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PRESSURE SWING ABSORPTION OF CARBON DIOXIDE IN DMEPEG SOLUTIONS

The mass transfer rates during CO_2 absorption and desorption from DMEPEG solutions were measured at a temperature ranging from 293.15 to 323.15 K in a baffled agitated reactor with a flat gas–liquid interface operating in a batchwise manner. Based on the measured values of pressure changes, the desorption rate was determined and compared with the absorption rate at the same driving force. Two distinct mechanisms of desorption were observed. The volumetric mass transfer coefficients for the bubbling desorption were determined from the measured overall and the diffusive desorption rates, and were correlated by a power relationship of supersaturation, the Reynolds and Weber numbers.

1. INTRODUCTION

The removal of acid gases, such as CO_2 and H_2S, from natural, refinery and synthesis gas streams by absorption with the use of different solvents is a significant operation in gas processing. Another important application of absorption-based technologies is CO_2 separation from flue gases, which takes place in many industries, including fossil-fuel power plants, steel and cement production, etc. According to the Intergovernmental Panel on Climate Change (IPCC), CO_2 is recognized as a major man-made greenhouse gas contributing to the global warming. The problem of the increasing emission of CO_2 has led to the international commitment to control this emission by all developed countries. The idea of CO_2 sequestration, which includes its capture and storage in underground rock formations, has progressed steadily over the past ten years. It is claimed that this solution could play an important role in solving the problem of the increasing emissions of greenhouse gas. The physical or chemical absorptions of CO_2 are generally recognized as the most efficient technologies of its separation at present. The most commonly used physical solvents are:

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methanol at low temperatures (Rectisol, Lurgi GmbH), propylene carbonate (Fluor-Solvent), *N*-methyl-2-pyrrolidone (Purisol, Lurgi GmbH) and dimethyl ether of polyethylene glycol (Selexol, Norton Chem) [1]. The common feature of these processes is that they are carried out in absorber-stripper mode, requiring two separate steps in CO_2 separation. This technology is known as a *pressure swing absorption process*, where low pressure allows CO_2 to desorb and the solvent to regenerate. Although in many practical situations the operational and capital costs of the desorption column may be greater than those of the absorption column, the studies devoted to desorption are not as numerous as those concerning absorption, and there is little information in the literature on the design aspects of desorption columns. The problem of predicting the desorption rates arises when the process is accompanied by the bubble nucleation in the liquid bulk. This phenomenon completely changes the hydrodynamic conditions in the liquid phase, and the diffusive mass transfer equations cannot describe the process rate in a way analogous to that of absorption.

Research on the measuring and calculation of the desorption rate under dynamic conditions accompanied by a typical mass transfer equipment is very limited, as compared to theoretical considerations of the bubble nucleation from quiescent supersaturated liquid solutions [2]. Only a few references report the quantitative results concerning the rates of physical gas desorption accompanied by the bubble nucleation from agitated liquid. WEILAND et al. [3] investigated the desorption of CO_2 from supersaturated aqueous solutions using a stirred cell apparatus. HIKITA and KONISHI [4] studied the same gas–liquid system in a baffled agitated vessel operating in a continuous manner. Recent literature sources contain no references to the problems under consideration.

The main scope of this paper was, therefore, to develop a reliable method for performing experiments of a gas desorption from supersaturated solutions initiated by the pressure release under dynamic conditions. The purpose of these measurements was to determine the influence of temperature, stirring speed and supersaturation of the solution on the CO_2 desorption rate from saturated dimethyl ether of polyethylene glycol solutions. DMEPEG 250 ($CH_3(CH_2CH_2O)_nCH_3$ – 250 kg·kmol^{-1} is an average molecular weight), commonly known as a Selexol solvent, is an important absorbent in gas purification technologies [1].

2. MATERIAL AND METHODS

Apparatus. The measurements were performed in the heat flow reaction calorimeter (Chemical Process Analyser, ChemiSens AB, Sweden), which is a fully automated and computer-controlled stirred reactor vessel with a possibility of an on-line measurement of thermal power developed by the process. Its heart is a mechanically agitated stainless steel/glass reactor with an effective volume of 250 cm^3. The schematic diagram of an experimental set-up is shown in figure 1. The reactor was equipped with four stainless steel baffles and an impeller stirrer. While in use, it is submerged in the thermostating liquid bath. A Peltier element mounted inside the bottom of the reactor serves as an efficient heating and cooling device, and keeps a temperature constant with an accuracy of ±0.1 K. The absolute pressure was measured by a pressure transducer mounted on the reactor flange. The measurement accuracy of the digital pressure transducer was 0.1% of the full range of 0–1.5 MPa. A separate tube on the top flange allows us either to evacuate the cell or to introduce the gas into the reactor.

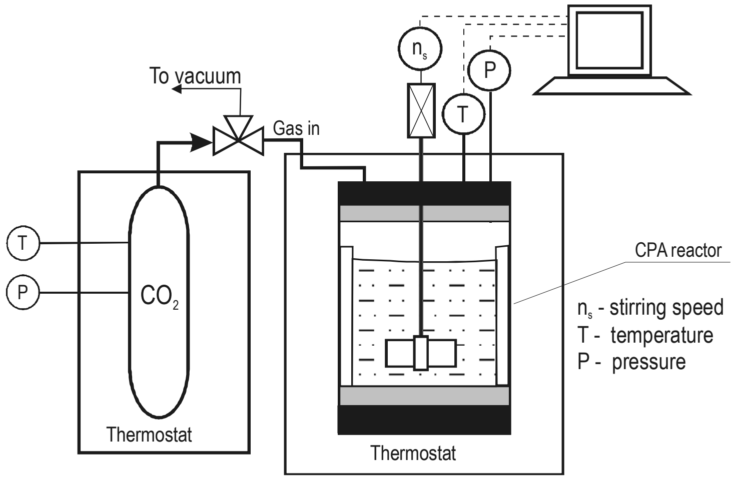

Fig. 1. Schematic of the experimental set-up

Procedure. Each experiment consisted of two steps, including the absorption and the subsequent desorption, initiated by the pressure release. 100 cm^3 of the solvent was introduced into the reactor. The gas feed lines and the content of the reactor were then vacuumed. When the vacuum was shut off, the system was allowed to come to the vapour–liquid equilibrium under stirring conditions at a given temperature. At this equilibrium, the stirring was stopped for a moment. Then, a controlled amount of acid gas was introduced into the upper part of the cell from the thermostated high-pressure gas reservoir through the insulated tubing. The total pressure at this state was recorded as the initial pressure (P_i). Then, the process was initiated by switching on the stirrer at the desired mixing speed. Pressure decay versus time was recorded as a result of the CO_2 absorption through the horizontal gas–liquid interface until the equilibrium state (P_f) was reached. This total pressure change ($P_i - P_f$) was necessary for calculating the equilibrium CO_2 solubility in the liquid expressed by Henry's law constant k_H (MPa·m^3·kmol^{-1}).

The desorption was conducted in the similar manner. The stirring was stopped for a moment while the system was rapidly decompressed via a release valve in order to reach the required supersaturation of the solution. The resulting supersaturation of the system subsequently led CO_2 to release from the liquid. The corresponding pressure increase was recorded, up to another gas–liquid equilibrium state. During the experiment, the CO_2 concentration in the solution was decreasing as bubbles were formed, which resulted in a decrease in the driving force and a consequent supersaturation of the solution. The relative supersaturation σ was defined by the following equation:

$$\sigma = \frac{c_{AL} - c_{AL}^*}{c_{AL}^*}, \tag{1}$$

where c_{AL}^* is the CO_2 concentration at the gas–liquid interface and c_{AL} is the gas bulk concentration. The equilibrium concentration c_{AL}^* is linearly related to CO_2 partial pressure (p_A) through Henry's law as follows:

$$c_{AL}^* = \frac{p_A}{k_H}. \tag{2}$$

By the CO_2 mass balance in the reactor, the continuous measurement of the pressure changes was related to the instantaneous rate of desorption, both CO_2 concentrations (c_{AL}^* and c_{AL}) and supersaturation σ. In these calculations, it was assumed that the initial CO_2 liquid concentration during desorption was known and equal to the final (equilibrium) CO_2 concentration reached during absorption.

The experiments were carried out at three temperatures: 293.15, 323.15 and 333.15 K. Various stirring speeds were applied: 100, 150, 200, 250 min^{-1}. The pressure change during absorption or desorption ranged from 0.1 to 1 MPa. The chemicals employed, i.e. CO_2 (99.995 vol % pure) and DMEPEG 250 (Fluka, 98.5 mass % pure), were of analytical reagent grade and used without any further purification.

The mass balance equation for the gas component entering the liquid phase predicts a linear dependence of the gas absorption rate ($N_{A,\text{abs}}$) on the concentration driving force, and has the following form

$$N_{A,\text{abs}} = (k_L a) V_L (c_{AL}^* - c_{AL}), \tag{3}$$

where $k_L a$ is the volumetric mass transfer coefficient in the liquid phase and V_L stands for the liquid volume. For the gas desorption, a similar equation can be written

$$N_{A,\text{des}} = (k_L a)_{\text{des}} V_L (c_{AL} - c_{AL}^*), \tag{4}$$

where $(k_L a)_{\text{des}}$ is the volumetric mass transfer coefficient for a gas desorption. For relatively low supersaturations occurring in the low bubbling region, the coefficient

$(k_La)_{\mathrm{des}}$ can be divided into the contributions of the diffusive mass transfer through the flat gas–liquid interface and the interface of the bubbles generated in the liquid, according to

$$(k_La)_{\mathrm{des}} = k_La + k_La_b\,. \tag{5}$$

The volumetric mass transfer coefficient k_La_b representing the contribution of generated bubbles to the process rate could be thus determined from the experimental absorption rate and overall desorption rate by combining equations (3)–(5). During an every desorption run, several instantaneous values of k_La_b were evaluated for the decreasing values of supersaturation of the solution as the process was carried out under unsteady conditions.

For the analysis and correlation of the experimental data, the physicochemical properties of the system in the temperature range applied were required. Most of them were collected from an available literature [5]–[6], while viscosity and surface tension of the solvent were independently measured. Viscosities were measured with a CVO 120 rheometer (Bohlin Instruments). Surface tension of the solvent was determined by a ring method using Kruss K-100 tensiometer.

3. RESULTS AND DISCUSSION

A typical example of mass transfer rates for CO_2 desorption from supersaturated DMEPEG solutions with different stirring speeds is shown in figure 2, where the process rate is plotted against the concentration driving force. For the comparison, the corresponding linear relation for the absorption process is plotted by dashed lines. It can be seen that higher desorption rates were achieved with higher stirring speeds. A higher stirring speed produces greater turbulence and promotes the gas bubbles detachment from the heterogeneous surface, which are contributing factors to the solvent regeneration rate. As may be noticed, there exist two different regions with respect to the effect of the driving force. In the initial stage of desorption, which corresponds to the high values of supersaturation, the desorption rate deviates upward from the absorption rate, represented by the dashed line. In this region, the bubble nucleation was visually observed through the glass walls of the reactor. The bubble nucleation in the liquid phase increases the turbulence in that phase and results in the subsequent increase of mass transfer coefficient and interfacial area. The rate of desorption observed under bubbling conditions is significantly faster than the absorption rate for the same driving force. This observation is in agreement with the previous findings [3]–[4]. Then, as the driving force and the substantial supersaturation decrease while approaching the equilibrium state, the rate of CO_2 desorption clearly decreases and becomes well represented as a linear function of the driving force similarly to the absorption process. In this region, designated as diffusive or quiescent desorption, the mass transfer takes place by a diffusive mechanism and the absorption model can be successfully used to predict the desorption rates. Consequently, the volumetric mass transfer coefficient $(k_La)_{\text{des}}$ in the quiescent desorption is equal to the relevant coefficient k_La in the absorption process.

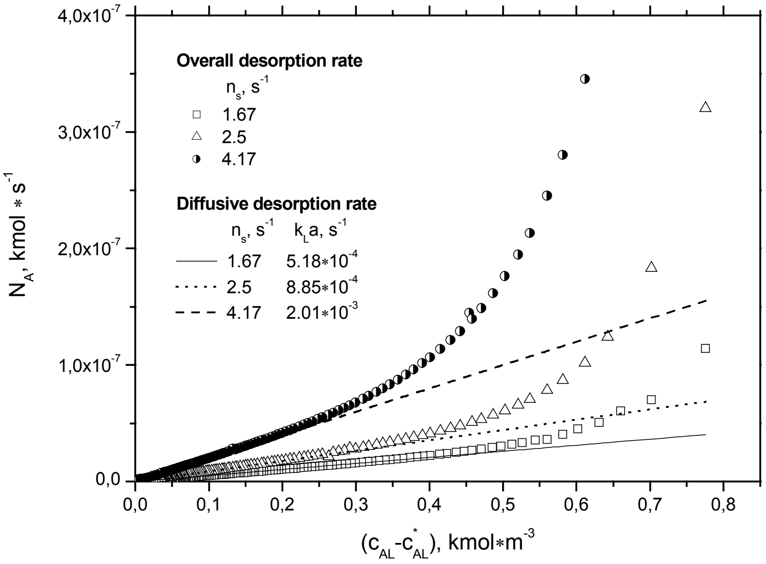

Fig. 2. Effect of stirring speed on CO_2 desorption rate at 293.15 K

The point of transition from bubbling to quiescent desorption can be determined from figure 2 as the value of the mass transfer driving force at which the desorption rate approaches absorption rate. As evidenced by the results presented in figure 2, the inception of bubbling is not sharp and takes place smoothly. The transition concentration driving force between bubbling and diffusive desorption decreased slightly with the increase of the stirring speed. The increased turbulence in the system due to higher stirring speeds enhances the desorption rate and lowers the threshold for bubbling desorption. For higher stirring speeds, the bubbles find it easier to detach themselves from the walls of the vessel and its bottom. As discussed above, the effect of stirring speed is thus to promote the bubble heterogeneous nucleation.

Figure 3 shows the selected data of volumetric mass transfer coefficients k_La_b over a wide range of operational conditions, including different temperature and stirring speed versus supersaturation value. The experimental results show that k_La_b increases with the increase of supersaturation of the solution, temperature and stirring speed. According to the analysis of the experimental data, an empirical correlation of k_La_b data was derived using the method of dimensional analysis. The mass transfer coefficient can be related to other variables by the following functional equation:

$$k_L a_b = f(\sigma, n_s, d_s, \rho_L, \eta_L, \gamma_L)\,, \tag{6}$$

where n_s is the stirring speed, d_s – the stirrer diameter, ρ_L, η_L, γ_L stand for the liquid density, viscosity and surface tension, respectively. Dimensional analysis leads to the following equation:

$$\frac{k_L a_b}{n_s} = B Re^a We^b \sigma^c\,, \tag{7}$$

where the Weber and Reynolds numbers are defined by:

$$Re = \frac{n_s d_s^2 \rho_L}{\eta_L}\,, \tag{8}$$

$$We = \frac{\rho_L n_s^2 d_s^3}{\gamma_L}\,. \tag{9}$$

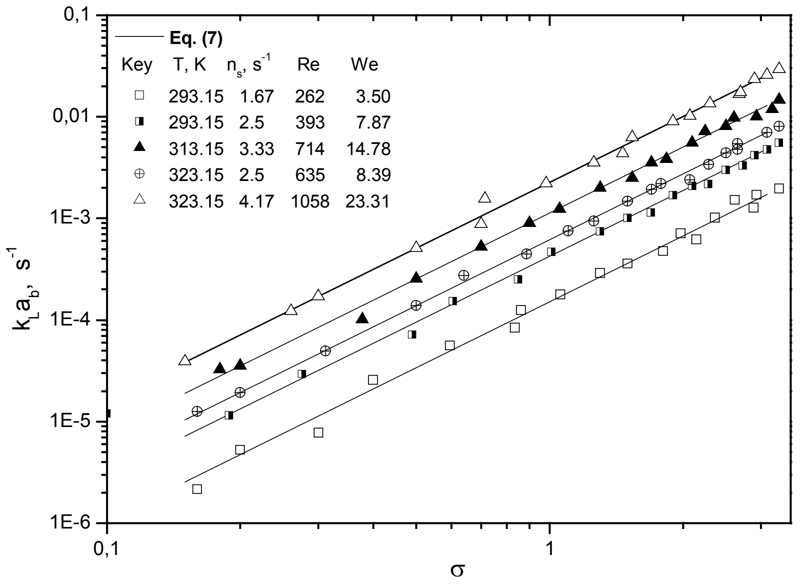

Fig. 3. Volumetric mass transfer coefficient $k_L a_b$ under different operational conditions as a function of supersaturation

A multiple least-square regression of 156 experimental data points in equation (7) gave the following results: $B = 7.8 \cdot 10^{-7}$, $a = 0.72$, $b = 0.43$, $c = 2.12$. The straight lines in figure 3 represent the fitted relations for $k_L a_b$ with a correlation coefficient (r^2) of 0.91, with the standard deviation (SD) of 16.4% for the absolute relative error (ARE).

The empirical correlation developed in the paper corresponds reasonably well with the wide variety of experimental data, with the mean deviation (MD) of 19.8% for the absolute relative error.

The ranges of dimensionless numbers in the above equation are:

$$3.50 < We < 23.31, \quad 262 < Re < 1058, \quad 0 < \sigma < 4.$$

The correlation can predict the values of the volumetric mass transfer coefficient for different physicochemical properties of the liquid under different operational conditions. The capability of k_La_b prediction will be further examined using different gas–liquid systems. It should be noted, however, that the correlation proposed is specific to the similar reactor types used in this study.

4. CONCLUSIONS

The rates of CO_2 desorption from supersaturated DMEPEG solutions were investigated in an agitated reactor under batchwise conditions. The results obtained show that the CO_2 desorption rate increases with an increase of the stirring speed and supersaturation of the solution. In the non-bubbling region of the process, desorption can be regarded as reverse to absorption. The desorption rate under bubbling conditions was faster than that of diffusive desorption. The overall desorption rate measured was divided into the contributions of the interface of the free surface of the liquid (diffusive desorption) and the interface of generated bubbles. The volumetric mass transfer coefficients for the bubbles k_La_b were determined in the wide range of operational conditions and correlated as a function of supersaturation of the solution, the Reynolds and Weber numbers. The correlation proposed is found to be consistent with the available experimental results within ±20%. The present study has provided an improved understanding of the desorption process and its quantitative description, which would be helpful for the design considerations of the regeneration step in several industrial processes for separating CO_2 based on physical solvents.

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ABSOPRCJA I DESORPCJA CO_2 W ROZTWORACH DMEPEG

Wykonano badania szybkości absorpcji i desorpcji CO_2 w rozpuszczalniku DMEPEG 250 (eter dimetylowy polietylenoglikolu), który jest stosowany komercyjnie w technologii Selexol do usuwania CO_2 z gazów odlotowych. Badania prowadzono w reaktorze zbiornikowym z mieszadłem, w zakresie temperatur 293.15–323.15 K. Podczas desorpcji CO_2 z przesyconych roztworów DMEPEG zaobserwowano wystąpienie obszaru desorpcji dyfuzyjnej i nukleacyjnej. Porównanie szybkości desorpcji w obu obszarach pozwoliło wyznaczyć objętościowy współczynnik wnikania masy dla desorpcji nukleacyjnej, k_La_b. Otrzymane wartości skorelowano za pomocą równania kryterialnego jako funkcję przesycenia roztworu, liczb Reynoldsa i Webera.