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Simulation and pilot plant measurement for CO_2 absorption with mixed amines

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Abstract

CO2 solubility in an aqueous tertiary amine solution was measured, and thermodynamic models Kent-Eisenberg and Clegg-Pitzer were used to correlate CO2 solubility. Process simulation was also carried out with these models, and simulation results are compared with pilot plant measurement data. The results show that the mixed amine solution of the tertiary amine with MEA could save regeneration energy about 20% compared with 30% MEA aqueous solution.

Keywords: CO_2 Capture, absorption, mixed amines, simulation, pilot plant

Introduction

Because of global warming, CO_2 capture and sequestration (CCS) now is looked as the main method to reduce the amount of greenhouse gases released into the atmosphere. For CO_2 capture, absorption, adsorption and membrane separations are main separation technologies. But now CO_2 capture with absorption still suffers high energy consumption during regeneration of solvents. In order to reduce the energy consumption and then cost for CO_2 capture, new absorbents, mass transfer packing and process intensification methods are important for the improvement of the process technologies.

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In this presentation CO_2 capture with various aqueous solutions of mixed amines was studied. Usually, primary and secondary amine solutions have fast reaction rates with CO_2, but they always suffer from smaller solubility for CO_2 because of carbarmate formation. Tertiary amines and sterically hindered amines usually have large solubility for CO_2, but unfortunately they suffer from slow reaction rates. So solutions of different amines are suggested to be used for CO_2 capture with both advantages of greater solubility and faster reaction rates.

CO_2 solubility in aqueous solutions of various amine mixtures were studied, and Chen-NRTL and Clegg-Pitzer thermodynamic models were used to calculate CO_2 solubilities. In reality, the absorption systems are gas-liquid equilibrium systems of mixed-solvent electrolytic solutions with several chemical reactions. The solubility calculation should include reaction equilibrium equations besides phase equilibrium for gases and solvents. The calculation procedures for gas absorption in different mixed amine solutions were established and the correlation results are in good agreement with experimental data.

The process simulation was also carried out with the thermodynamic models and relative models for reaction kinetics and mass transfer models for tray towers. The simulation results are compared with measured data from pilot plants. In the pilot plant, there is a packing column absorber and a packing column stripper, both in diameter 80 mm, and there is a heat exchanger between rich solution and lean solution. The liquid flow rates are automatically controlled, and all data including temperature, pressure, flow rates, CO_2 concentrations in gas phases are shown and recorded automatically.

The solution studied is the aqueous solution of a primary amine as monoethanolamine (MEA) and a tertiary amine 3-dimethylamine-1-propanol (DMAP).

The composition of these mixtures has a strong effect on energy consumption for CO_2 absorption. The best points for the mixture composition of the above solution were found both in pilot plant measurement and process simulation. Compared with the widely used MEA solution, above solutions with best compositions can save more than 20% energy for CO_2 capture from flue gas at atmosphere pressure.

From the results, it is suggested that further development in solvents and process technologies might give further improvement in saving of energy consumption for CO_2 capture.

1 Thermodynamic Model

For the prediction of acid gas solubility in aqueous alkanolamine solutions, Kent and Eisenberg [1] proposed a thermodynamic model, which took the equilibrium of absorption into account. In their study, general equations for equilibrium constants and Henry constant were used without consideration of the activity coefficients of components. Their model is accurate when the acid gas loading (the mole ratio of CO_2 to amine) is larger than 0.1. Deshmukh and Mather [2] established a stricter model based on the extended Debye-Huckel theory and Edwards' model [3]. In Deshmukh and Mather's model, the activity coefficient is calculated using the electrostatic interaction and short-range interaction contributions, and the fugacity coefficient in the gas phase is calculated by Peng-Robinson equation. Austgen [4] used electrolytic-NRTL model [5] to calculate the activity coefficients of components in the liquid phase of alkanol-amine solution. Li and Mather [6] used the Clegg-Pitzer equation [7] for correlation and prediction of CO_2 solubility in a mixed alkanolamine solution.

In this study, Kent-Eisenberg and Clegg-Pitzer equations for electrolytic mixed-solvent solution were applied also and the equilibrium model of gas absorption in the system of CO_2-MEA-DMAP-H_2O was established. The parameters in Kent-Eisenberg and Clegg-Pitzer equations were carefully selected and obtained through regression. With the parameters derived from gas absorption equilibrium data, solubilities of CO_2 in the mixed amine solutions can be directly predicted.

1.1 Chemical reaction equilibria

There are several chemical reactions, as listed in Table 1, in the liquid phase of the CO_2-MEA-DMAP-H_2O system. All these reactions should be included in the calculation of gas solubility for CO_2 in these systems.

Table 1. Chemical reactions in the liquid phases of the system

Protonation of MEA	$MEA + H^+ \Leftrightarrow MEAH^+$
Protonation of DMAP	$DMAP + H^+ \Leftrightarrow DMAPH^+$
Carbarmate formation for MEA*	$MEA + CO_2 \Leftrightarrow MEACOO^- + H^+$
Dissociation of water	$H_2O \Leftrightarrow H^+ + OH^-$
First grade hydrolysis of CO_2	$CO_2 + H_2O \Leftrightarrow HCO_3^- + H^+$
Second grade hydrolysis of CO_2	$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+$

1.2 Vapor-liquid equilibria

The vapor-liquid equilibrium in the systems involves five molecular components: CO_2, AMP, MEA, DEA and H_2O. The fugacity of a component in the gas phase should be equal to the fugacity in the liquid phase.

The fugacity of CO_2 in the liquid phase can be calculated by the following equation:

$$f_{1(\mathrm{G})} = f_{1(\mathrm{L})} = x_1 \gamma_1 H_1^0 \tag{1}$$

where H_1^0 is the Henry constant of CO_2 in water, γ_1 is the activity coefficient of CO_2 in the liquid phase, with the reference state defined as the infinite dilution concentration of CO_2 in pure water.

The fugacities of H_2O and amines are calculated by the saturated vapor pressure method:

$$f_{i(G)} = f_{i(\mathrm{L})} = x_i \gamma_i P_i^0 \quad (i = 1,2) \tag{2}$$

where P_i^0 is the saturated vapor pressure. The fugacity $f_{i(\mathrm{G})}$ of components in the gas phase can be calculated by Peng-Robinson equation (Peng and Robinson, 1976). And the activity coefficient γ_i of components in the liquid phase can be calculated by Clegg-Pitzer equation. For Kent-Eisenberg, the activity coefficients γ_i of all components are equal to 1.0.

1.3 Clegg-Pitzer model

The excess Gibbs free energy in liquid phase can be calculated by the Clegg-Pitzer equation for electrolytic mixed-solvent solution [7]:

$$\frac{G^E}{RT}=\frac{G^{DH}}{RT}+\frac{G^S}{RT} \tag{3}$$

where the term $\frac{G^{DH}}{RT}$ is Debye-Huckel term for the long distance interaction. It can be expressed as:

$$\frac{G^{DH}}{RT}=-\frac{4A_xI_x}{\rho}\ln(1+\rho I_x^{1/2})+\sum_c\sum_a x_cx_aB_{ca}g\left(\alpha I_x^{1/2}\right) \tag{4}$$

The term $\frac{G^S}{RT}$ stands for the short distance interaction contribution, which includes contributions of all pairs of particles in the solution:

$$\frac{G^S}{RT}=x_I\sum_n x_n\sum_c\sum_a F_cF_aW_{nca}+\sum_{n>}\sum_{n'} x_nx_{n'}(A_{n'n}x_n+A_{nn'}x_{n'}) \tag{5}$$

where subscripts c, a, n and n' represent cation, anion, and neutral species and,

$$x_I=1-\sum_n x_n\ ,\ F_c=2x_c/x_I\ ,\ F_a=2x_a/x_I$$

B, W and *A* are the interaction parameters between particles (molecules and ions) used in the Clegg-Pitzer equation. Activity coefficients of particles in the liquid phase can be expressed as:

$$\ln\gamma_i=\left(\frac{\partial G^E/RT}{\partial n_i}\right)_{T,P,n_{j\neq i}} \tag{6}$$

In the calculation of activity coefficient, the reference state must be taken into account. For H_2O and amines, the reference states in Eq.(7) are the same as those in Eq.(2). But for CO_2 and ions, we use their infinite dilution states in pure water (noted as subscript 1) as the reference state, consistent with the reference state in Eq. (1) and equilibrium constant equations:

$$\ln\gamma_i=\left(\frac{\partial G^E/RT}{\partial n_i}\right)_{T,P,n_{j\neq i}}-\left(\frac{\partial G^E/RT}{\partial n_i}\right)_{T,P,x_1=1.0} \tag{7}$$

1.4 Correlation and prediction of CO_2 solubility in amine solutions

With the thermodynamic model described above, the gas absorption equilibrium for the system CO_2-DMAP-H_2O can be correlated. The interaction parameters in the Clegg-Pitzer equation can be obtained by regression from literature solubility data. The calculated solubility data are in agreement with the experimental ones in Fig. 1, which shows the model is reliable. The model is also applicable to the simulation of MEA-DMAP-H_2O system at all kinds of absorption conditions. Because absorption equilibrium data in the low loading range of CO_2 are important for gas purification and solvent regeneration, the logarithmic coordinates are used in the figure.

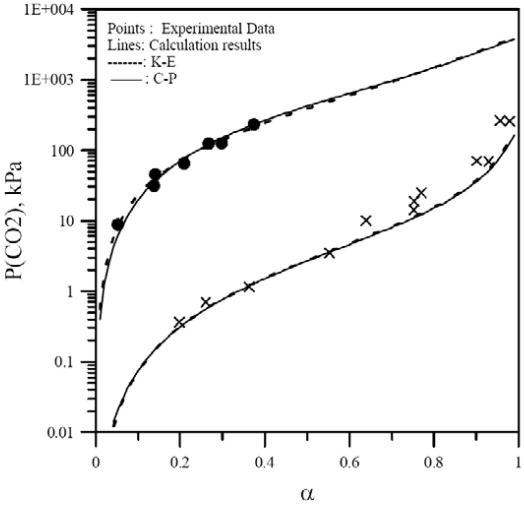

Fig.1 Gas absorption equilibria for CO_2-DAMP (2.5M)-H_2O system at 313.15K and 393.15K. Points: Experimental data; Lines: calculated results with Kent-Eisenberg and Clegg-Pitzer model.

The thermodynamic models can be used for prediction of CO2 solubility in the mixed amine solution MEA-DMAP-H_2O. An example is shown in Fig.2 with the Kent-Eisenberg model for 0%, 5%, 10%, 20% and 30% MEA with total MEA+DMAP of30%.

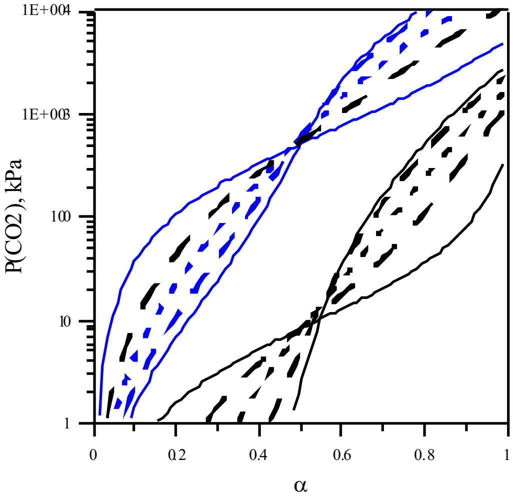

Fig.2 Gas absorption equilibria for CO_2-MEA-DAMP-H_2O system at 313.15K and 393.15K. Lines: predicted results with Kent-Eisenberg model for 0%, 5%, 10%, 20% and 30%MEA with 30% MEA+DMAP.

2 Process simulation and Pilot Plant Measurement

2.1 Pilot Plant Measurement

This experimental scale facility of the CO_2 capture by the reactive absorption was designed and set up in 2007 in our laboratory. Figure 3 is the picture of the experimental scale facility.

Fig.3 Pilot plant facility for CO2 absorption in Tsinghua University.

As shown in Figure 3, the absorber is built at the left of the facility. Its diameter is 0.089m, and the total height is 1.6m, and it's packed with θ cycle random packing with diameter of 5mm. The CO_2 gas mixture, with the flow rate of about 3kg/h-12kg/h and the volume concentration about 10%, entering the absorber from the bottom, and the amine solution (lean solvent), with the flow rate of around 20kg/h-70kg/h and after cooled to 40 ° C by the heat exchanger, entering the absorber from the top, have the liquid-gas mass exchange in the absorber, achieving the absorption process. The desorber is built at the right of the facility. Its diameter is also 0.089m, and the height of the packing section is 1.5m, and it's packed also with θ cycle random packing with diameter of 5mm. The upper part of the desorber is the coil-type water condenser and the bottom of the desorber has a 10KW electrical heater. The amine solution (rich solvent), with the flow rate of around 30kg/h-80kg/h and after pre-heated to 105 °C by the heat exchanger, entering the packing section from the top. After heating, the amine solution evaporates and has the liquid-gas mass exchange in the desorber, achieving the desorption process. Between the absorber and the desorber, there are the heat exchanger and the gas mixing tank. Heat exchanger is used for heat transferring with the lean solvent and the rich solvent, improving the thermal efficiency. The gas mixing tank is used for mixing the two kinds of treated gas which are respectively from absorption and desorption, to obtain the CO_2 gas mixture with the volume concentration about 10%, and to achieve the circulating absorption. Of course, before reaching the steady state, it's necessary to compound the mixed gas by using the pure CO_2 and air. Measuring instruments and computer data collectors are installed at every key points of the whole experimental facility, measuring and collecting the temperature, pressure, flow rates and the CO_2 gas volume concentration during the experiment. The regeneration energy is measured and collected by the digital electrical meter. Consequently, after reaching the steady state, this experimental procedure system is a completely closed loop system.

2.2 Process simulation for CO2 absorption

A simulation program was established based on our earlier works [8]. The thermodynamic models and parameters regressed in this work are used. The simulation results will be compared with the pilot plant measurement data.

Fig.4 shows the simulation results for CO2 absorption with the solution of MEA-DMAP-H2O. With the input of regeneration energy saved by 20% compared with that of 30% MEA solution, the simulation results for CO2 capture percentage are shown with the mixed solution MEA-DMAP-H2O with different concentrations. These results are agreed with the pilot plant measurement results.

To explain the results in Fig.4, the lines of fig.2 should be used. As an activator of absorption kinetics, the concentration of MEA less than 5% should be enough. But at the regeneration partial pressure of 100kPa for CO2 at 120℃, the loading of CO2 is around 0.3 for 5% MEA solution, while at 40℃ the CO2 loading is even lower at the CO2 partial pressure of 1kPa. This means that at the top of absorber, there is no mass transfer space for CO2 absorption, and the CO2 capture percentage is low. The best CO2 capture percentage appears around 8%. Higher MEA concentration will makes more CO2 captured as carbarmate with MEA and leads higher energy consumption.

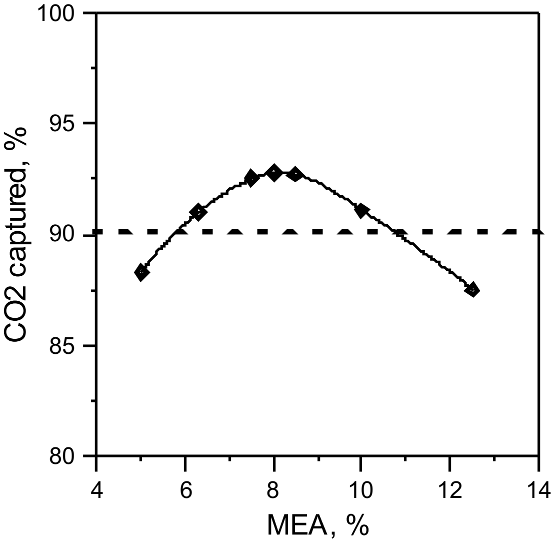

Fig.4 CO2 Capture ratio with energy consumption 20% saved than MEA.

3 Conclusions

Thermodynamic models have been established for calculation of gas solubility of CO_2 in aqueous amine solution with Kent-Eisenberg and Clegg-Pitzer equations as the activity coefficient model. The gas solubilities of CO_2 in MEA-DMAP-H_2O can be predicted directly with equations in which the parameters are obtained by regression of single amine absorption equilibrium data. The process simulation software is established based on gas solubility thermodynamic models. Simulation prediction results are in good agreement with pilot plant experimental ones, which shows that the best concentration of the solvent can save energy consumption with about 20% for CO_2 capture, compared with usual 30% MEA aqueous solution.

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