Supporting Information

"A comparative study of the CO_2 absorption in some solvent-free alkanolamines and in aqueous monoethanolamine (MEA)"

Authors: Francesco Barzagli, Fabrizio Mani*, Maurizio Peruzzini

^{13}C NMR experiments

The pulse sequence with proton decoupling and NOE suppression was used to acquire the $^{13}C\{^{1}H\}$ with the following acquisition parameters: pulse angle = 90.0°, acquisition time = 1.3632 s, delay time = 2-30 s, data points = 65K, number of scans = 250-500. Increasing the acquisition time and/or the relaxation delay (up to 60 s) does not produce substantial changes in the relative peak areas of the $-CH_2-$ carbon atoms that contain the same number of attached protons. The ^{13}C atoms of R'-CO_2- functionalities have no attached hydrogen and exhibit longer relaxation times than those of $-CH_2-$ and CH_3 groups, thus resulting in lower intensity resonances.

The ^{13}C NMR resonances (δ, ppm) of the carbon atoms of the carbamate and protonated amines (in parentheses) saturated by CO_2 were: MMEA, 163.55, 60.32, 50.93, 34.80; (56.74, 50.93, 32.54); EMEA, 163.21, 61.88, 48.68, 42.15, 13.42; (57.26, 49,21, 42.15, 11.17); IPMEA, 162.33, 63.22, 51.43, 43.51, 20.00 (58.38, 48.82, 46.02, 20.67); BZMEA, 164.17, 139.71, 128.87, 127.69, 126.44, 61.78, 51.38, 49.23 (135.63, 128.37, 128.11. 126.90, 58.67, 51.81, 49.52); BUMEA, 163.55, 62.37, 49.39, 47.83, 30.64, 19.57, 13.42 (57.69, 49.93, 47,51, 28.53, 19.57, 13.12).

The couples of resonances in the range 60.32 and 32.54 ppm (MMEA), 61.88 and 11.17 ppm (EMEA), 63.22 and 20.00 ppm (IPMEA), 139.71 and 49.23 ppm (BZMEA), 62.37 and 13.12 ppm (BUMEA) assigned to the CH, CH_2 and CH_3 carbon atoms of the amine carbamates and of the fast exchanging protonated amines and free amines. The low-intensity resonances in the range 164.17-162.23 ppm were ascribed to the carbonyl group of the carbamate

Comparison of the sensible heat of 30% MEA and neat BUMEA

For the comparison, we used the results obtained in the cyclic experiments carried out with two absorber configuration and 93.5 % efficiency of both absorbents. The flux of 0.100 $dm^3\ h^{-1}$ of aqueous 30 wt % MEA [d(50 °C) = 1.07 kg dm^{-3}] corresponds to 0.0749 kg of water and 0.0321 kg of MEA (heat capacity 4.18 kJ kg^{-1} $°C^{-1}$ and 2.6 kJ kg^{-1} $°C^{-1}$, respectively[1]) to be heated from 50 °C (absorber) to 105 °C (desorber). Meanwhile 0.168 mol h^{-1} of CO_2 was captured from the gas mixture (flux rate 29.0 $dm^3\ h^{-1}$ at 22 °C, 15.0 v/v % CO_2 and 93.5 % of absorption efficiency). From these figures, 129 kJ/mol CO_2 were required to heat aqueous MEA. The same calculus for neat BUMEA and 0.120 $dm^3\ h^{-1}$ [d(50 °C) = 0.904 kg dm^{-3}; heat capacity 2.47 kJ kg^{-1} $°C^{-1}$ [2]] gave 75 kJ/molCO_2.

Comparison with solvent-free MEA

It has been already reported[3] that the reaction of CO_2 with neat MEA gave a liquid carbonated species, most likely the ionic couple MEA carbamate and protonated MEA. The experiments of absorption-desorption we carried out with neat MEA in the same experimental conditions of these used with BUMEA gave absorption efficiency in the range 50-54%. The low absorption efficiency of solvent free MEA was due to the very high viscosity of the carbonated species (458 cP measured at 50 °C) that strongly reduces the gas to liquid mass transfer and, consequently the reaction rate.

References

(1) Chiu, L. F.; Liu, H. F.; Li, M. H. Heat capacity of alkanolamines by differential scanning calorimetry. *J. Chem. Eng. Data* **1999**, 44 (4), 631-636.

(2) Shaikh, I. W. N. Molar heat capacities and heats of mixing of aqueous solutions of 2-(propylamino)ethanol, 2-(butylamino)ethanol, 1-(2-hydroxyethyl)piperidine, bis(2-

methoxyethyl)amine and other alkanolamines of importance to carbon dioxide capture. *MD Thesis in Process Systems Engineering, University of Regina, CDN* **2012**.

(3) Jassim, M. S.; Rochelle, G. T.; Eimer, D.; Ramshaw, C. Carbon dioxide absorption and desorption in aqueous monoethanol amine solutions in a rotating packed bed. *Ind. Eng. Chem. Res.* **2007**, 46, 2823-22833.