Measurement and Calculation of Thermodynamic Properties for Aqueous Solutions of CO2 absorbents

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Thermodynamic properties as vapor-liquid equilibrium and mixing enthalpy H^E are very important for process design and simulation of CO_2 capture. In this work, these properties were measured for aqueous solution of new developed CO2 absorbents. A thermodynamic model was established through simultaneously correlating the vapor-liquid equilibrium data and the mixing enthalpy data with the Non-Random Two-Liquid (NRTL) model. The excess molar enthalpies H^E of water + (2-ethylamino) ethanol have been measured at temperatures 303K and 323K over the whole range of mole fractions. The experimentally measured H^E values and the vapor-liquid equilibrium data were simultaneously correlated using the NRTL model. The calculated results reached a good agreement with the experimental data.

Keywords: CO2 absorption, aqueous alkanolamine, vapor-liquid equilibrium, mixing enthalpy.

1. Introduction

Based on the fact that global warming is creating a series of problems on our environment, it is putting more and more importance on how to efficiently capture greenhouse gases, headed by carbon dioxide. In industry, the method of chemical absorption is the most maturely and successfully applicable comparing with all the other technologies. High energy consumption is the bottleneck in large-scale application, which is closely related to the solvent inherent properties, especially the thermodynamic properties, which play an important role, not only on the selection of new absorbent, but also on the simulation and optimization of the absorption process.

Alkanolamines and their mixtures with water are used for removal of acidic gases such as carbon dioxide in the natural gas and petroleum refining processes, due to their variable weak basicity. Taking into consideration of molecular structure, the solution with water demonstrates non-ideality.

One of the most important absorbent thermodynamic properties is the heat of mixing (the excess molar enthalpy H^E), which reflects the change of the intermolecular interaction in mixing process, as while is an indication in solution

non-ideality. The thermodynamic model, built from the experimental mixing heat data, will be useful in testing the feasibility of existing models, building new model, modeling of multi-stage and multi-component equilibrium in absorption/desorption column, and modeling of gas solubility in alkanolamine solutions.

2. Experiment and Calculation

The apparatus used in measuring excess molar enthalpy in our experiment is C80 calvet-calorimeter. Its working principle is based on Tian-Calvet heat flux principle. The heat flux between the reference cell and sample cell is precisely measured owing to the contribution of hundreds of thermocouple, which are located around the cells. The sensitivity is 0.10μW. The cells are a couple of membrane mixing cells, which are set up and designed in a perfectly symmetrical manner to cancel out the effect of residual deviation in the calorimetric unit's temperature and of outside electrical interference. The actual temperature of each measurement was within 0.05 K of the stated temperature. The accuracy of the analytic balance is ±0.1mg, the uncertainties of the mole fraction and mixing heat is ±0.0001 and 2%.

To examine the accuracy of the calorimeter, we measured the mixing heat of solvent diethanolamine and methyldiethanolamine. The error was within 2%. After examination of the built model and the instrument, the excess molar enthalpies of solutions such as water + (2-ethylamino) ethanol have been measured at temperatures 303K and 323K over the whole range of mole fractions.

We built a thermodynamic model through simultaneously correlating the vapor-liquid equilibrium data and the molar enthalpy data on the basis of Non-Random Two-Liquid (NRTL) model. And we calculated the monoethanolamine and methyldiethanolamine solution in a self-compiled Fortran program, the excess molar enthalpies and vapor-liquid equilibrium data of which were from literature. The result errors of both were same with the literature.

The experimentally measured H^E values and the vapor-liquid equilibrium data were simultaneously correlated using the NRTL model. The calculated results reached a good agreement with the experimental data. The thermodynamic model of aqueous alkanolamine is expected to apply in the calculation of CO_2 absorption processes.