

## ABSTRACT

---

### VAPOUR - LIQUID EQUILIBRIUM OF CARBON DIOXIDE IN AQUEOUS ALKANOLAMINES

BY

MADHUSREE KUNDU

For the rational design of gas treating processes, the knowledge of vapour-liquid equilibrium of acid gases in aqueous alkanolamines is essential. In this work a rigorous thermodynamic model has been developed in order to predict the vapour-liquid equilibria of CO<sub>2</sub> in aqueous single and blended alkanolamines. The analytical tool involved the use of a non-traditional optimization algorithm, simulated annealing (SA), for parameter estimation for the model, beside the use of the traditional deterministic technique, Levenberg Marquardt (LM). The results of using SA for parameter estimation, which is a multivariable optimization problem, are very encouraging. The model is validated with the data available in the open literature and the experimental data generated in this work.

The model is used to predict the VLE of CO<sub>2</sub> in aqueous solution of diethanolamine (DEA), N-methyldiethanolamine (MDEA) and sterically hindered amine, 2-amino-2-methyl-1-propanol (AMP). In view of the increasing commercial interest of blended alkanolamine solvents, the model is also used to predict the VLE of CO<sub>2</sub> in (DEA + AMP + H<sub>2</sub>O) and (DEA + MDEA + H<sub>2</sub>O) solutions. By using thermodynamic data, e.g. freezing point depression and heat of mixing, besides the VLE data, the binary amine-water models are improved, thus solvent-solvent interaction parameters are estimated confidently, which are used in predicting the VLE of the ternary systems. The model predicted results for aqueous single amine solvents as well as aqueous blended amine solvents are consistent and are in very good agreement with the available literature data and the VLE data generated in this work. Parametric sensitivity analyses using the model are done to determine the effects of different pertinent model parameters on the accuracy of predicted VLE data of CO<sub>2</sub> in alkanolamine solvents.

The energy required for regeneration of the loaded amine solutions is one of the major operating costs of gas treating processes. The amount of energy required for regeneration is directly related to the enthalpy of solution of the acid gases in the aqueous amine solvents. The developed model for (CO<sub>2</sub> - aqueous single amine systems) has been successfully extended to estimate the enthalpy of solution and reaction.

Measurement of solubility of CO<sub>2</sub> in aqueous single amine, DEA, MDEA, and AMP and aqueous amine blends DEA/AMP, DEA/MDEA have been done in this work up to a maximum CO<sub>2</sub> partial pressure of 100 kPa for various temperatures and amine concentrations using the VLE measurement set-up developed in this work.

Henry's constant for CO<sub>2</sub> in aqueous blended alkanolamines and densities of these alkanolamine solutions have been determined in this work. For Henry's constant of CO<sub>2</sub>, the physical solubility of N<sub>2</sub>O has been measured in the aqueous solutions of (DEA/MDEA), and (DEA/AMP). Then "N<sub>2</sub>O analogy" has been used to determine the physical solubility of CO<sub>2</sub> in these solvents ( $H_{CO_2-amine}$ ). The densities of aqueous blends of (DEA/MDEA) and (DEA/AMP) for various relative amine compositions have been measured over a wide range of temperature and relative amine composition, and useful correlations developed for prediction of densities of the amine blends. These data were necessary as model parameters. However, it is expected that the physico-chemical parameters thus generated will also be useful for the database for process design.