Thermodynamics of CO_2 Absorption in Aqueous Ethanolamine Solutions: Experimental Study of the Enthalpy of Solution by Flow Calorimetry

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The capture of carbon dioxide from post combustion emission is one of the challenges for reducing the release of greenhouse gases into the atmosphere, and, aqueous amine solutions are known to be efficient chemical solvents for this purpose. Energetic effects involved in such processes are of large interest for the industry as the energy cost for CO_2 removal is directly related to the enthalpy of solution of CO_2 into the absorbing fluid. This paper reports measurement of enthalpy of solution of CO_2 into aqueous solutions of ethanolamines (w = 0.1500 and 0.300) at temperatures of 323 K and 373 K, and for pressures from 0.2 to 5 MPa for different loading (mol CO_2 / mol amine). Experiments were conducted at constant temperature and pressure, using a custom-made flow-mixing unit in the SETARAM C-80 calorimeter. Three different amines were selected (monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA)). A thermodynamic model considering all reactions taking place, and, adjusted only on vapour-liquid-equilibrium properties, was used to model the enthalpy of solution of CO_2 in the different absorbent. In the case of DEA, different literature equilibrium constant correlations for the amine protonation and the carbamate formation were tested. The energetic contributions from each chemical reaction involved during the capture process are discussed. The reaction of amine protonation was found to provide the most important energetic contribution just after the carbamate formation when that reaction was possible. In the case of DEA, the enthalpy calculation was strongly dependent on the choice of the correlation used for the equilibrium constants. Accurate protonation constant measurements are needed to resolve this issue, so that the calorimetric data can be used as the basis of a comprehensive model that covers a wide range of temperature and pressure.