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Influence of Poly(ethylene oxide) 400 (PEG400) on the Absorption of CO_2 in Diethanolamine (DEA)/H_2O Systems

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ABSTRACT: An experimental device coupling vapor−liquid equilibrium (VLE) measurements and liquid phase analysis by Fourier transform infrared (FTIR) spectroscopy has been used to study the absorption of CO_2 in water/diethanolamine (DEA)/poly(ethylene oxide) 400 (PEG400) systems. The concentration of the molecular form of absorbed CO_2 and the evolution of the carbamate species are measured with the IR spectroscopic method. The partial pressure of carbon dioxide and the liquid phase speciation have been determined at $T = 298.1$ K for various PEG400 concentrations (with a mass fraction ranging from 0 to 0.3), the mass fraction of DEA being 0.3. At fixed pressure, the CO_2 solubility decreases for increasing PEG400 concentrations, which expresses the decrease in solvent polarity. For a given loading and at constant concentration of DEA, the CO_2 molecular concentration increases with the PEG400 concentration increase, whereas the ion repartition is not significantly influenced by the solvent composition.

INTRODUCTION

Acid gas absorption is an important step of the natural gas treatment process. It generally involves alkanolamine as the chemical solvent. Most of the new gas sources contain high quantities of acid gases, and the thermodynamics modeling currently used are not accurate enough for a realistic representation of these high loaded systems needed for the optimization of the industrial process. The water/amine/acid gases systems are characterized by the presence of numerous chemical species, most of them being ions. In the case of the water/diethanolamine (DEA, IUPAC name: 2,2′-iminoethanol) /CO_2 system, the involved equilibria are the following:

$$\text{Amine protonation}: (C_2H_5OH)_2NH + H_3O^+ \leftrightarrow (C_2H_5OH)_2NH_2{}^+ + H_2O \quad (1)$$

$$\text{Carbon dioxide hydrolysis}: CO_2 + 2H_2O \leftrightarrow HCO_3{}^- + H_3O^+ \quad (2)$$

$$\text{Hydrogen carbonate hydrolysis}: HCO_3{}^- + H_2O \leftrightarrow CO_3{}^{2-} + H_3O^+ \quad (3)$$

$$\text{Carbamate formation}: (C_2H_5OH)_2NH + HCO_3{}^- \leftrightarrow (C_2H_5OH)_2NCOO^- + H_2O \quad (4)$$

To adjust the parameters of the model, solubility data are generally used. The concentration of the species produced by the reactions between DEA and acid gas can only be calculated by the model, without any assurance about its accordance with real values. Nevertheless, these data are important, especially if the model is used in connection with the representation of the absorption kinetics. Therefore, a realistic model can be obtained only if the database used for the determination of parameters model includes values related to the liquid phase speciation.

We wish to present herein the development of an original device that combines a Fourier transform infrared (FTIR) spectroscopy analysis of the liquid phase with a vapor−liquid equilibrium (VLE) measurement. This kind of apparatus has been used previously for studying water/DEA/CO_2 systems.[1]

The major disadvantage of traditional solvents containing water and alkanolamines is the very high energy needed for their regeneration. That is why new solvents are developed by adding a physical solvent to the chemical previous ones. The regeneration energy cost is then lowered.[2] In a previous work, we studied the influence of methanol on the absorption of CO_2 in water/DEA systems.[3] In this work, we wish to extend this type of study to another physical solvent, poly(ethylene oxide) 400 (PEG400), instead of methanol (derivatives of polyethylene glycol are used in the Selexol process). Results from both mixed solvents will be compared.

Four mixtures have been studied at $T = 298.1$ K, with the following compositions, expressed in mass fraction:

$$-\ 0.7112\ \text{water} + 0.2888\ \text{DEA}$$

$$-\ 0.1032\ \text{PEG400} + 0.5955\ \text{water} + 0.3013\ \text{DEA}$$

$$-\ 0.2023\ \text{PEG400} + 0.4963\ \text{water} + 0.3014\ \text{DEA}$$

$$-\ 0.2930\ \text{PEG400} + 0.4024\ \text{water} + 0.3046\ \text{DEA}$$

Finally, to check the experimental reproducibility, we have also considered the following system:

$$-\ 0.2978\ \text{PEG400} + 0.3970\ \text{water} + 0.3032\ \text{DEA}$$

In the following discussion, the composition of the solutions will be expressed in mass fraction.

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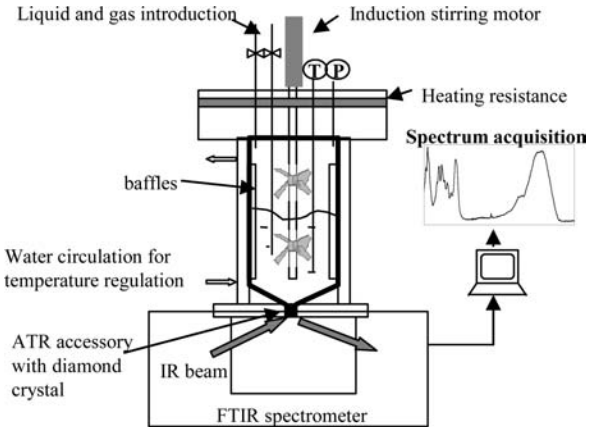

Figure 1. Schematic view of the experimental apparatus.

EXPERIMENTAL SECTION

Materials. CO_2 ($w = 0.99$ in mass fraction) was supplied by Air Liquide. DEA and PEG400 (both $w = 0.99$ in mass fraction) from Fluka were used. The molar mass of PEG400 varies from (0.380 to 0.420) $kg \cdot mol^{-1}$, the average molar mass being 0.4 $kg \cdot mol^{-1}$. Distilled water was used.

Apparatus. A schematic view of the experimental device is presented in Figure 1. The equilibrium cell is a double-jacketed cylindrical reactor ($V = 294.2 \pm 0.1 \cdot 10^{-6}$ m^3), made of stainless steel. The stainless steel lid is equipped with two valves, allowing the introduction of gas and liquid, and a connection to the vacuum pump. Pressure and temperature are measured with a pressure transducer and a Pt100 temperature probe, respectively. The temperature is controlled by circulating a thermostatic fluid from a thermostatic bath (CC1 model from Huber). The lid is heated by a heating resistance at a temperature slightly higher ($\Delta T = 3$ K) than the cell temperature to avoid any condensation phenomenon. To ensure the homogeneity of the liquid and vapor phases, two four-blade impellers driven by a motor and baffles are used. A hole has been made in the bottom of the reactor to allow the liquid phase to be in contact with an ATR (attenuated total reflectance) cell, used for the IR analysis. O-rings in nitrile are used between the top of the cell and its lid and between the bottom of the cell and the ATR device to ensure the pressure tightness. The whole apparatus is placed in a FTIR spectrometer (Avatar from Thermonicolet). The ATR device is a Durasample cell with diamond crystal. Contrary to most of the matter used when working in IR transmission spectroscopy, diamond allows us to analyze the aqueous solution. Moreover, the ATR technique does not need any sample preparation and is then well-adapted for in situ measurement. The IR compartment is closed and flushed with air free of CO_2 and free of water, to avoid interference with the CO_2 contained in ambient air.

Procedure. The solvents are individually degassed. For this purpose, water and PEG400 are cooled into liquid nitrogen and pumped under vacuum during 30 min, this procedure being repeated three times. DEA is heated at 323 K under vacuum during 5 h. The solutions are then prepared by weighing.

At the beginning of each experiment, the solution containing DEA, PEG400, and water is introduced into the cell under vacuum. When the VLE temperature is reached, the solvent vapor pressure P_{sol}^{vap} is measured. CO_2 is then added to the cell. Both amounts of CO_2 and alkanolamine solution introduced in the cell are known by weighing.

Pressure and IR spectra are then regularly recorded, and when no change occurs within one hour, we assume that the equilibrium is reached. The equilibrium pressure P_{tot} allows us to determine the CO_2 partial pressure at equilibrium (see hereafter), and the IR spectrum is analyzed for the determination of speciation data. Then a new amount of CO_2 is added to increase the loading, noted α, which represents the ratio between the mole number of absorbed CO_2 and the amine mole number in the liquid phase.

Partial Pressure and CO₂ Loading Determination. The CO_2 partial pressure P_{CO_2} is calculated according to Raoult's expression:

$$P_{CO_2} = P_{tot} - P_{sol}^{vap}(1 - x_{CO_2}^{app}) \qquad (5)$$

where $X_{CO_2}^{app}$ is the apparent molar fraction of CO_2 in the liquid phase.

The validity of such an approximation has been verified by comparison with the partial pressure deduced from gas chromatography measurement. During the study of the system (0.7112 water + 0.2888 DEA), a gas chromatograph (Perichrom PR 2100) equipped with an automatic sampling loop has been connected to the equilibrium cell. The analyzer was a thermal conductivity detector. Calibration of the TCD response has been realized by connecting the sample loop to a tank containing CO_2 at known pressure. The CO_2 peak area has been plotted versus P_{CO_2}, and a line has been obtained. The average deviation between P_{CO_2} measured in the tank and calculated with the calibration line is 0.5 %. Finally, the average deviation between the value estimated using eq 5 and the value of P_{CO_2} indicated by the pressure indicator for the system (0.7112 water + 0.2888 DEA) was calculated at 1.3 %. We assume then the validity of eq 5.

The evaluation of the CO_2 loading α requires the determination of both the DEA and the CO_2 global concentrations in the liquid phase. Because of the very low partial pressure of DEA, its mole number in the liquid phase is considered as equal to the quantity initially introduced in the cell. Since the CO_2 is present both in vapor and in liquid phases, a vapor phase correction has to be applied. α is finally expressed as follows:

$$\alpha_{CO_2} = \frac{n_{CO_2,\,in} - \left[\dfrac{P_{CO_2}\varphi_{CO_2}^{vap}(V_{reactor} - V_{solution})}{RT}\right]}{n_{Am,\,in}} \qquad (6)$$

where $n_{CO_2,in}$ is the total mole number of CO_2 introduced, $V_{reactor}$ the volume of the reactor, $V_{solution}$ the volume of the liquid phase, and $\varphi_{CO_2}{}^{vap}$ the fugacity coefficient of CO_2 in the vapor phase. $\varphi_{CO_2}{}^{vap}$ has been calculated as follows, using the virial equation of state: $\varphi_{CO_2}{}^{vap} = \exp(B/RT)$ with T as the temperature, R the constant of ideal gas, and B the CO_2 virial second coefficient from Van Huff et al.[4]

IR Spectrum Description and Concentration Calculation. Figure 2 gives the IR spectra of aqueous solutions of a mixture of DEA (mass fraction: 30.13 %) and PEG400 (mass fraction: 10.32 %) at various loadings. The spectra present numerous peaks, but in a previous study[3] three peaks have been selected for the determination of the quantity of species produced by the reaction between CO_2 and DEA:

At 1360 cm^{-1}, a peak associated to HCO_3^- is observed. As it can be observed on the spectrum reported in Figure 2, it always increases with increasing CO_2 loading, as expected.

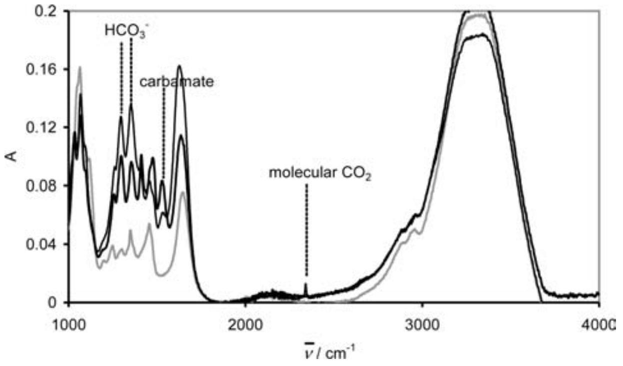

Figure 2. IR spectra of an aqueous solution of (0.3013 DEA + 0.1032 PEG400) mass fraction, at various loading (α) at 298.1 K: thin —, $\alpha = 0$; medium —, $\alpha = 0.578$; thick —, $\alpha = 0.844$.

Table 1. Solubility of CO_2 in Aqueous Solutions of Mass Fractions (0.2988 DEA + 0.0000 PEG400) at $T = 298.1 \pm 0.1$ K

p_{CO_2}/kPa	loading (α_{CO_2})	$h_{carbamate}$/a.u.	c_{CO_2}/mol·L^{-1}
< 1.8	0.1207 ± 0.0008	0.144 ± 0.006	
< 1.8	0.2212 ± 0.0010	0.245 ± 0.006	
< 1.8	0.3292 ± 0.0014	0.343 ± 0.006	
2.2 ± 1.8	0.4263 ± 0.0018	0.408 ± 0.006	
4.4 ± 1.8	0.5187 ± 0.0022	0.432 ± 0.006	
10.9 ± 1.8	0.5961 ± 0.0024	0.417 ± 0.006	
22.9 ± 1.8	0.6594 ± 0.0026	0.376 ± 0.006	
51.3 ± 1.8	0.7351 ± 0.0030	0.327 ± 0.006	0.013 ± 0.010
97.5 ± 1.8	0.7999 ± 0.0032	0.284 ± 0.006	0.026 ± 0.010
150.4 ± 1.8	0.8459 ± 0.0034	0.240 ± 0.006	0.039 ± 0.012
186.4 ± 1.8	0.8676 ± 0.0034	0.225 ± 0.003	0.048 ± 0.014

Table 2. Solubility of CO_2 in Aqueous Solutions of Mass Fractions (0.3013 DEA + 0.1032 PEG400) at $T = 298.1 \pm 0.1$ K

p_{CO_2}/kPa	loading (α_{CO_2})	$h_{carbamate}$/a.u.	c_{CO_2}/mol·L^{-1}
< 1.8	0.3793 ± 0.0026	0.027 ± 0.006	
14.1 ± 1.8	0.5777 ± 0.0028	0.030 ± 0.006	
47.1 ± 1.8	0.6718 ± 0.0028	0.027 ± 0.006	
88.1 ± 1.8	0.7300 ± 0.0030	0.024 ± 0.006	0.023 ± 0.016
180.1 ± 1.8	0.7994 ± 0.0032	0.019 ± 0.006	0.055 ± 0.022
275.1 ± 1.8	0.8447 ± 0.0034	0.018 ± 0.006	0.075 ± 0.026
379.1 ± 1.8	0.8775 ± 0.0036	0.016 ± 0.006	0.102 ± 0.028
500.1 ± 1.8	0.9072 ± 0.0038	0.015 ± 0.006	0.139 ± 0.034
602.1 ± 1.8	0.9269 ± 0.0038	0.014 ± 0.006	0.159 ± 0.036
865.1 ± 1.8	0.9772 ± 0.0042	0.013 ± 0.006	0.222 ± 0.046

At 1530 cm^{-1}, a peak representative of carbamate ($(C_2H_5OH)_2NCOO^-$) is observed. Its variation with increasing CO_2 loading is not monotonous and presents a maximum at a loading value of about 0.5, which corresponds to the stoichiometry of the carbamate formation: two molecules of DEA for one molecule of CO_2, as it can be seen by combining eqs 1, 2, and 4:

$$CO_2 + 2(C_2H_5OH)_2NH \leftrightarrow (C_2H_5OH)_2NCOO^- + (C_2H_5OH)_2NH_2^+ \qquad (7)$$

At 2340 cm^{-1}, the peak characteristic of molecular CO_2 can be detected. This peak is located in a wavenumber range where no other peak occurs, and its height and area are easy to estimate. On the contrary, a deconvolution process is needed for the other two peaks.

The height h_i of a peak is connected to the species concentration C_i by the relation:

$$C_i = k_i \cdot h_i$$

where k_i has to be determined through calibration experiments.

For molecular CO_2, the calibration has been previously done by Sidi-Boumedine et al.[5] The system CO_2/water has been studied, the dissolved CO_2 concentration being perfectly known from literature[6] or by mass balance. It has been verified that the height of the CO_2 peak is proportional to the molecular CO_2 concentration, up to at least $c_{CO_2} = 0.2$ mol·L^{-1}. Moreover, we have checked that k_i does not depend significantly on the solvent, by determining k_{CO_2} in pure water and in the solution 0.7 water/0.3 PEG400. We have obtained $(k_{CO_2})_{water} = 6.98$ mol·L^{-1} and $(k_{CO_2})_{water/0.3PEG400} = 6.64$ mol·L^{-1}.

Unfortunately, it was not possible to estimate the height of the HCO_3^- peak with a sufficient accuracy, because of the complexity of the deconvolution process: the amine, and also the protonated amine contribute to the absorbance in this area.

The carbamate peak is easier to deconvoluate, and we could consequently determine its height. But due to the lack of calibration for $(C_2H_5OH)_2NCOO^-$, we could not convert the peak height to a concentration so chose simply to work with peak height, which should be approximately proportional to concentration.

Uncertainty in Measured Quantities and Results. The temperature of the equilibrium cell was measured with a Pt100 sensor from TC SA, calibrated with a high precision Pt100 probe and a PHP 601 thermometer from AOIP, in a high precision calibration bath (HPB from Hart Scientific). The high precision Pt100 probe and the PHP 601 thermometer are periodically calibrated by a COFRAC accredited laboratory. The uncertainty of the temperature in the cell is ± 0.1 K. The total pressure for each run was measured with a transducer PTX 611 from Druck ((0 to 1000) kPa) with an uncertainty within ± 0.7 kPa, the sensor being also calibrated by a COFRAC accredited laboratory. The solutions were prepared by mass using a Mettler Toledo analytical balance (model XP1203S) with an uncertainties of 0.001 g. The uncertainties of quantities deduced from directly measured quantities were estimated using the error propagation method. The uncertainties related to the overall solution composition and to the loading are then respectively ± 0.05 % and 0.1 %. The peak height (in arbitrary unit) is determined with a precision of ± 0.003. In Tables 1 to 4, the expanded ($k = 2$) uncertainty is reported for all of the measurements. The detection limit for molecular CO_2 concentration is $c = 0.005$ mol·L^{-1}. The 0.3 PEG400/0.3 DEA system has been studied twice, to check the repeatability of the measurements. It can be observed on the corresponding figure (see after) that the values are within the experimental deviation.

RESULTS AND DISCUSSION

The values of loading α, P_{CO_2}, c_{CO_2}, and the height of the carbamate peak are presented in Tables 1 to 4.

CO_2 Solubility. The evolution of CO_2 solubility versus loading is presented in Figure 3. For all of the systems, the solubility variation is low for loadings lower than 0.5, whereas it is important for loading higher than 0.5, P_{CO_2} increasing rapidly because carbamates are transformed into HCO_3^-. At fixed P_{CO_2}, the loading and then the global solubility decrease when the PEG400

Table 3. Solubility of CO_2 in Aqueous Solutions of Mass Fractions (0.3014 DEA + 0.2023 PEG400) at $T = 298.1 \pm 0.1$ K

p_{CO_2}/kPa	loading (α_{CO_2})	$h_{carbamate}$/a.u.	c_{CO_2}/mol·L^{-1}
< 1.8	0.2683 ± 0.0018	0.021 ± 0.006	
2.0 ± 1.8	0.3898 ± 0.0018	0.028 ± 0.006	
4.0 ± 1.8	0.4608 ± 0.0020	0.031 ± 0.006	
9.0 ± 1.8	0.5089 ± 0.0022	0.032 ± 0.006	
17.0 ± 1.8	0.5550 ± 0.0022	0.031 ± 0.006	
31.1 ± 1.8	0.6004 ± 0.0024	0.030 ± 0.006	
57.6 ± 1.8	0.6480 ± 0.0026	0.028 ± 0.006	
92.1 ± 1.8	0.6914 ± 0.0028	0.026 ± 0.006	0.028 ± 0.018
135.1 ± 1.8	0.7286 ± 0.0028	0.025 ± 0.006	0.038 ± 0.020
183.1 ± 1.8	0.7597 ± 0.0030	0.023 ± 0.006	0.060 ± 0.024
241.1 ± 1.8	0.7879 ± 0.0030	0.021 ± 0.006	0.077 ± 0.026
311.1 ± 1.8	0.8151 ± 0.0032	0.021 ± 0.006	0.093 ± 0.028
398.1 ± 1.8	0.8416 ± 0.0032	0.020 ± 0.006	0.124 ± 0.032
503.1 ± 1.8	0.8673 ± 0.0034	0.019 ± 0.006	0.149 ± 0.036
598.1 ± 1.8	0.8885 ± 0.0034	0.016 ± 0.006	0.180 ± 0.040
822.1 ± 1.8	0.9269 ± 0.0038	0.014 ± 0.006	0.235 ± 0.028

Table 4. Solubility of CO_2 in Aqueous Solutions of Mass Fractions (0.3046 DEA + 0.2930 PEG400) at $T = 298.1 \pm 0.1$ K

p_{CO_2}/kPa	loading (α_{CO_2})	$h_{carbamate}$/a.u.	c_{CO_2}/mol·L^{-1}
< 1.8	0.1083 ± 0.0008	0.011 ± 0.006	
2.0 ± 1.8	0.3342 ± 0.0016	0.030 ± 0.006	
6.0 ± 1.8	0.4461 ± 0.0020	0.034 ± 0.006	
13.1 ± 1.8	0.4998 ± 0.0020	0.034 ± 0.006	
26.1 ± 1.8	0.5487 ± 0.0022	0.033 ± 0.006	
55.1 ± 1.8	0.6003 ± 0.0024	0.032 ± 0.006	0.020 ± 0.018
102.1 ± 1.8	0.6514 ± 0.0026	0.030 ± 0.006	0.035 ± 0.020
161.1 ± 1.8	0.6973 ± 0.0028	0.028 ± 0.006	0.063 ± 0.024
265.1 ± 1.8	0.7466 ± 0.0030	0.024 ± 0.006	0.087 ± 0.026
361.1 ± 1.8	0.7815 ± 0.0030	0.022 ± 0.006	0.119 ± 0.032
442.1 ± 1.8	0.8070 ± 0.0032	0.021 ± 0.006	0.150 ± 0.036
647.1 ± 1.8	0.8593 ± 0.0034	0.018 ± 0.006	0.209 ± 0.044
777.1 ± 1.8	0.8862 ± 0.0036	0.017 ± 0.006	0.256 ± 0.050

concentration increases, the term global solubility meaning the quantity of absorbed CO_2, whatever its chemical form. This behavior is the consequence of a less favorable ion formation when the composition in PEG increases and is consistent with the decreasing polarity of the solvent, the dielectric constant of PEG400 being $\varepsilon = 14.27$[7] instead of 78.78[8] for water. The methanol addition and PEG addition can be compared on Figure 3. In this figure, it may be noticed that the solubility of CO_2 is greater in the case of DEA aqueous solutions containing 30 wt % of methanol compared to DEA solutions with 30 wt % of PEG. This result is in accordance with the value of the methanol dielectric constant: $\varepsilon = 32.63$,[9] the proportion of ion formation through chemical reactions being larger in more polar solutions.

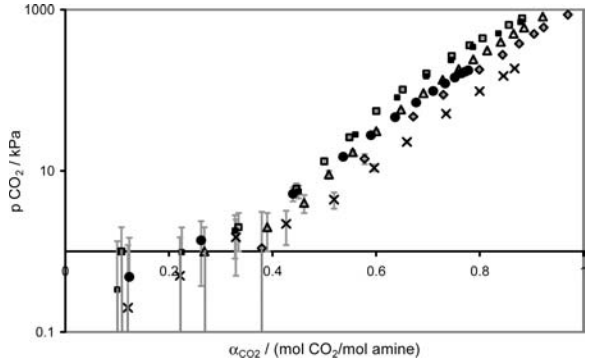

Figure 3. Solubility of CO_2 in DEA aqueous solutions with the following mass fractions as a function of the loading (α) at 298 K: ×, 0 PEG400 + 0.2988 DEA; ◇, 0.1032 PEG400 + 0.3013 DEA; △, 0.2023 PEG400 + 0.3014 DEA; □, 0.2930 PEG400 + 0.3046 DEA; ■, 0.2978 PEG400 + 0.3032 DEA; ●, 0.2945 methanol + 0.3013 DEA; Archane et al.[3]

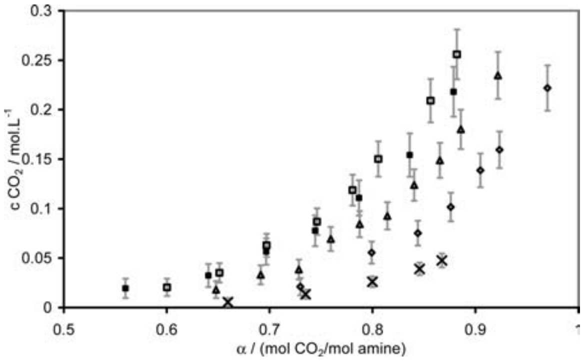

Figure 4. Concentration of molecular CO_2 in DEA aqueous solutions with the following mass fractions as a function of the loading (α) at 298 K: ×, 0 PEG400 + 0.2988 DEA; ◇, 0.1032 PEG400 + 0.3013 DEA; △, 0.2023 PEG400 + 0.3014 DEA; □, 0.2930 PEG400 + 0.3046 DEA; ■, 0.2978 PEG400 + 0.3032 DEA.

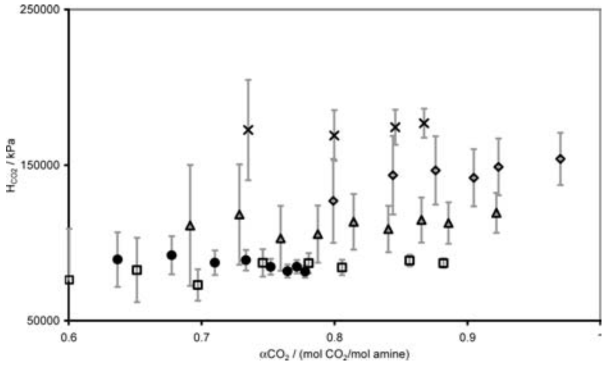

Figure 5. CO_2 Henry's constant evolution in DEA aqueous solutions with the following mass fractions as a function of the loading (α) at 298 K: ×, 0 PEG400 + 0.2988 DEA; ◇, 0.1032 PEG400 + 0.3013 DEA; △, 0.2023 PEG400 + 0.3014 DEA; □, 0.2930 PEG400 + 0.3046 DEA; ●, 0.2945 methanol + 0.3013 DEA; Archane et al.[3]

Liquid Phase Composition. *Molecular CO_2 Concentration.* The evolution of molecular CO_2 concentration is presented in Figure 4. For increasing loadings, the concentration of the molecular form of CO_2 increases, and at fixed loading, the molecular CO_2 concentration increases for increasing PEG400 concentrations, as the CO_2 partial pressure did. At fixed pressure, the solubility of molecular CO_2 is higher in pure PEG400 than in water. This result is emphasized in Figure 5 where the Henry's constant H_{CO_2} (defined as $H_{CO_2} = P_{CO_2}/x_{molecular\ CO_2}$ where $x_{molecularCO_2}$ is the molecular CO_2 mole fraction) is presented as a function of the loading and the solvent composition. H_{CO_2} is

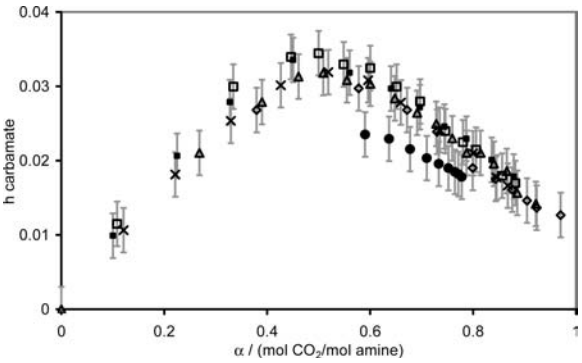

Figure 6. Evolution of the carbamate peak height in DEA aqueous solutions with the following mass fractions as a function of the loading (α) at 298 K: ×, 0 PEG400 + 0.2988 DEA; ◇, 0.1032 PEG400 + 0.3013 DEA; △, 0.2023 PEG400 + 0.3014 DEA; □, 0.2930 PEG400 + 0.3046 DEA; ■, 0.2978 PEG400 + 0.3032 DEA; ●, 0.2945 methanol + 0.3013 DEA; Archane et al.[3].

significantly lower for systems containing a physical solvent. This explained that mixed solvents are more efficient than chemical solvents for the purification of gases containing high concentration of acid gases: the bulk removal properties of the physical solvent are combined with the amine's ability to achieve very low residual acid gas specifications.

Methanol has quite the same influence than PEG400, since the decrease of H_{CO_2} in the mixed systems is mainly due to the decrease of the water content, which has a higher H value ($(H_{CO_2})_{water}$ = 165 600 kPa[6]) than $(H_{CO_2})_{methanol}$ = 14 800 kPa[10] and $(H_{CO_2})_{PEG400}$ = 1300 kPa.[11]

Carbamate Evolution. Figure 6 presents the evolution of the height of the carbamate peaks versus loading, for a DEA aqueous solution free of physical solvent and for systems containing PEG400. As expected, for a given system, the peak height reaches a maximum for $\alpha \approx 0.5$. When $\alpha > 0.5$, the carbamates are decomposed into HCO_3^-. At fixed α, there are no significant differences between the three systems containing PEG400 and the system without PEG400. As the concentration of molecular CO_2 is very low if compared to HCO_3^- and carbamate, the nondependence of the height of the carbamate peak traduces the fact that the reaction between HCO_3^- and carbamate is not significantly affected by the replacement of a part of the water by PEG400.

■ CONCLUSION

The addition of increasing amounts of PEG400 in water/DEA systems leads to a lowering of the acid gas solubility, for loadings less than 1. The molecular CO_2 concentration simultaneously increases, whereas the HCO_3^- and carbamate repartition are not modified by the PEG400 composition change. This kind of data is very scarce in the literature: ^{1}H NMR spectroscopy has been used by Böttinger et al.[12] and Poplsteinova Jakobsen et al.[13] to determine the true composition of CO_2 loaded aqueous solutions of monoethanolamine (MEA), DEA, methyl diethanolamine (MDEA), and butylethanolamine. Suda et al.,[14] again with ^{1}H NMR experiments, have published a few experimental points of $H_2O-MEA-CO_2$ systems, and Jackson et al.[15] have published a qualitative study using FT-IR spectroscopy of systems containing MEA, MDEA, or AMP (2-amino-2-methyl-1-propanol), with similar attribution for the various peaks.[3] These speciation data are nevertheless very important, for instance in kinetics modeling, where the driving forces for CO_2 absorption are driven by the concentration of molecular CO_2 at the liquid interface. The presented experimental device is particularly well-suited for coupled measurements of solubility and liquid phase speciation.

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