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Chemical Absorption and Mass Transfer of Greenhouse Gas Carbon Dioxide

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The findings regarding CO_2 emissions and efficient absorption of CO_2 have important implications for controlling the greenhouse effect. This paper describes the preparation of a mixture with mono ethanol amine (MEA) and N-methyldiethanolamine (MDEA) for chemical adsorption of CO_2. This study involves the concentration of mixed MEA/N-MDEA solution and how the mass transfer property of chemical reactions is subject to gas and liquid flows. The findings suggest that the mass transfer and volumetric mass transfer coefficients significantly increase when the liquid flow accumulates, while lets up when the gas flow builds up. If the concentration of MEA climbs up, chemical absorption rate of CO_2 will show a significant boost; while it bumps up a little if the concentration of N-MDEA increases. Here, the Ha quasi-number is introduced into the formula for calculating CO2 absorption volume mass transfer coefficient. The test comparison results show that the average error of the proposed prediction model is only 8.5%, so that it has a better prediction effect. This study provides the clues to chemical absorption of CO_2.

1. Introduction

Recent years have seen rapid development of industrial sphere, posing a sharp consumption for fossil energy (oil, coal, natural gas, etc.), which has led to an increase of CO_2 in atmosphere, thus causing a train of threats to ecological environment, for example, global greenhouse effect and melting glaciers, rising sea levels and global temperature rising (Douglas and Costas, 2005). In this context, how to control CO_2 emissions and reduce the greenhouse effect has so far been challenging in various countries.

In industrial production, a chemical absorption method has always been used to capture CO_2, thanks to its higher absorption rate and more mature technology than the membrane and physical separation methods (Adibi, 2018; Park, Lee and Park, 2013; Mangalapally and Hasse, 2011). It works based on the principle that alkaline substances react with CO_2 to form a stable polymer, thereby achieving the purpose of removing CO_2. By far, there are several methods for chemical absorption of CO_2, mainly including: (1) The alcohol amine process, which has the longest service life, usually uses organic amines including MEA and N-MDEA, etc. These two organic amines have a higher absorption efficiency for CO_2. However, MEA needs to react with CO_2 at a high temperature, it consumes lots of energy in the production. The bicarbonate formed by the reaction of MEA and CO_2 will contaminate the actified solution; the MDEA absorbs CO_2 at a relatively slow rate (Yang et al, 2014; Yang et al, 2014; Lewis et al, 2011; Mccrellis et al, 2016). (2) hot potassium carbonate process, which mainly uses an aqueous solution of potassium carbonate to react with CO_2 to achieve the purpose of absorbing CO_2 (Tang, Fei and Yi, 2011; Atkins et al., 2018). (3) ammonia process, which uses a chemical reaction between ammonium hydroxide and CO_2 to produce non-polluting ammonia carbonate and amine nitrate, and features less corrosivity, easy degradation of reaction products, etc., but has a low CO_2 absorption efficiency, severe escapes of ammonia (Xiang et al, 2013; Derks and Versteeg, 2009; Qin et al, 2010; Zhang and Guo, 2013).

Based on the existing literature, a mixed MEA/N-MDEA solution for chemical absorption of CO_2 has been prepared and applied to the practices. This study involves the concentration of the components and how the mass transfer property of the chemical reaction is subject to the gas and liquid flows, providing the clues to the chemical absorption of CO_2 in the future.

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2. Establishment of calculation model

2.1 Calculation of CO_2 mass transfer coefficient

The tester for the mixed MEA/N-MDEA absorption solution of CO_2 is shown in Fig. 1. In the test, a T-channel is used, and the CO_2 and the mixed MEA/N-MDEA solution enter the tester from the inlets of gas and liquid phases, respectively. Test is conducted at room temperature.
Based on the slug flow theory, a single bubble volume V_B can be expressed as

$$V_{\mathrm{B}} = \pi w^3/6 + 0.9w^2\left(L_{\mathrm{B}} - w\right) \tag{1}$$

Single bubble surface area A_B is

$$A_{\mathrm{B}} = \pi w^2 + \left[2\pi r + 4\left(w - 2r\right)\right]\left(L_{\mathrm{B}} - w\right) \tag{2}$$

Based on the two-film theory, when the input CO_2 has no impurities, the gas film resistance can be ignored in the calculation process. At this time, the mass transfer flux N is

$$N = k_{\mathrm{L}}\left(C_{\mathrm{e}} - C\right) \tag{3}$$

k_L represents the mass transfer coefficient on the liquid side of the gas film; C_e represents the equilibrium concentration of CO_2 in the mixed solution.

$$C_{\mathrm{e}} = \bar{P}He \tag{4}$$

H_e is the correlation coefficient; P is the average pressure. When considering the resistance on the gas side, the mass transfer flux N is

$$N = \frac{1}{A_{\mathrm{s}}}\frac{\mathrm{d}n_{\mathrm{g}}}{\mathrm{d}t} \tag{5}$$

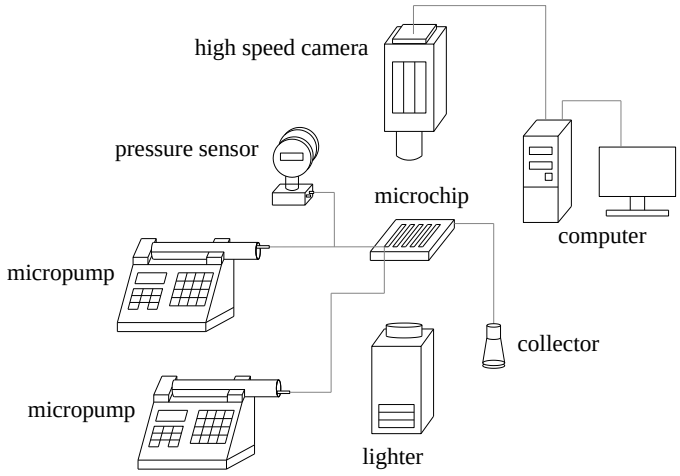

Figure 1: Tester for mixed MEA/N-MDEA absorption solution of CO_2

n_g represents the molar mass of absorbed CO_2. Combine formulas 3 and 5 and perform a series of conversions, then

$$\frac{\mathrm{d}n_{\mathrm{g}}}{\mathrm{d}t} = V_{\mathrm{c}}k_{\mathrm{L}}aC_{\mathrm{e}} \qquad \Delta n_{\mathrm{g}} = V_{\mathrm{c}}k_{\mathrm{L}}aC_{\mathrm{e}}t \tag{6}$$

Within the time t, the molar masses Δn_{in} and Δn_{out} of CO_2 entering the device and the output CO_2 are respectively expressed as

$$\Delta n_{\text{in}} = \frac{P_{\text{in}} V_0 \, ft}{RT} \qquad \Delta n_{\text{out}} = \frac{P_{\text{out}} V_{\text{out}} \, ft}{RT} \tag{7}$$

Then Δn_g can be converted into

$$\Delta n_{\text{g}} = \frac{\left(P_{\text{in}} V_0 - P_{\text{out}} V_{\text{out}} \right) ft}{RT} \tag{8}$$

According to formula 5, the expression of the mass transfer coefficient k_L is

$$k_{\text{L}} = \frac{\left(P_{\text{in}} V_0 - P_{\text{out}} V_{\text{out}} \right) f}{A_{\text{s}} C_{\text{e}} RT} \tag{9}$$

2.2 Volumetric mass transfer coefficient model

The chemical reaction process between CO_2 and mixed MEA/N-MDEA solution is as follows

$$\text{MDEA} + \text{H}^+ \leftrightarrow \text{MDEAH}^+ \tag{10}$$

$$\text{CO}_2 + \text{MDEA} + \text{H}_2\text{O} \leftrightarrow \text{MDEAH}^+ + \text{HCO}_3^- \tag{11}$$

$$\text{MEA} + \text{H}^+ \leftrightarrow \text{MEAH}^+ \qquad \text{MEA} + \text{CO}_2 \leftrightarrow \text{MEACOO}^- + \text{H}^+ \tag{12}$$

$$\text{MEACOO}^- + \text{H}_2\text{O} \leftrightarrow \text{MEA} + \text{HCO}_3^- \tag{13}$$

$$\text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \qquad \text{CO}_2 + \text{OH}^- \leftrightarrow \text{HCO}_3^- \tag{14}$$

$$\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-} \qquad \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^- \tag{15}$$

From the chemical reactions in Formulas 9~14, it is known that N-MDEA does not chemically react with CO_2, and only acts as a catalyst for CO_2 hydrolysis, but MEA does to form aminoglycolic acid. H_a in the chemical reaction process is greater than 3.

The relevant literature proposes different prediction models for the volumetric mass transfer coefficient k_L.

$$Shad_{\text{H}} = 0.084 \, \text{Re}_{\text{G}}^{0.213} \, \text{Re}_{\text{L}}^{0.937} \, Sc_{\text{L}}^{0.5} \tag{16}$$

$$Shad_{\text{H}} = 10.201 \, \text{Re}_{\text{G}}^{0.206} \, \text{Re}_{\text{L}}^{0.218} \, Sc_{\text{L}}^{0.5} \tag{17}$$

$$Shad_{\text{H}} = m_1 \, \text{Re}_{\text{G}}^{m_2} \, \text{Re}_{\text{L}}^{m_3} \, Sc_{\text{L}}^{0.5} \tag{18}$$

Where, Re_g and Re_g are gas-liquid Reynolds numbers for characterizing gas-liquid flow conditions; Sc_L is Simidt number for characterizing liquid phase properties. Based on the relevant studies, this paper takes full account of strengthening effect of CO_2 on mass transfer in the reaction process of mixed MEA/N-MDEA solution. The prediction formula of mass transfer coefficient is corrected by using H_a quasi-number.

$$Shad_{\text{H}} = n_1 \, \text{Re}_{\text{G}}^{n_2} \, \text{Re}_{\text{L}}^{n_3} \, Sc_{\text{L}}^{0.5} Ha^{n_4} \tag{19}$$

3. Test results and analysis

As shown in Fig. 2, the relationship between gas flow and mass transfer coefficient k_L under different liquid flow conditions is shown in the form of curve. The molar masses of fixed MEA and N-MDEA are 1kmol/m^3 and 0.3kmol/m^3, respectively. It is clear from the figure that, when the liquid flow is constant, k_L grows up slowly as the gas flow increases; when Q_G increases from 80 ml/h to 280 ml/h, the average amplification of k_L is only 8%; when the liquid flow gradually builds up, k_L significantly increases; Q_L changes from 20 ml/h to 60 ml/h, and when Q_G is 280 ml/h, k_L goes up by about 57%. It is attributed to the fact that the bubble gets longer and liquid slug volume decreases as the gas flow increases, so that the mass transfer efficiency from the liquid film to the liquid slug declines. For this reason, k_L increases less; when the liquid flow bumps up, the bubble

shortens, while liquid slug volume increases, so that the mass transfer efficiency from the liquid film to the liquid slug is improved. In other way, k_L greatly increases. It can also be observed from the figure that, when the Q_L takes lower value, Q_L presents a very significant effect on the increase of k_L; when Q_L takes a higher value, its effect on the increase of k_L gradually decreases.

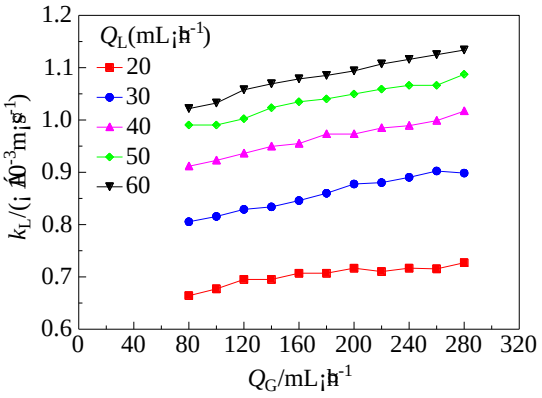

Figure 2: Relationship between gas flow and mass transfer coefficient k_L under different liquid flow conditions

As shown in Fig. 3, the relationship between gas flow and volumetric mass transfer coefficient k_La under different liquid flow conditions is shown in the form of curve. The volumetric mass transfer coefficient k_La grows up rapidly with the increase of Q_G and then eases up. When Q_G>220 ml/h, k_La keeps constant. When the gas flow builds up, the specific surface area of the bubble also increases gradually, so does the volumetric mass transfer coefficient k_La; when the gas flow further increases, the specific surface area of the bubble tends to decrease, k_La basically remains unchanged. When the gas flow is lower, k_La is substantially unaffected by the liquid flow.

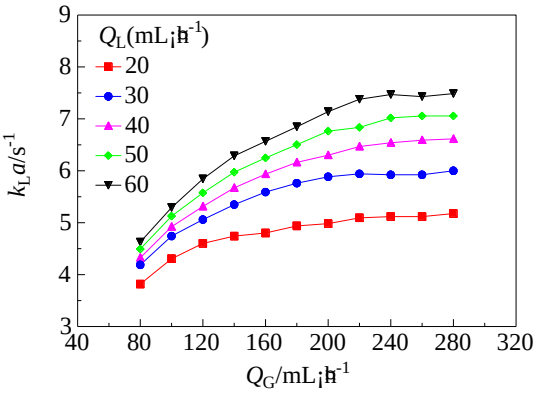

Figure 3: Relationship between gas flow and volumetric mass transfer coefficient k_La under different liquid flow conditions

Further, we discuss how the mass transfer coefficient k_L and volumetric mass transfer coefficient k_La are subject to the concentration of MEA. The test results are shown in Fig. 4. It is observed that, when the content of MEA in the mixed solution increases, k_L and k_La all significantly increase, due to the fact that the increase of MEA will cause the reactant concentration to build up, promoting the chemical reaction to move toward the reaction product with lower concentration. In this case, the bubble volume rapidly decreases, and the number of bubbles remarkably builds up, thereby strengthening the mass transfer property.

As shown in Fig. 5, we know about how the mass transfer coefficient is subjected to change with the increase in the concentration of N-MDEA. Similar to the MEA, since the N-MDEA can be used as a catalyst for the reaction between CO_2 and MEA, the mass transfer coefficient tends to increase with the faster reaction. From Fig. 4 and Fig. 5, it is known that N-MDEA has less effect on the mass transfer and volumetric mass transfer coefficients than the MEA.

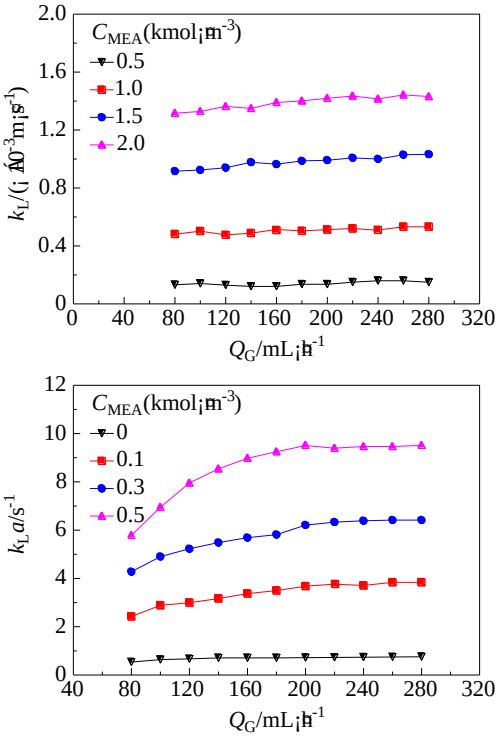

Figure 4: Effect of MEA on mass transfer and volumetric mass transfer coefficients k_L and k_La

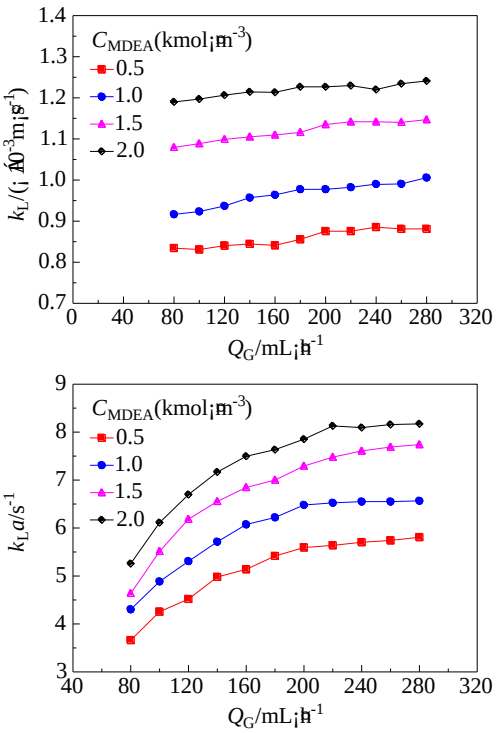

Fig. 5 Effect of N-MDEA on mass transfer and volumetric mass transfer coefficients k_L and k_La

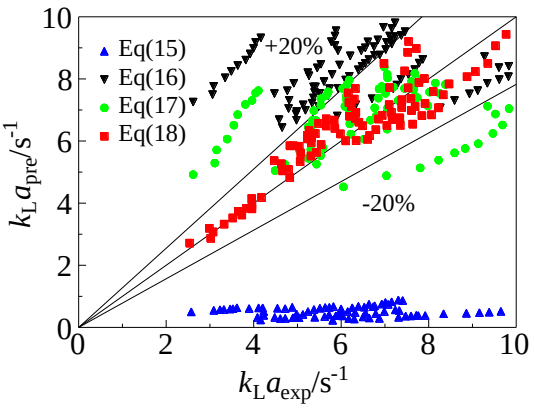

Figure 6: Comparison results between theoretical value and test value of volumetric mass transfer coefficient

The volumetric mass transfer coefficient is calculated according to the formulas 15 – 18. Then the result is compared with the value available from the test, as shown in Fig. 6. It is known from the figure that the comparison results obtained using formulas 15 - 17 have a higher error since both of them do not consider the effect of volume change when MEA and CO_2 react with each other, and worse, formula 17 ignores the amplitude effect of the mixed solution on the chemical reaction rate. Formula 18 proposed in this paper can fully involve this amplitude effect due to the introduction of *Ha* quasi-number. As shown above, the average error between the theoretically calculated value from this proposed algorithm and the test value is only 8.5%, much lower than the corresponding values from the other three formulas, which shows that it has the best prediction effect.

4. Conclusion

In this paper, a mixed MEA/N-MDEA absorption CO_2 solution is prepared and applied for chemical adsorption of CO_2. This study also involves the concentration of the mixed MEA/N-MDEA solution and how the mass transfer properties of chemical reactions are subject to the gas and liquid flows. Here are some conclusions:
(1) When the liquid flow builds up, the mass transfer and volumetric mass transfer coefficients increase greatly; when the gas flow gets strong, both increase less.
4.2 If the concentration of MEA bumps up, the chemical absorption rate of CO_2 significantly increases; while the concentration of N-MDEA rises up, the chemical absorption rate of CO_2 lessens.
4.3 The Ha quasi-number is introduced into the formula for calculating chemical absorption volume mass transfer coefficient of CO_2. The test comparison results show that the average error of the proposed prediction model is only 8.5%, so that it has a better prediction effect.

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