VIP CO_2 Capture

DOI: 10.1002/anie.201101250

CO_2 Capture in Amine-Based Aqueous Solution: Role of the Gas–Solution Interface**

*Tanza Lewis, Manfred Faubel, Bernd Winter, and John C. Hemminger**

Aqueous amine-based solutions are the cheapest currently employed solvents to capture CO_2 emitted into the atmosphere from industrial processes, as occurring for instance in coal-operated power plants.[1] CO_2 capture involves flowing flue gas through an aqueous solution containing a relatively nontoxic compound such as monoethanolamine (MEA) that reacts selectively with CO_2. The technique has been used in the chemical industry for more than 60 years,[2] and will likely continue to play an important role for some time. However, the overall process is costly because of the energy required for CO_2 recovery,[1b] and poses several technical problems, for example, solvent disposal.[1b,3] Moreover, the properties that are essential for efficient capture are not well understood,[4] and there is an especially high demand to better understand the CO_2–amine solution interactions at the molecular level. This will be of great relevance for the development of more energy-efficient processes and the design of capture solutions. The reactivity of the ternary mixture $MEA + H_2O + CO_2$, including the complex chemical equilibria between the various species that are formed in solution at ambient conditions, has been the subject of intensive research. Several kinetic models and reaction mechanisms have been proposed,[1a,5] and thermodynamic properties determined.[1d,4] Surprisingly, very few studies have explicitly addressed the role of the solution–gas interface, although it is of key importance for properly modeling absorption kinetics. This fact has motivated the present experimental study of the electronic structure and composition of the aqueous MEA and CO_2-treated MEA gas–solution interface. Our experiments show that neutral MEA exhibits a relatively enhanced concentration at the surface of the aqueous solution, whereas the products of the reaction of MEA with CO_2, carbamate and carbamic acid, show a preference for the bulk solution. These observations indicate that a detailed understanding of the behavior of CO_2 at the liquid/vapor interface and the interface-to-bulk transport of the products will be important for understanding CO_2 capture.

We report soft-X-ray photoelectron spectroscopy (PE) measurements from a vacuum liquid microjet of aqueous solutions of pure MEA ($HOC_2H_4NH_2$) and CO_2-treated MEA (CO_2 loading 0.24 mol mol^{-1}MEA), probing both the solution surface and into bulk solution. Surface-sensitive PE measurements require that the inelastic mean free path (IMFP) of the detected photoelectrons is minimal, which is the case when electron kinetic energies (eKEs) are near 60–100 eV.[6] We acquired N 1s and C 1s spectra from the solution surfaces with 500 and 378 eV photon energies, respectively, corresponding to around 90 eV eKE, where the IMFP is 10 Å, resulting in a very interface-sensitive experiment.[7] Higher photon energies up to 1017 eV for N 1s and 898 eV for C 1s were also applied and correspond to probing predominantly the bulk aqueous solution.[8]

At low to mid CO_2 loading, the reaction between CO_2 and MEA produces a carbamate species as the major product as shown in Reaction (1):[1a]

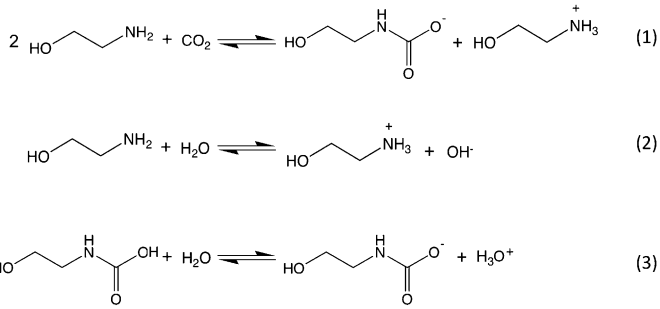
$$2\,MEA + CO_2 \rightleftharpoons MEA\text{-}COO^- + MEA\text{-}H^+ \quad (1)$$

There is a known acid/base equilibrium that occurs between neutral and protonated MEA (Reaction (2); MEA and MEA-H$^+$) which has a pK_a of 9.55. An equilibrium must also exist between carbamate and carbamic acid (Reaction (3); MEA-COO$^-$ and MEA-COOH). The molecular formula for these reactions are shown in Scheme 1.

$$MEA + H_2O \rightleftharpoons MEA\text{-}H^+ + OH^- \quad (2)$$

$$MEA\text{-}COOH + H_2O \rightleftharpoons MEA\text{-}COO^- + H_3O^+ \quad (3)$$

Experimental measurements of the pK_a value associated with Reaction (3) have not been reported, but calculations



Scheme 1. The structural formula of the species in Reactions (1)–(3).

[*] T. Lewis, Prof. Dr. J. C. Hemminger
Department of Chemistry, University of California, Irvine
1201 Natural Sciences II, Irvine, CA 92679 (USA)
Fax: (+1) 949-824-3168
E-mail: jchemmin@uci.edu
Dr. M. Faubel
Max-Planck-Institut für Dynamik und Selbstorganisation
37037 Göttingen (Germany)
Dr. B. Winter
Helmholtz-Zentrum Berlin für Materialien und Energie
and BESSY, 12489 Berlin (Germany)

[**] This work was supported by AirUCI from the NSF (grant CHE 0431312) and the Deutsche Forschungsgemeinschaft (project WI 1327/3-1).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201101250.

suggest it is between 7 and 9.[4] We will report an experimental value herein. Differences in the local electronic environment of the nitrogen site make it possible to distinguish MEA and MEA-H^+ in water by the different N1s binding energies (BEs; chemical shift), whereas the carbamate and carbamic acid species are distinguished by their C1s BEs, reflecting local electronic structure changes at the carbon atoms. With careful consideration of experimental parameters, we can determine the approximate relative concentration of the species from the measured PE signal intensities, for both surface and bulk solution.

Figure 1 shows N1s PE spectra acquired from untreated and CO_2-treated MEA solutions. The bottom spectrum (Figure 1A) is a surface-sensitive measurement of untreated 4.9 M MEA (corresponding to 30 wt% MEA, the concentration commonly used in CO_2 capture) at pH 12.8. Here the MEA is in its neutral form, and the signal is fitted by a single Gaussian function (in red) at 406.4 eV BE with a full width at half maximum (FWHM) of 1.3 eV. Figure 1B shows an analogous measurement of 4.9 M MEA where the pH value has been adjusted to equal the pK_a value of the bulk (9.5). The emerging peak at 408.8 eV thus identifies contributions from protonated MEA; the respective Gaussian curve (in blue) has a FWHM value of 1.5 eV. The higher binding energy for the protonated MEA is a result of decreased electron density at the nitrogen site and also of the added Coulomb charge of the extra proton. Measured peak intensity ratios are a reasonably good reflection of relative concentrations of the two species[7–8] and can be used to quantitatively track differences in the equilibrium between MEA and MEA-H^+ at the surface and in bulk solution. Figure 1E shows the ratio of the MEA and MEA-H^+ N1s signals obtained for the solution with equal pH and pK_a values as a function of the eKE, that is, the experimental probe depth. In our bulk probe (750 eV KE) we measure the 1:1 ratio of neutral to protonated MEA as expected when the pH equals the pK_a. However, our surface-sensitive measurements at a eKE of 90 eV show an increased ratio of around 1.6, implying surface segregation of neutral MEA, and a preference of MEA-H^+ for the bulk solution. This has consequences for the reaction of CO_2 impinging on the MEA solution surface and for reactions at the interface between the solution and the CO_2 gas bubbles.

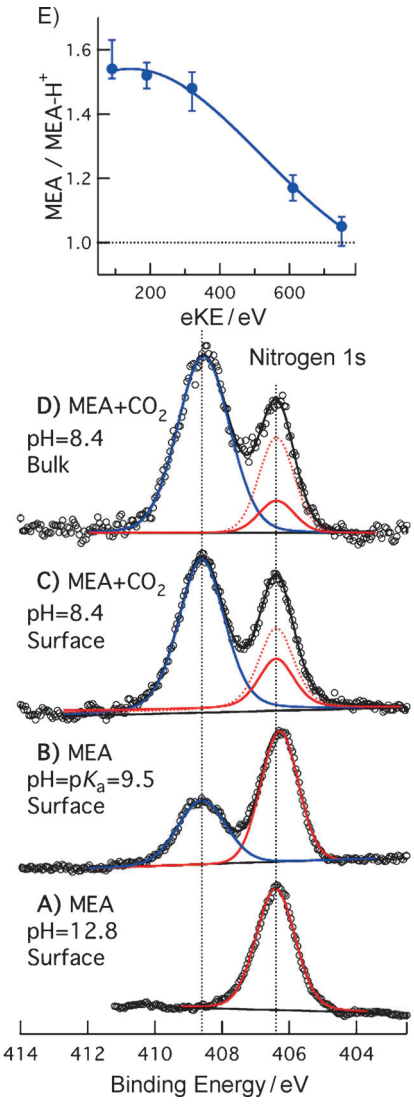


Figure 1. N1s PE spectra of A,B) 4.9 M MEA and C,D) CO_2-treated MEA solutions identify contributions from MEA in its neutral (low BE, solid red) and protonated (high BE, blue) form. The dotted red Gaussian curve represents a signal from carbamate reaction products. E) Relative concentrations of neutral and protonated MEA as a function of the depth into a solution of MEA with equal pH and pK_a values of 9.5.

The two remaining spectra (Figure 1C and 1D) were acquired from a 4.9 M MEA solution that was treated with CO_2 at a loading of 0.24 mol mol^{-1} MEA. The final pH of the solution was 8.4. Contributions from carbamate reaction products cannot be readily distinguished from those of the MEA reactant in the N1s PE spectra because they have a very similar local electronic structures at the nitrogen sites and thus have the same N1s BEs. Thus, the 406.4 eV BE peak in Figure 1C,D is composed of two overlapping Gaussian functions of same width (represented by dotted and solid lines). To illustrate relative peak intensities here we assume a CO_2 loading of 0.24 mol mol^{-1} throughout the solution, although relative concentrations of MEA and the reaction products in surface and bulk solution will later be explicitly determined. However, here we can immediately see a difference in the relative signals of MEA and MEA-H^+ when we compare the spectrum of the solution interface (Figure 1C) to that of the bulk solution (Figure 1D). A more complete understanding of the CO_2-treated MEA solutions can be obtained from the C1s PE spectra.

Figure 2 shows C1s PE spectra acquired from untreated and CO_2-treated solutions of MEA. In 4.9 M MEA solution at pH 12.8 (Figure 2A) and in 4.9 M MEA solution at pH 9.5 (Figure 2B) we see a single peak at 291 eV, and the respective Gaussian fit (in red) of FWHM at 1.4 eV. After reaction with CO_2 (Figure 2C,D), we detect two additional peaks to the high BE side of MEA. We attribute the lower BE peak to carbamate (MEA-COO^-) and the higher BE to carbamic acid (MEA-COOH), where the difference in the BE (ca. 0.8 eV) is nearly identical to the C1s BE shift observed between acetate (CH_3COO^-) and acetic acid (CH_3COOH; see the Supporting

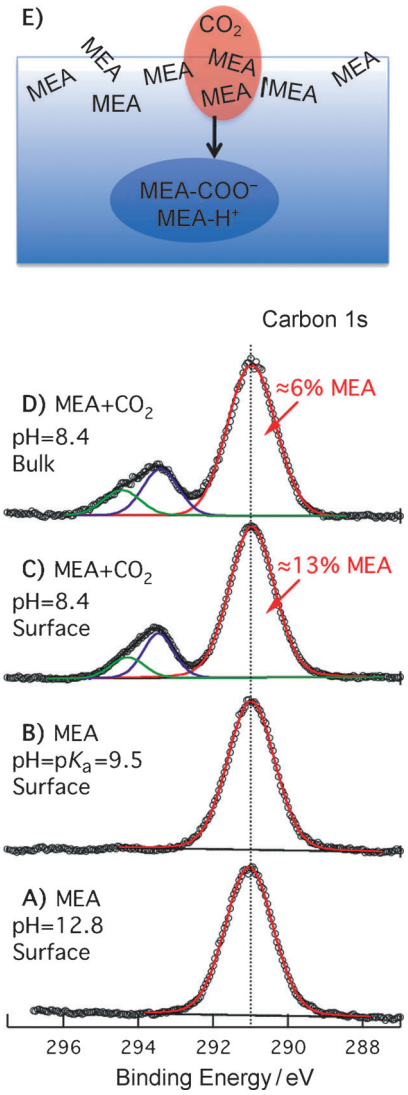


Figure 2. C1s PE spectra of A,B) 4.9 M MEA and C,D) CO_2-treated MEA. In CO_2-treated MEA, intensities from carbamate (low BE, purple) and carbamic acid (high BE, green) emerge, and the peaks labeled in red show the percentage of the contribution of neutral MEA. E) Model for CO_2 absorption at the MEA surface.

Information), thus providing strong support for our spectral assignment.

Our measurements first make it possible to calculate the pK_a of MEA carbamic acid (MEA-COOH). From the relative intensities of carbamate and carbamic acid in bulk solution (Figure 2D) and the measured pH of the solution, we calculate the pK_a of MEA-COOH as 8.2, consistent with theoretical calculations[4] and representing the first reported experimental determination of the pK_a value of carbamic acid. Second, our measurements make it possible to determine the relative spatial distributions of MEA and the reaction products in bulk solution and at the solution interface. However, we first need to note that several species contribute to the peak highlighted in red: MEA, MEA-H^+, and the signal from the two noncarboxylic carbons in MEA-COO^- and MEA-COOH. The contribution from carbamate products is directly obtained by the intensity of the carboxylic C1s (peaks highlighted in green and purple in Figure 2C,D), and the additional relative contribution from MEA and its protonated form is determined from the N1s spectra (peaks highlighted by solid red and blue lines in Figure 1C,D). Then, the contribution from neutral MEA to the signal intensity shown in red in Figure 2C,D is 13 and 6% of the total peak area, respectively. We find that the ratio of the signal of neutral MEA over that of the summed product (MEA-COO^- and MEA-COOH) is around 0.22 when we probe the surface, and decreases to around 0.09 in bulk solution. This indicates a propensity of MEA for the solution surface and a preference of the carbamate species for the bulk solution.

In conclusion, our experiments show that neutral MEA exhibits a relatively enhanced concentration at the surface of the aqueous solution, whereas protonated MEA, carbamate, and carbamic acid show a preference for the bulk solution. This suggests a model for CO_2 absorption at the MEA surface (Figure 2E) where CO_2 encounters pure MEA at the solution surface, and the reaction products and MEA-H^+ move into the bulk of the solution once they are formed. The higher concentration of the neutral MEA at the solution surface suggests an increased scavenging rate for CO_2, and hence more efficient CO_2 capture. Because CO_2 absorption kinetics in MEA will be different at the solution surface and in the bulk solution, accurate modeling of the kinetics should include both surface and bulk reactions. Our results also suggest that the structure of the CO_2-capturing solvent at the interface is important, and needs to be considered for optimizing the solvent performance.

Experimental Section

Photoemission measurements were recorded from a 15 μm sized liquid vacuum jet at the soft-X-ray U41 PGM undulator beamline of BESSY, Berlin.[9] The velocity of the laminar jet was approximately 50 ms^{-1}, and the temperature was 4 °C. Electrons were detected normal to both the synchrotron-light polarization vector and the flow of the liquid jet. At operation conditions the pressure in the interaction chamber was about 1.5×10^{-4} mbar. The energy resolution of the U41 beamline is better than 300 meV at the incident photon energies used here, and the resolution of the hemispherical energy analyzer is constant with kinetic energy (about 200 meV at 20 eV pass energy). The aqueous solutions were prepared from 99% MEA (Sigma Aldrich) diluted in de-ionized water. CO_2-treated MEA solutions were prepared by bubbling CO_2 gas through aqueous solutions of MEA and recording the mass uptake. The reaction was carried out in an open container at a CO_2 pressure of 1 atm. The reaction proceeded until no further CO_2 uptake was observed.

Received: February 18, 2011
Published online: June 7, 2011

Keywords: aqueous solution interfaces · carbon dioxide · photoelectron spectroscopy

[1] a) N. McCann, D. Phan, X. G. Wang, W. Conway, R. Burns, M. Attalla, G. Puxty, M. Maeder, *J. Phys. Chem. A* **2009**, *113*, 5022; b) C. Lastoskie, *Science* **2010**, *330*, 595; c) R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi, T. K. Woo, *Science* **2010**, *330*, 650; d) N. Mac Dowell, F. Llovell, C. S.

Adjiman, G. Jackson, A. Galindo, *Ind. Eng. Chem. Res.* **2010**, *49*, 1883.
[2] G. T. Rochelle, *Science* **2009**, *325*, 1652.
[3] P. Singh, J. P. M. Niederer, G. F. Versteeg, *Int. J. Greenhouse Gas Control* **2007**, *1*, 5.
[4] P. Jackson, A. Beste, M. Attalla, *Struct. Chem.* **2010**, *21*, 985.
[5] A. Aboudheir, P. Tontiwachwuthikul, A. Chakma, R. Idem, *Chem. Eng. Sci.* **2003**, *58*, 5195.
[6] S. Hüfner, *Photoelectron Spectroscopy: Principles and Applications*, Springer, Berlin, **1995**.
[7] N. Ottosson, M. Faubel, S. E. Bradforth, P. Jungwirth, B. Winter, *J. Electron Spectrosc. Relat. Phenom.* **2010**, *177*, 60.
[8] M. A. Brown, B. Winter, M. Faubel, J. C. Hemminger, *J. Am. Chem. Soc.* **2009**, *131*, 8354.
[9] B. Winter, *Nucl. Instrum. Methods Phys. Res. Sect. A* **2009**, *601*, 139.

