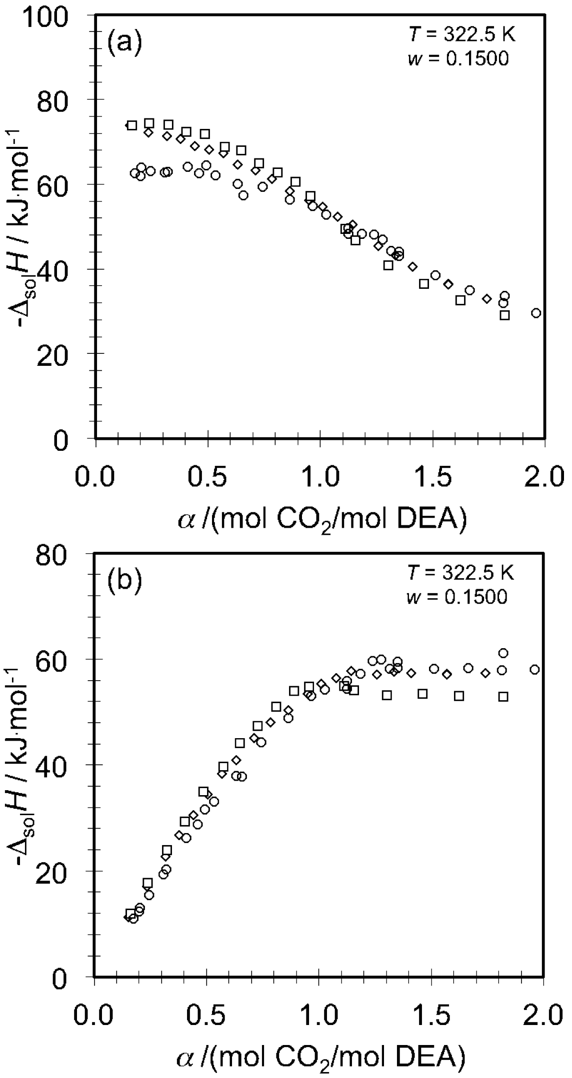

Figure 2. Enthalpy of solution ($-\Delta_{sol}H$) versus CO$_2$ loading for an aqueous solution of DEA ($w_{DEA} = 0.1500$) at $T = 322.5$ K: □, 0.5 MPa; ◇, 1.0 MPa; ○, 2.0 MPa. (a) $\Delta_{sol}H$/(kJ·mol^{-1} of CO$_2$); (b) $\Delta_{sol}H$/(kJ·mol^{-1} of DEA).

Combining eqs 16 and 17, the enthalpy of reaction for the CO$_2$ dissolution (eq 18) was obtained:

$$\Delta_{r_k}H(\text{kJ}\cdot\text{mol}^{-1}\,\text{CO}_2) = -RT^2 \cdot\left(\frac{\partial \ln(k_{H,CO_2}(T, p_w^s))}{\partial T}\right) + RT^2 \cdot\left(\frac{\partial \ln \gamma_{CO_2}}{\partial T} - \frac{\partial \ln \phi_{CO_2}}{\partial T}\right) + RT^2 \cdot\left(\frac{\partial(v_{CO_2}^{\infty}(p - p_w^s)/RT)}{\partial T}\right) \qquad k = \text{E8} \tag{18}$$

The enthalpy of solution of CO$_2$ in the aqueous solution of diethanolamine, $\Delta_{sol}H$, was calculated as a combination of the physical dissolution $\Delta_{r_k}H$ and the different total heat of absorption Q_i for every single chemical reaction occurring during the absorption process. Each heat of absorption Q_i was normalized to one mole of gas dissolved (eq 19).

$$\Delta_{sol}H(\text{kJ}\cdot\text{mol}^{-1}\,\text{CO}_2) = \Delta_{r_k}H + \frac{1}{n_{CO_2}^{dis}}\sum_i Q_i \qquad i = \text{E1 to E5} \qquad k = \text{E8} \tag{19}$$

where $n_{CO_2}^{dis}$ is the number of moles of CO$_2$ completely dissolved once the thermodynamic equilibrium is reached.

Table 8. Average Values for the Enthalpies of Solution at Low Loadings ($\alpha < 0.4$) in Aqueous DEA Solutions ($w_{DEA} = 0.1500$ and 0.3000) at (322.5 and 372.9) K

p	$-\Delta_{sol}H^{av}$	$\delta\Delta_{sol}H^{av}$	p	$-\Delta_{sol}H^{av}$	$\delta\Delta_{sol}H^{av}$
MPa	kJ·mol^{-1}	of CO$_2$	MPa	kJ·mol^{-1}	of CO$_2$
		$T = 322.5$ K			
	$w_{DEA} = 0.1500$			$w_{DEA} = 0.3000$	
0.55	74	4	0.54	77	4
1.04	72	4	1.03	76	4
2.07	63	3	1.97	72	4
		$T = 372.9$ K			
	$w_{DEA} = 0.1500$			$w_{DEA} = 0.3000$	
0.55	73	4	0.55	77	4
1.04	70	3	1.02	76	4
3.08	58	3	3.09	71	4

Table 9. Experimental Values for the Solubility of CO$_2$ in Aqueous DEA Solutions ($w_{DEA} = 0.1500$ and 0.3000) at (322.5 and 372.9) K

p/MPa	s/(mol CO$_2$/mol amine)	δs	p/MPa	s/(mol CO$_2$/mol amine)	δs
	$w_{DEA} = 0.1500$			$w_{DEA} = 0.3000$	
		$T = 322.5$ K			
0.53	0.956	0.05	0.54	0.840	0.04
1.04	1.079	0.06	1.03	0.914	0.05
2.07	1.187	0.06	1.97	1.041	0.05
		$T = 372.9$ K			
0.55	0.647	0.03	0.55	0.515	0.03
1.04	0.745	0.04	1.02	0.658	0.03
3.08	1.107	0.05	3.09	0.899	0.04

Table 10. Deviation between the Experimental Pressures at Equilibrium[16] and the Calculated Values Using Different Combinations of Literature Formulations of Amine Protonation (eq E2) and Carbamate Formation (eq E5) Constants

$K_{m,r=E2}$[a]	$K_{m,r=E5}$[b]	$\sum_i^n \lvert P_{i,exp.} - P_{i,calc.}\rvert / n \cdot P_{i,exp.}$
Oscarson et al.[4]	Oscarson et al.[4]	0.259
Oscarson et al.[4]	Böttinger et al.[37]	0.072
Oscarson et al.[4]	Aroua et al.[38]	0.130
Böttinger et al.[37]	Oscarson et al.[4]	0.254
Böttinger et al.[37]	Böttinger et al.[37]	0.070
Böttinger et al.[37]	Aroua et al.[38]	0.125
Benamor and Aroua[20]	Oscarson et al.[4]	0.246
Benamor and Aroua[20]	Böttinger et al.[37]	0.068
Benamor and Aroua[20]	Aroua et al.[38]	0.121

[a] Reaction E2 corresponds to the amine protonation: $(C_2H_5)_2NH + H^+ \leftrightarrows (C_2H_5)_2N^+H_2$. [b] Reaction E5 corresponds to the carbamate formation: $(C_2H_5)_2NH + HCO_3^- \leftrightarrows (C_2H_5)_2NCOO^- + H_2O$.

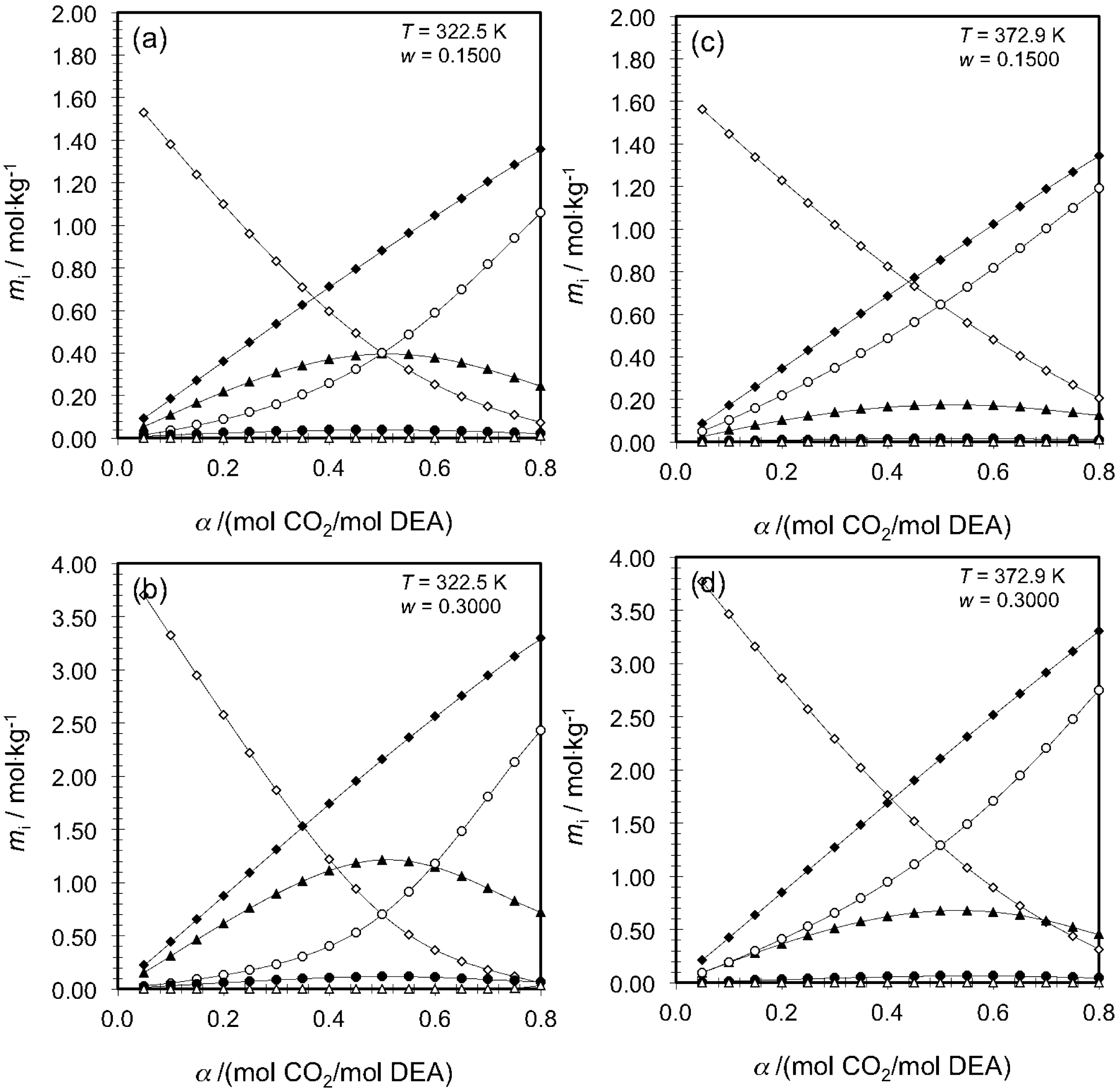

Figure 3. Speciation at equilibrium for the system {CO_2 + DEA + H_2O} calculated from our thermodymanic model. ◊, $(C_2H_5)_2NH$; ♦, $(C_2H_5)_2N^+H_2$; ▲, $(C_2H_5)_2NCOO^-$; ○, HCO_3^-; ●, CO_3^{2-}; Δ, CO_2. (a) T = 322.5 K and w_{DEA} = 0.1500; (b) T = 322.5 K and w_{DEA} = 0.3000; (c) T = 372.9 K and w_{DEA} = 0.1500; (d) T = 372.9 K and w_{DEA} = 0.3000.

4. RESULTS

4.1. Experimental Data.

The enthalpy of solution of CO_2 in the aqueous amine (DEA) solutions (w_{DEA} = 0.1500 and 0.3000) was measured at (322.5 and 372.9) K at pressures from (0.5 to 3) MPa. The experimental data were obtained for different gas–solvent flow rate ratios; they are presented in Tables 4 to 7. The uncertainties in the enthalpy were determined as indicated above (see Section 2.3). As an example, experimental enthalpies (measured at T = 322.5 K and w_{DEA} = 0.1500) have been plotted versus loading α (moles of CO_2/mol of amine); large exothermic effects were observed at both temperatures. Figure 2b (which plots the enthalpy (/kJ·mol^{-1} of amine) versus the loading) typically shows two domains that correspond to:

(1) A total dissolution of CO_2 injected (unsaturated solution).
(2) A partial dissolution of CO_2 injected (saturated solution).

When the enthalpy of solution $\Delta_{sol}H$ is expressed in kJ·mol^{-1} of CO_2 (Figure 2a) the graphs exhibit plateaus for the lowest loadings, up to 0.5, and then the exothermic effect decreases as the loading increases. At the lowest loadings (Figure 2a), the energetic effect per mole of gas seems to be constant, within experimental uncertainty, and independent of CO_2 loading. This behavior was also observed and reported in the literature.[4,23−29] Average enthalpy values $\Delta_{sol}H^{av}$, for $\alpha < 0.4$, expressed in kJ·mol^{-1} of CO_2 are reported in Table 8.

The calorimetric data were also used for an indirect determination of the solubility limits of CO_2 in the aqueous amine solutions. Numerical values were graphically determined from Figure 2b and are reported in Table 9 for the different conditions of temperature, pressure, and composition investigated in this study. Up to the saturation of the DEA solution, the enthalpy expressed per mole of amine increases with loading until it reaches a plateau. The plateau indicates that no more carbon dioxide can be dissolved into the solution, and the solution is therefore saturated (two-phase region). The solubility limit corresponds thus to the point where the plateau is reached.[25−29] Since the experimental uncertainty depends on the identification precision of the first point of the plateau and is based on the reproducibility of the measurements and possibility of systematic errors affecting the enthalpy of solution or the flow rates reliability of the pumps, it is expected that this

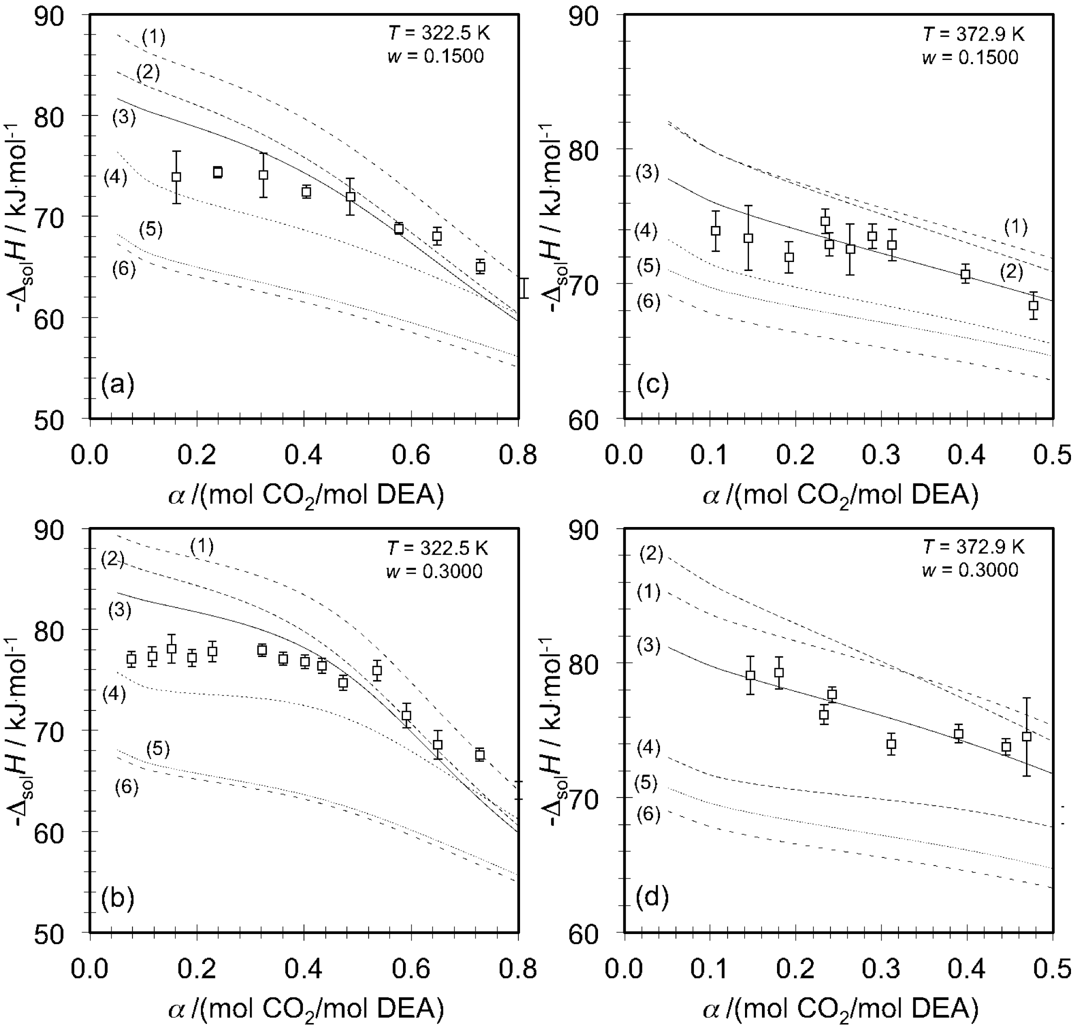

Figure 4. Enthalpy of solution ($-(\Delta_{sol}H/(\text{kJ}\cdot\text{mol}^{-1}$ of $CO_2))$) versus CO_2 loading for aqueous solution of DEA: □, experimental data at 0.5 MPa; thermodymanic model using: (1) ($K_{m,r=E2}$) given by Böttinger et al.[37] and ($K_{m,r=E5}$) given by Aroua et al.;[38] (2) ($K_{m,r=E2}$) given by Benamor et Aroua[20] and ($K_{m,r=E5}$) given by Aroua et al.;[38] (3) ($K_{m,r=E2}$) given by Oscarson et al.[4] and ($K_{m,r=E5}$) given by Aroua et al.;[38] (4) ($K_{m,r=E2}$) given by Böttinger et al.[37] and ($K_{m,r=E5}$) given by Böttinger et al.;[37] (5) ($K_{m,r=E2}$) given by Benamor and Aroua[20] and ($K_{m,r=E5}$) given by Böttinger et al.;[37] (6) ($K_{m,r=E2}$) given by Oscarson et al.[4] and ($K_{m,r=E5}$) given by Böttinger et al.[37] (a) $T = 322.5$ K and $w_{DEA} = 0.1500$; (b) $T = 322.5$ K and $w_{DEA} = 0.3000$; (c) $T = 372.9$ K and $w_{DEA} = 0.1500$; (d) $T = 372.9$ K and $w_{DEA} = 0.3000$.

method allows a determination of the solubility limit within (5 and 9) %.

4.2. Thermodynamic Model. First of all, the binary interactions parameters $\beta_{i,j}^0$ and $\beta_{i,j}^1$ (see the Supporting Information) were regressed from Lawson and Garst solubility data:[16] 39 vapor−liquid equilibrium experimental data points measured at temperatures between (310 and 394) K and for equilibrium pressures up to 5 MPa. We tested three different formulations for the amine protonation (Oscarson et al.,[4] Benamor and Aroua,[20] and Böttinger et al.,[37] eq E5) as well as for the carbamate formation (Oscarson et al.,[4] Böttinger et al.,[37] and Aroua et al.,[38] eq E6) which lead to 9 (3 × 3) sets of interactions parameters. Lists of the different parameters are reported in Tables A5−A13. For the DEA protonation, Oscarson et al.[4] and Benamor and Aroua[20] adjusted their constants on potentiometric data.[47,48] Böttinger et al.[37] considered them as adjustable parameters in their thermodynamic model, but they fitted both VLE data and spectroscopic (Raman) data.[37] Regarding the carbamate formation constants, the ones proposed by Oscarson et al.[4] and Böttinger et al.[37] were obtained during the optimization of their thermodynamic model as adjustable parameters. Aroua et al.[38] used a potentiometric technique to measure neutralization of $(C_2H_5)_2NCOO^-$ by NaOH.

For each set of interaction parameters, the pressures at equilibrium calculated with the model were compared to the experimental data[16] that was used to fit the adjustable parameters using eq 20:

$$\text{deviation} = \frac{1}{n}\cdot\sum_{i}^{n}\left|\frac{p_{i,\text{exp.}} - p_{i,\text{calc.}}}{p_{i,\text{exp.}}}\right| \qquad (20)$$

The obtained deviation on the total equilibrium pressure (Table 10) varied from ~7 % to ~25 % depending on the combination used for formulation of the DEA protonation constant ($K_{m,r=E2}$) and the carbamate formation ($K_{m,r=E5}$). It appeared that the deviation was strongly dependent on the correlation used for the carabamate formation constant (Table 10), and looking at the deviation, it was evident that the correlation

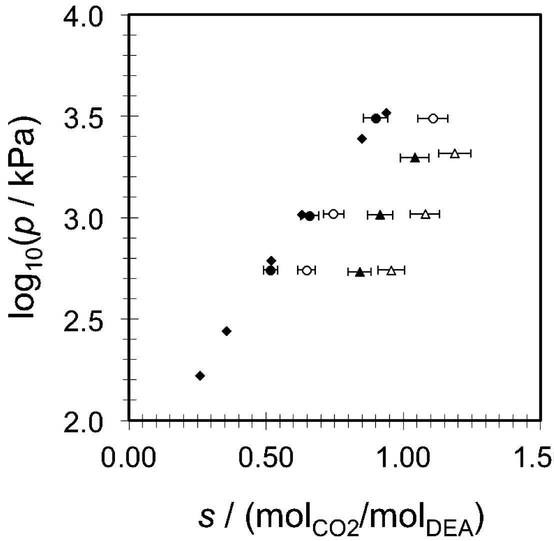

Figure 5. Solubility of CO_2 in DEA solutions vs total pressure: △, this work, $w_{DEA} = 0.1500$, T = 322.5 K; ▲, this work, $w_{DEA} = 0.3000$, T = 322.5 K; ○, this work, $w_{DEA} = 0.1500$, T = 372.9 K; ●, this work, $w_{DEA} = 0.3000$, T = 372.9 K; ◆, Kennard and Meisen,[12] $w_{DEA} = 0.30$, T = 373 K.

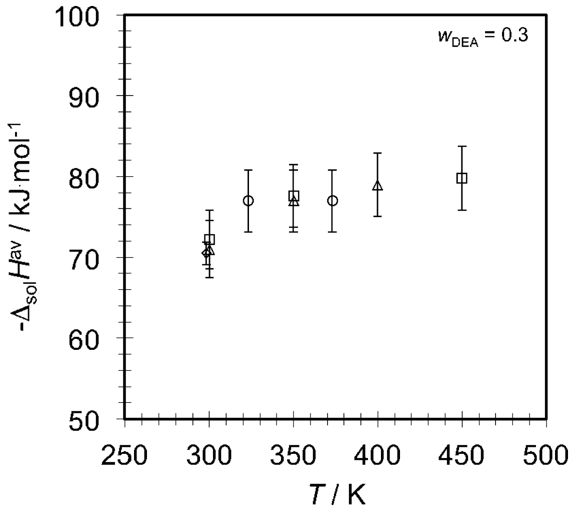

Figure 6. Average enthalpy of solution $(-(\Delta_{sol}H^{av}/(\text{kJ}\cdot\text{mol}^{-1}\text{ of }CO_2))$ versus temperature for aqueous solution of DEA: □, Oscarson et al.,[4] $w_{DEA} = 0.35$; ◇, Carson et al.,[23] $w_{DEA} = 0.30$; △, Helton et al.,[24] $w_{DEA} = 0.35$; ○, this work, $w_{DEA} = 0.30$.

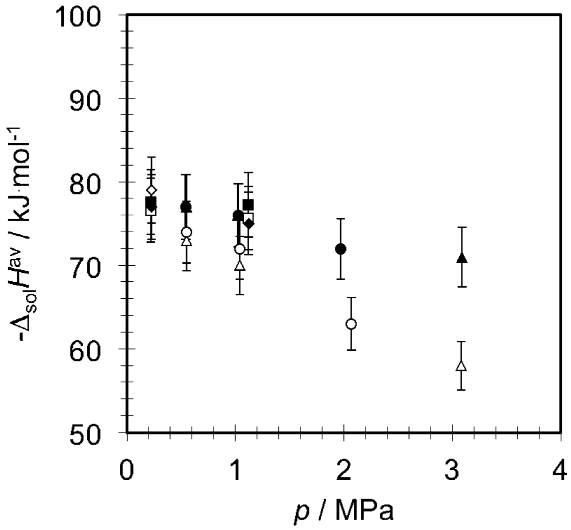

Figure 7. Average enthalpy of solution $(-(\Delta_{sol}H^{av}/(\text{kJ}\cdot\text{mol}^{-1}\text{ of }CO_2))$ versus pressure for aqueous solution of DEA: ○, this work, T = 322.5 K and $w_{DEA} = 0.1500$; ●, this work, T = 322.5 K and $w_{DEA} = 0.3000$; △, this work, T = 372.9 K and $w_{DEA} = 0.1500$; ▲, this work, T = 372.9 K and $w_{DEA} = 0.3000$; □, Oscarson et al.,[4] T = 350 K and $w_{DEA} = 0.20$; ■, Oscarson et al.,[4] T = 350 K and $w_{DEA} = 0.35$; ◇, Helton et al.,[24] T = 350 K and $w_{DEA} = 0.20$; ◆, Helton et al.,[24] T = 350 K and $w_{DEA} = 0.35$.

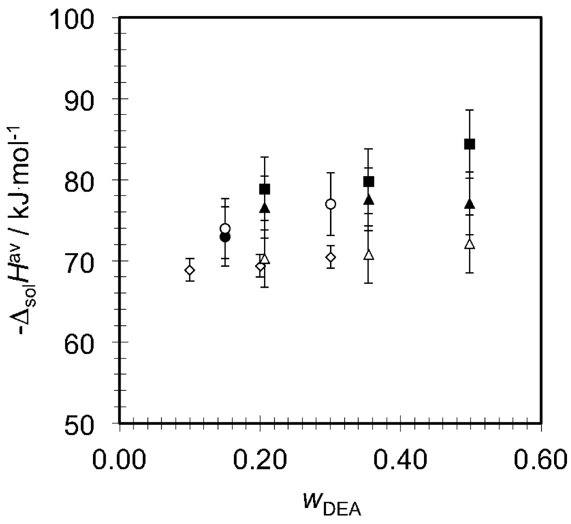

Figure 8. Average enthalpy of solution $(-(\Delta_{sol}H^{av}/(\text{kJ}\cdot\text{mol}^{-1}\text{ of }CO_2))$ versus composition of the aqueous solution of DEA: ○, this work, T = 322.5 K and p = 0.5 MPa; ●, this work, T = 372.9 K and p = 0.5 MPa; ◇, Carson et al.,[23] T = 298 K and p = 0.1 MPa; △, Oscarson et al.,[4] T = 300 K and p = 0.2 MPa; ▲, Oscarson et al.,[4] T = 350 K and p = 0.2 MPa; ■, Oscarson et al.,[4] T = 450 K and p = 0.2 MPa.

proposed by Oscarson et al.[4] did not allow a good fit of the data, so it was omitted.

The six remaining different sets of interaction parameters were then used in the model to calculate the speciation in the same conditions of temperature ((322.5 and 372.9) K), pressure (up to 3 MPa), and composition (w_{DEA} = 0.1500 and 0.3000) than our experimental data points. The choice of the correlation used in the model for $K_{m,r=E2}$ and $K_{m,r=E5}$ did not have a significant influence on the correlation of vapor−liquid equilibrium data and speciation plots appeared to be similar. Speciation was calculated using classical thermodynamic relations described above (see part 3). As an example, results when using the DEA protonation constant ($K_{m,r=E2}$) given by Oscarson et al.[4] and the carbamate formation ($K_{m,r=E5}$) given by Aroua et al.[38] are reported in Figure 3. The speciation obtained using each of the six sets of interaction parameters was then used to calculate the enthalpy of solution of CO_2 in aqueous DEA solutions using the classical thermodynamic relations described above (see part 3). Results are plotted in Figure 4.

5. DISCUSSION

5.1. Solubility Data. Experimental limits of solubility of CO_2 in the aqueous solutions of DEA were plotted versus the equilibrium total pressure p on a pressure-logscale in Figure 5, as well as literature values from Kennard and Meisen.[12] Our solubility limits derived from enthalpy data and theirs obtained by methods specifically designed for solubility work agreed

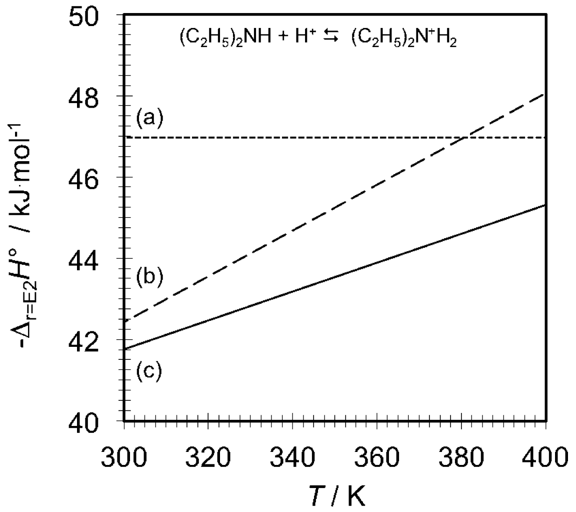

Figure 9. Standard reaction enthalpy $(-(\Delta_{r=E2}H°/(kJ \cdot mol^{-1}))$ for the reaction of amine protonation (eq E2) from T = 300 K to T = 400 K. (a) Benamor and Aroua;[20] (b) Böttinger et al.;[37] (c) Oscarson et al.[4]

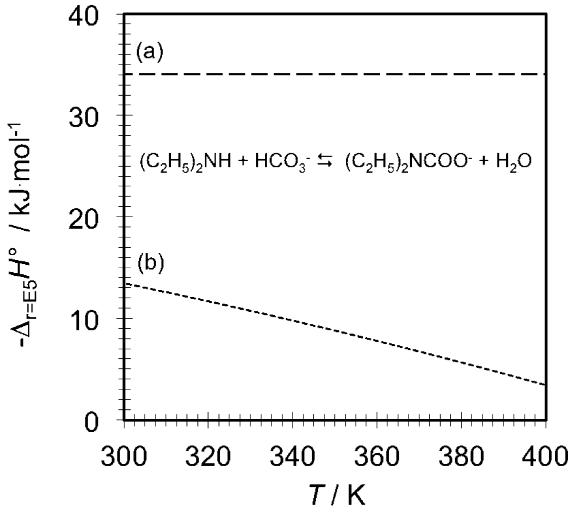

Figure 10. Standard reaction enthalpy $(-(\Delta_{r=E5}H°/(kJ \cdot mol^{-1}))$ for the reaction of carbamate formation (eq E5) from T = 300 K to T = 400 K. (a) Böttinger et al.;[37] (b) Aroua et al.[38]

within less than 5 %. We also used our thermodynamic model to predict the solubilty limit of CO_2 in our aqueous solutions of DEA (T = (322.5 and 372.9) K and w_{DEA} = (0.1500 and 0.300)): Experimental and calculated values agreed within less than 5 %. The solubility of CO_2 in the aqueous solutions of DEA was found to decrease as temperature increases; this can be related to the diminution of amine basicity and carbamate stability.[49] The general tendency observed with the composition of the absorbent was a decrease of the CO_2 solubility (expressed in moles of CO_2 per mole of DEA) in the aqueous DEA solutions.

As the amine concentration increased, the number of water molecules necessary to solvate the ions in solution also increased, resulting in a diminution of the number of molecules of water available to solvate the CO_2.

5.2. Temperature, Pressure, and Composition Effects on the Enthalpy of Solution at Low Loadings (α < 0.4).

A discussion of the effects of temperature, pressure, and absorbent composition on the dissolution of carbon dioxide will be carried out by comparison of enthalpies of solution when they were found to remain constant (i.e., average enthalpy values $\Delta_{sol}H^{av}$ expressed in kJ·mol^{-1} of CO_2, estimated on the plateaus). Numerical values are reported in Table 8.

The temperature and pressure effects on the enthalpy of solution of CO_2 in aqueous solutions of DEA are represented in Figures 6 and 7; comparisons were made with the available literature data.[4,23,24] Literature values,[4,23] obtained around 298 K, were found to be significantly lower than those obtained at higher temperatures, as noticed in Figure 6. A comparison between our values and literature data[4,23,24] showed that, from (323 to 450) K, the enthalpy of solution of CO_2 in aqueous DEA solutions seems to be independent of the temperature within the experimental uncertainty (Figure 6). The increase in the enthalpy observed from (298 to 313) K was not investigated because of the limitations of our experimental apparatus setup. A similar conclusion was made regarding the pressure effect (Figure 7): up to 2 MPa, the enthalpy seems to be independent of the pressure within the experimental uncertainty. Although the pressure and temperature effects on the enthalpy of solution of CO_2 in DEA solutions were concluded to be not significant regarding the experimental uncertainty, we noticed a decrease of the enthalpy at p = 2.07 MPa and at p = 3.08 MPa for the dissolution of CO_2 in solution of mass composition w_{DEA} = 0.1500. This diminution was attributed to a limitation of the experimental technique.[29] Indeed, technical difficulties when experiments were carried out for low gas loadings were observed. In these conditions, the difference in volume flow rates of carbon dioxide and absorbent solution was an important factor, leading to problems of mixing. This difference increases with the volumic mass of CO_2, i.e. with pressure, or when decreasing amine composition. Therefore, we average the enthalpy of solution (when it remained constant) regardless of the temperature and the pressure by omitting the two points mentioned above (for w_{DEA} = 0.1500 at p = (2.07 and 3.08) MPa). The enthalpy of solution $\Delta_{sol}H^{av}$ was estimated to be 72 ± 2 kJ·mol^{-1} of CO_2 and 75 ± 4 kJ·mol^{-1} of CO_2 for w_{DEA} = 0.1500 and w_{DEA} = 0.3000, respectively. The composition dependency of the DEA aqueous solution is represented in Figure 8; we compared our experimental values with data from Carson et al.[23] and from Oscarson et al.[4] The general effect appeared to be a slight increase of the exothermic effect; however this augmentation stayed within the experimental uncertainty.

5.3. Influence of the Equilibrium Constant Used for the Amine Protonation and the Carbamate Formation on the Prediction of the Enthalpy of Solution.

Six different sets of interaction parameters adjusted on VLE literature data[16] were used to calculate the enthalpy of solution of CO_2 in aqueous DEA solutions up to the solubility limit of CO_2 (see Section 4.2). The resulting predicted enthalpies of solution are compared with our experimental data in Figure 4. The model reproduced the general shape of the experimental data, with a plateau less pronounced at low loadings, as observed by others authors.[4,7−9]

Although the choice of the formulation used in the model for $K_{m,r=E2}$ and $K_{m,r=E5}$ did not have a significant influence on the correlation of vapor−liquid equilibrium data, noticeable differences were observed on the enthalpy of solution, depending on the set of interaction parameters/equilibrium constants used. The enthalpy of solution varied from (−60 to −90) kJ·mol^{-1} at T = 322.5 K and from (−65 to −90) kJ·mol^{-1} at T = 372.9 K. The analysis of the different contributions to the heat of solution, which is discussed in more detail in the next section, showed that the major energetic effects were the ones

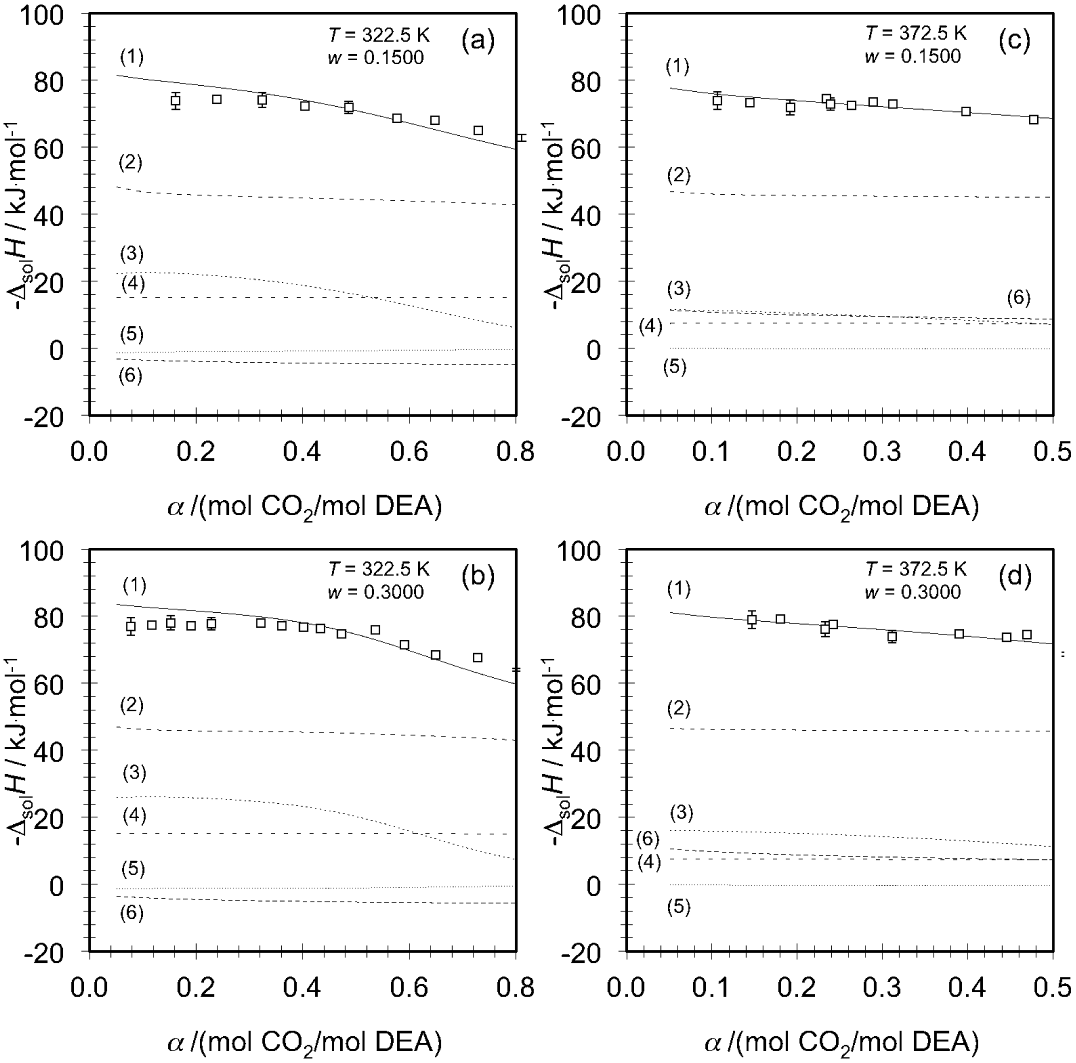

Figure 11. Enthalpy of solution ($-(\Delta_{sol}H/(\text{kJ·mol}^{-1}$ of CO_2)) versus CO_2 loading for the aqueous solution of DEA: □, experimental data at 0.5 MPa. From the thermodymanic model: (1) total enthalpy of solution. Enthalpic contribution from reaction: (2) amine protonation E2; (3), carbamate formation E5; (4) CO_2 vapor–liquid equilibrium E8; (5) second ionization of CO_2 E4; (6) first ionization of CO_2 E3. (a) T = 322.5 K and w_{DEA} = 0.1500; (b) T = 322.5 K and w_{DEA} = 0.3000; (c) T = 372.9 K and w_{DEA} = 0.1500; (d) T = 372.9 K and w_{DEA} = 0.3000.

due to the reactions of amine protonation (eq E2) and carbamate formation (eq E5). In Figure 4, the differences observed within the different predicted enthalpy of solution (using the different sets of interaction parameters) looked greater at T = 322.5 K compared to T = 372.9 K; this was found to be mainly due to the carbamate formation which was found to decrease as the temperature increased (Figure 3).

The choice of the equilibrium constant correlation (for eqs E2 and E5) was found to lead to relatively big differences when calculating the standard reaction enthalpy, $\Delta_r H°$. Evolutions of the standard reaction enthalpy with respect to the temperature are shown in Figures 9 and 10 for eq E2 and E5, respectively. For the amine protonation, differences up to ~8.5 % and ~6.4 % were observed at T = 322.5 K and T = 372.9 K, respectively, and, for the carbamate formation, the disparity was even more important: ~68 % at T = 322.5 K and ~82 % at T = 372.9 K. Even if the primary purpose of these correlations is to give a good estimation of the thermodynamic constant over a wide range of temperature, more work ought to be done regarding its derivative properties. For this purpose, great care should be taken when fitting data points to make the correlation over a wide temperature range, including, for example, enthalpic data for the reaction involved in the fit. The "best" correlations to predict the enthalpy of solution of CO_2 were found to be, respectively, the one given by Oscarson et al.,[4] ($K_{m,r=E2}$) for the amine protonation and by Aroua et al.,[38] ($K_{m,r=E5}$) for the carbamate formation.

5.4. Relative Importance of the Different Reactions to the Enthalpy of Solution. Figure 11 shows the relative contributions of every single chemical/physical reaction involved in the dissolution of CO_2 in aqueous DEA solutions. At both temperatures (T = (322.5 and 372.9) K) the amine protonation (eq E2) clearly appears to provide the most important contribution with more than 60 % of the total energetic effect, the smallest being due to the formation of the bicarbonate (eq E4). The enthalpy associated to the physical dissolution of CO_2 (eq E8) remained constant at ~ −15 kJ·mol^{-1} (T = 322.5 K) and ~ −7.5 kJ·mol^{-1} (T = 372.9 K). At T = 322.5 K (Figure 11), the enthalpy released by the formation of the carbonate (eq E3) was found to be rather small and endothermic, oscillating respectively between (0 and 5) kJ·mol^{-1}. At this temperature, the behavior of the enthalpy of solution as a function of the loading was mostly driven by the contribution due to the carbamate formation (eq E5) that contributed ~30 % to the enthalpy of solution. The enthalpy associated to the carbamate formation remained constant up to $\alpha \sim 0.25$ and then decreased slowly. This behavior became more evident when looking at the speciation plots (Figure 3): as the loading increased the quantity of carbamate in the solution increased linearly until $\alpha = 0.25$ and then more slowly until it reached a maximum for $\alpha = 0.5$ to finally decrease. This observation agreed with the literature description of chemical absorption of CO_2 in aqueous solutions of secondary amines (DEA),[50,51] where a carbamate formation (eq 21) was involved.

$$CO_2 + 2(C_2H_5)_2NH \leftrightarrows (C_2H_5)_2NCOO^- + (C_2H_5)_2N^+H_2 \quad (21)$$

The solubility of the gas into the solution is thus limited by stoichiometry to a maximum loading $\alpha = 0.5$ moles of CO_2/moles of amine. However, due to possible carbamate hydrolysis (eq 22), the loading can exceed 0.5 when increasing CO_2 pressure.[51]

$$(C_2H_5)_2NCOO^- + H_2O \leftrightarrows (C_2H_5)_2NH + HCO_3^- \quad (22)$$

In that case the dissolution process is not controlled anymore by the carbamate formation but by the carbon dioxide, which reacts with the amine to form a carbonate. At $T = 372.9$ K (Figure 11), the same general behavior was observed regarding the energetic contribution related to the formation of the carbamate, but that time it provided only ~(15 to 20)% of the total energetic effect. That was explained by the much smaller proportion of carbamate into the solution (Figure 3): From $T = 322.5$ K to $T = 372.9$ K at $\alpha = 0.5$ the molality decreased from (0.40 to 0.18) $\text{mol}\cdot\text{kg}^{-1}$ and from (1.22 to 0.68) $\text{mol}\cdot\text{kg}^{-1}$ at $w_{\text{DEA}} = 0.1500$ and $w_{\text{DEA}} = 0.3000$, respectively. These results agreed with previous literature studies,[49] where the stability of the carbamate was found to decrease with increasing temperature. At $T = 372.9$ K, an interesting matter was observed regarding the enthalpy released by the formation of the carbonate, which was found to be exothermic. Moreover it contributed to ~(13 to 15) % to the total energetic effect (Figure 9). This effect could explain why our experimental enthalpy of solution did not change from $T = 322.5$ K to $T = 372.9$ K. As the temperature increased, it was clear that a competition was involved between the carbamate and the carbonate formation to dissolve the carbon dioxide into the aqueous solution of DEA (Figure 3): At $T = 322.5$ K, up to $\alpha = 0.5$, carbamates were predominant in the solution, but at $T = 372.9$ K, this phenomenon appeared to be reversed, and CO_2 was solubilized mainly under the form of carbonate.

The change of energetic behavior observed as a function of the loading was clearly associated to the change of governance for the different chemical mechanisms involved in the CO_2 dissolution process.

6. CONCLUSION

In this paper we have provided new experimental enthalpy of solution data for the system $\{CO_2 + \text{DEA} + H_2O\}$. The solubility data derived from our enthalpy data were found to be consistent with the direct phase equilibria measurements from the literature within the estimated experimental uncertainty. The enthalpy of solution, $\Delta_{\text{sol}}H$ ($\text{kJ}\cdot\text{mol}^{-1}$ of CO_2) was found to be constant at low CO_2 loading within experimental uncertainty. In this domain an average enthalpy of solution, $\Delta_{\text{sol}}H^{\text{av}}$, was estimated. These values were used to discuss pressure, temperature, and absorbent composition effects. The enthalpy of solution of carbon dioxide in aqueous solutions of DEA was observed to be independent of pressure within the experimental uncertainty. However the enthalpies obtained at the low loadings and highest pressures, above 2 MPa, seemed to be experimentally underestimated. This could be due to CO_2−absorbent mixing difficulties. No significant temperature or composition effect was observed.

A VLE thermodynamic model was applied to the system $\{CO_2 + \text{DEA} + H_2O\}$. The solubility data derived from this model were found to agree with our experimental results within the estimated experimental uncertainty. The thermodynamic model was then used to predict the enthalpy of solution in the same conditions as we ran our experiments, using six sets of interaction parameters regressed on literature data.[16] The "best" correlations to predict the enthalpy of solution of CO_2 were found to be respectively the one given by Oscarson et al.[4] ($K_{\text{m,r=E2}}$) for the amine protonation and that by Aroua et al.[38] ($K_{\text{m,r=E5}}$) for the carbamate formation. At both temperatures (T = (322.5 and 372.9) K) the amine protonation was found to provide the most important contribution with ~60 % of the total energetic effect. Then the second most important enthalpic contribution was from the carbamate formation (~30 % at $T = 322.5$ K and ~15 % at $T = 372.9$ K). The carbonate formation was found to create an endothermic effect at $T = 322.5$ K and an exothermic effect at $T = 372.9$ K, which explained mainly why our experimental enthalpy of solution did not change from $T = 322.5$ K to $T = 372.9$ K. Tests of several equilibrium constant formulations showed that, at $T = 322.5$ K and $T = 372.9$ K, differences up to ~8.5 % and ~6.4 %, respectively, for the amine protonation and ~68 % at $T = 322.5$ K and ~82 % at $T = 372.9$ K for the carbamate formation arose when calculating the enthalpy of solution. The thermodynamic model was able do describe the enthalpy of solution for loading up to $\alpha = 0.8$ at $T = 322.5$ K and $\alpha = 0.5$ at $T = 372.9$ K. The change of energetic behavior observed when increasing the loading has been described using the model and was found to be correlated to the change of governance for the chemical mechanisms involved in the CO_2 dissolution.

As a final remark, this work showed that a thermodynamic model adjusted using only VLE properties could represent the dissolution of CO_2 in aqueous solutions of DEA over a wide range of temperature. However it was pointed out that the enthalpy of solution derived from such models is largely dependent on the accuracy of equilibrium constants and particularly those of amine protonation and carbamate formation. Therefore direct measurements of enthalpies of solution are still of interest to test the consistency of the model and its ability to predict solution properties. Direct enthalpic measurements for these reactions would be very helpful to complete the other experimental data used in the fit of the equilibrium constant considered in the CO_2 capture process.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables of the coefficients and explanation of the thermodynamic constants used in the modeling of the system $\{CO_2 + \text{DEA} + H_2O\}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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