Electronic Supplementary Information

^{13}C NMR spectroscopy

Normally, the integration of the ^{13}C NMR resonances does not allow for a reliable quantification of species having carbon atoms in different environments, due to the different spin-lattice T_1 relaxation time which has a marked dependence on the number of protons attached to the carbon.[15] In the species we are dealing with, *i.e.* DEA carbamate and the rapidly exchanging (free ammine)/(protonated amine), the ^{13}C atoms of the CH_2-CH_2 backbone (DEA, MDEA) and of CH_2OH (AMP) have the same number of hydrogen atoms directly attached and likewise exhibit similar T_1, as shown by the similar integrals featuring each CH_2 resonance (less than 2% of error). On the other hand, the ^{13}C atoms of HCO_3^-/CO_3^{2-} pair and of CO_2^- functionality of DEA carbamate have no attached hydrogen and exhibit much higher relaxation times than those of CH_2 groups, thus resulting in lower intensity resonances. For these reasons the relative amounts of carbamate, free amine and protonated amine have been determined by NMR integration of the corresponding signals of the CH_2 carbons whose chemical shifts are markedly dependent on the chemical environment. As a matter of fact, we have carried out several ^{13}C NMR spectra on standard solutions containing free DEA, fully protonated DEA, DEA carbamate and accurately weighted amounts of these species in different molar ratios and we have found a quantitative relationship (less than 3 % error) between the relative peak areas of CH_2 carbon atoms and the known concentrations of each species. The quantification method is therefore empirically quite reliable likely reflecting similarities of the relaxation rate for similar CH_2 carbons in both carbamate and the rapidly exchanging (free amine)/(protonated amine).

In order to measure the relative amounts of fast equilibrating free amine and protonated amine by NMR analysis we have carried out a quantitative ^{13}C NMR study on D_2O standard solutions of neat amine, protonated amine and their 1:1 molar mixture. Plotting of the chemical shifts of the ^{13}C-resonance due to CH_2OH group provides a straight line with limiting values assigned to free amine [$\delta(CH_2OH)$: DEA, 60.86 ppm; MDEA, 59.19 ppm; AMP, 71.75 ppm] and to protonated amine [$\delta(CH_2OH)$: $DEAH^+$, 57.05 ppm; $MDEAH^+$, 55.71 ppm, AMPH+, 66.40 ppm]. As already reported for the HCO_3^-/CO_3^{2-} system,[12] the straight line featuring these plots suggest that the frequency of the resonance assigned to the carbon atom of the CH_2CH_2 unit is proportional to the relative concentration of the two species.

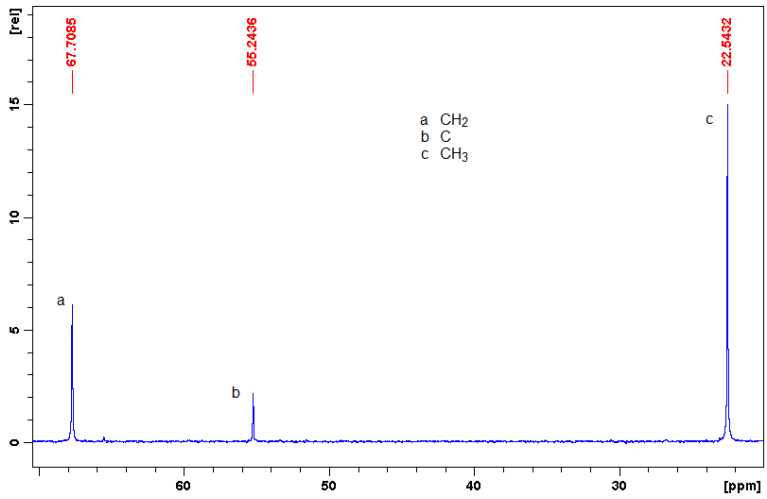

Fig. 1. ^{13}C NMR spectrum of 2.00 M AMP at absorption equilibrium. The resonance of HCO_3^-/CO_3^{2-} is not reported.

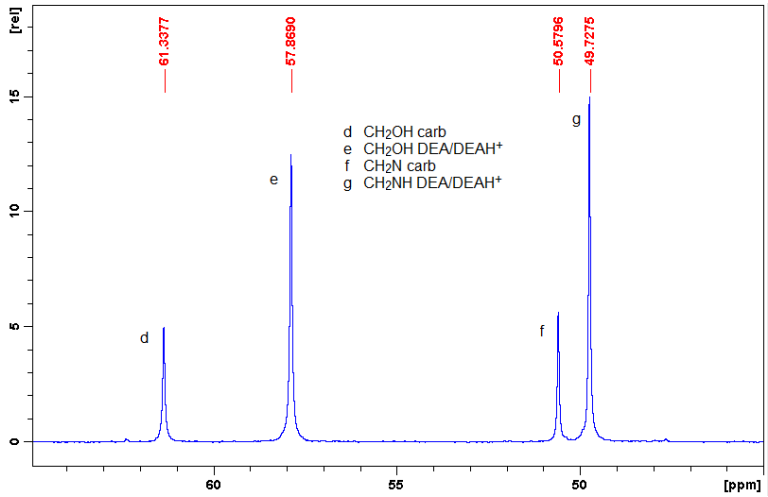

Fig.2. ^{13}C NMR spectrum of 2.00 M DEA at absorption equilibrium. The resonances of HCO_3^-/CO_3^{2-} and of $-CO_2^-$ are not reported.

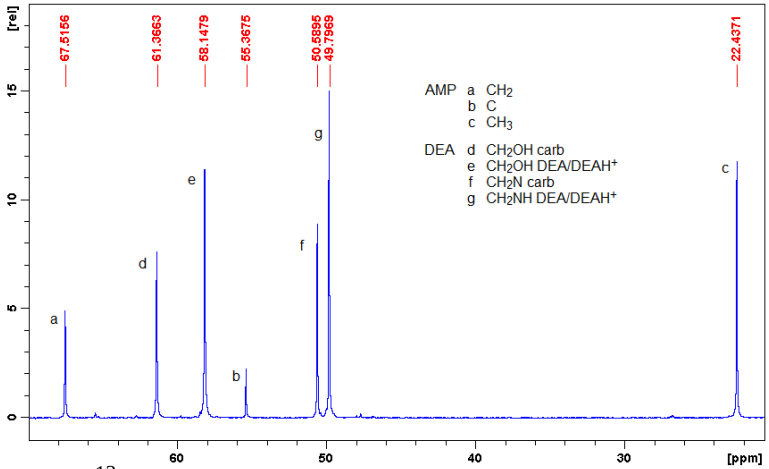

Fig.3. ^{13}C NMR spectrum of 2.00 M AMP/DEA blend (2/1 molar ratio) at absorption equilibrium. The resonances of HCO_3^-/CO_3^{2-} and of $-CO_2^-$ of DEA carbamate are not reported.

^{13}C NMR analysis

As an example of the method used to compute the species in solution from ^{13}C NMR data, we report the computations related to the final absorption equilibrium of DEA solution 1.33 M.

On the basis of the CH_2OH carbon resonance frequency[8] of $DEAH^+$/DEA (δ = 58.07) and of carbon resonance[12] of HCO_3^-/CO_3^{2-} (δ = 161.58), we computed 0.367 DEA/$DEAH^+$ and 7.49 HCO_3^-/CO_3^{2-} molar ratios. Moreover, from the peak integration of the signals at 58.07 ppm and at 61.38 ppm [$\delta(CH_2OH)$ of $DEACO_2^-$], 0.0884 mol of $DEACO_2^-$, 0.228 mol of $DEAH^+$ and 0.0836 mol of residual free DEA have been computed.

The charge neutrality of the solution requires:

$DEAH^+ = HCO_3^- + 2CO_3^{2-} + DEACO_2^-$ (1)

From equation (1) we obtain $DEAH^+ - DEACO_2^- = HCO_3^- + 2CO_3^{2-} = 0.140$ mol.

Indicating as *x* the amount of HCO_3^- and *y* that of CO_3^{2-} we have the relations:

$x + 2y = 0.140$ mol and $x/y = 7.49$ (2)

Solving the system (2) we obtain HCO_3^- = 0.110 mol and CO_3^{2-} = 0.0147 mol. From these figures and from the amount of DEA carbamate, 0.0884 mol, we compute the relative distribution of CO_2 in solution as HCO_3^- (51.6 %), CO_3^{2-} (6.9 %) and $DEACO_2^-$ (41.5 %).

The method is simpler for MDEA and AMP solutions, due to the absence of the carbamate derivative.

The method to compute the average amine regeneration efficiency is based on the amounts of CO_2 measured during the absorption experiments and of the amounts of protonated amine, bicarbonate and carbonate as inferred from ^{13}C NMR spectral analysis. As an example, the regeneration efficiency of the AMP solution 1.33 M is computed as follows. The amount of absorbed CO_2 (0.787 mol) in the entire experiment is computed from the average absorption efficiency (91.0%) and the overall amount of CO_2 flowed through the absorbent (12 h; 0.827 mol), summed to the amount of CO_2 flowed in the starting desorber solution (0.0344 mol). The reaction of 0.787 mol of CO_2 with AMP produces protonated amine and HCO_3^- [reaction (3); $CO_{2(abs)}/AMPH^+$ = 1/1] and CO_3^{2-} [reaction (4); $CO_{2(abs)}/AMPH^+$ = 1/2]

$AMH + CO_2 + H_2O \rightleftarrows HCO_3^- + AMH_2^+$ (3)

$2AMH + CO_2 + H_2O \rightleftarrows CO_3^{2-} + 2AMH_2^+$ (4)

From the ^{13}C NMR analysis we derive the average values of 0.117 mol of HCO_3^- (69.6%) and of 0.0511 mol of CO_3^{2-} (30.4%): from these percentages we compute the overall amount of protonated

AMP (1.026 mol). At the end of the experiment the overall amount of protonated AMP contained in both the absorber and the desorber solution is 0.587 mol (from ^{13}C NMR analysis). The difference 1.026 mol – 0.587 mol = 0.439 mol represents the amount of protonated amine that has regenerated free amine according to the reactions (5) and (6).

$$HCO_3^- + AMH_2^+ \rightleftarrows AMH + CO_2 + H_2O \qquad (5)$$

$$CO_3^{2-} + AMH_2^+ \rightleftarrows HCO_3^- + AMH \qquad (6)$$

From the 0.439/1.026 ratio we compute 42.8% of regenerated amine during the entire experiment: we have defined this value the amine regeneration efficiency. Obviously, at the end of any experiment when the equilibrium has been reached, the regeneration efficiency of all the amine is 100%.

For DEA solutions, the percentage of carbamate has been also considered to evaluate the overall amount of protonated DEA.

The loading capacity of the single amines has been computed as the molar ratio between the overall amount of absorbed CO_2 at the end of each experiment and the summed amounts of the starting and regenerated amine. In the above example of AMP 1.33 M combined with 373 K of desorber temperature, we have computed 0.439 mol of regenerated amine and 0.787 mol of absorbed CO_2. The overall amount of starting amine in both absorber and desorber is 0.800 mol. The ratio 0.787(mol)/1.239(mol) = 0.635 is the computed loading capacity.

We cannot compute the regeneration efficiency and loading capacity of blended amines as ^{13}C NMR analysis give us the overall amount of HCO_3^- and CO_3^{2-} produced by the reaction of the two amines.

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