148u Experimental Determination of the Liquid Phase Composition in the System CO2 / Methyldiethanolamine / H2o

Reda Sidi-Boumedine, Elise PROVOST, Walter FURST, Viep Hoang-Dinh, and Jean-Louis PEYTAVY

Absorption of acid gases by aqueous solutions of alkanolamine is an important industrial process. The accurate design and improvement of industrial absorption and solvent regeneration columns has to take into account couplings between kinetics, mass transfer and thermodynamics. This explains the need of a thermodynamic modelling that gives an accurate and realistic representation of the speciation in the liquid phase. Due to the complexity of the amine - Water - Acid gases systems, the use of solubility data for the determination of model parameters is probably not sufficient to get a realistic model. Hence we have develop a new method to get both solubility data and liquid phase speciation values in the case of Alkanolamine - Water - Acid gases systems. These new data will allow to get realistic modellings with two consequences: (i) The use of theses modellings in extrapolation conditions will be more reliable. (ii) It will also be an help to make a choice between numerous sets of literature solubility data, which present large discrepancies.

The new experimental device allows to get the equilibrium pressure at fixed temperature, amine concentration and acid gas loading but also to measure the concentration of the species produced, in the liquid phase, by absorption process. It consists of two parts: (1) a thermostated cell, equipped with pressure and temperature sensor, in which known quantities of the amine solution and of acid gas are introduced. The stirring is made through a magnetic stirrer. The pressure is recorded and, at equilibrium, it gives the gas solubility value. (2) The second part of the equipment is in a FT-IR spectrometer equipped with an ATR (Attenuated Total Reflectance) cell made of germanium. The liquid phase is circulated between the equilibrium cell and the ATR one. The analysis of the liquid phase IR spectrum gives us informations about the liquid phase composition. The equilibrium cell as well as the external loop are maintained at the same temperature to avoid equilibrium changes in the loop. The loop volume (40 µL)is negligible in comparison to the cell volume (460 mL). Using an air thermostated bath, some parts of the equipment are maintained at a temperature that is slightly higher than the cell temperature to avoid condensation on the metallic parts of the cell. As we considered CO_2 , a sweeping of the IR-Spectrometer with purified air (without CO_2 and moisture) is made to be sure that the CO_2 signal is relative to the circulating liquid phase.

In a first step, the method has been applied to the water - CO_2 system, because, as the relation between CO_2 partial pressure and molecular CO_2 solubility is well known, it allows to check the validity of the method. On IR spectra, a well defined peak at 2340 cm^{-1} is observed; it is characteristic of molecular CO_2. Its area increases linearly with CO_2 concentration, allowing to determine the response coefficient. This coefficient has been used to evaluate the concentration of molecular CO_2 in the systems with amines. It has to be pointed out that the amines have no IR peaks in the 2200-2400 cm^{-1} wavelength range. This explains that, even if molecular CO_2 corresponds to a very low proportion of the loading, its concentration may be measured using IR spectrum.

The method has been applied to systems CO_2 / MDEA (methyldiethanolamine) / water, and concentrations of molecular CO_2 and HCO_3^-, together with CO_2 partial pressure have been measured. We carried out original measurements for 25.7 and 46.8 Wt % of MDEA in water, at temperatures ranging between 25°C and 75°C and for CO_2 partial pressures up to 2 bars.

In the IR spectrum of the CO_2 loaded amines solutions, we selected two peaks: the one at 2430 cm^{-1}, already mentioned, and a large band at 1200-1450 cm^{-1}, devoted to HCO_3^-. The area of the first peak gives the molecular CO_2 concentration. A mass balance on carbonated species allows the calculation of the HCO_3^- concentration and an linear relationship between this value and the area of the band at 1200-

1450 cm^{-1} has been found. This linearity may be considered as a validation of the method. Furthermore, it allows the determination of the HCO_3^- response coefficient that may be used in the case of more complex systems. Together with the liquid phase composition determination, CO_2 partial pressure at equilibrium has been measured. We have compared our results with literature data and a these new values agree with the recent values of Sidi-Boumedine et al.[1] obtained independently using different equipments. Speciation experimental data have been compared with the values deduced from the application of two published models (NRTL electrolyte by Augsten et al.[2] and a model developed by Li and Mather[3]). At a given loading, xCO_2 molecular increases with the alkanolamine concentration and with the temperature, as expected by both models. Nevertheless, significant deviation can be observed between the models : at a given loading, xCO_2 deduced from Li's model are lower than those deduced from NRTL electrolyte model, and the difference increases with temperature. Our experimental results agree with the values obtained applying NRTL electrolyte model, especially at high loadings. The new method proved its ability to get speciation values in the MDEA - Water - CO_2 system. It may be extended to other amine systems and this development is actually in progress, especially in the case of secondary amines.

References

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