EXPERIMENTAL STUDY OF THE ABSORPTION OF ACID GASES IN POROUS PARTICLES IMPREGNATED WITH AQUEOUS ALKANOLAMINE SOLUTIONS

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(Received 16 January 1994; accepted for publication 19 April 1994)

Abstract—In the present study the absorption behaviour and the equilibria of CO$_2$ and H$_2$S in porous $\alpha$- and $\gamma$-alumina particles impregnated with inert solutions and alkanolamine solutions were investigated. From the equilibrium data it could be concluded that for CO$_2$ and H$_2$S also adsorption on the internal surface of liquid filled $\gamma$-alumina particles occurs. The experimental absorption rate data were compared with theoretical data obtained with an absorption model, which describes the mass transport accompanied by chemical reaction in porous particles impregnated with reactive solutions. The CO$_2$ and H$_2$S alkanolamine data necessary for this model were taken from literature, while the tortuosity and porosity were experimentally determined. The model could describe the experimentally observed absorption rates satisfactorily. Discrepancies mainly occurred for the process conditions where equilibrium was approached. These deviations probably must be attributed to the calculation of the equilibrium compositions (no correction for non-idealities) and the accuracy of the available thermodynamic data.

1. INTRODUCTION

Various gas-liquid processes are successfully applied in industry to separate components from gas mixtures. The absorption of the gaseous compounds in the liquid can be purely physical, but often chemically reactive species are added to the liquid. Chemically reactive components in the liquid increase the gas absorption capacity while simultaneously an enhancement of the gas absorption rate may occur. Both phenomena contribute to a better performance of the separation process. A well-known class of chemically reactive liquids applied in these processes are aqueous alkanolamine solutions which are used for the removal of CO$_2$ and/or H$_2$S from industrial gases.

Besides the solvent, the gas-liquid contactor also influences the efficiency of a separation process. Usually, a tray column or a packed column is used to realize the gas-liquid contact, however, on laboratory scale special reactors were developed to optimize specific absorption processes. Examples of such reactors are the cyclone spray scrubber and the centrifugal reactor (Versteeg and van Swaaij, 1987; Schrauwen and Thoenes, 1988; Bosch et al., 1989b). These special reactors often have specific drawbacks in comparison to traditional absorbers (Bosch et al., 1989b), but in some situations they might be advantageous. Especially, for the selective removal of H$_2$S from natural gas which also contains CO$_2$, the aforementioned reactors offer promising possibilities.

A new method for the continuous separation of gases with reactive liquids was proposed by Hogendoorn et al. (1993). Their idea was to impregnate the reactive absorption liquid in small porous particles which can be fluidized. The porous particles are used as liquid carriers, in which diffusion and simultaneous reaction of the gaseous components take place. Hogendoorn et al. (1993) showed that, from a theoretical point of view, impregnated small particles can effectively be used to remove gases selectively. By circulating the impregnated particles from an absorber to a desorber unit a new type of continuous separation process can be obtained. The particles can be kept in motion by various kinds of gas-solid contactors, like e.g. a bubbling fluidized bed, a riser or a trickle flow reactor.

Before studying the absorption behaviour in these types of reactors experiments in a model reactor where the particles are fixed are preferred. The problems involved with the handling of the flowing solid phase can be avoided and the absorption characteristics in the particles can be studied in more detail.

Physical absorption in liquid impregnated particles accompanied by adsorption on the internal surface of the particles has both theoretically and experimentally been studied by several authors (Edeskuty and Amundson, 1952; Ma and Evans, 1968; Komiyama and Smith, 1974a, b; Leyva-Ramos and Geankoplis, 1985; Lee et al., 1993). In the experimental studies the particles were suspended in a liquid which was stirred to reduce possible external mass transfer resistances. A pulse of a fluid tracer was added to the suspension and the tracer concentration was continuously monitored. For systems with linear adsorption isotherms effective diffusion coefficients could be derived by fitting the experimental results to analytical solutions (Crank, 1976; Komiyama and Smith, 1974a, b; Prasher and Ma, 1977). Komiyama
and Smith (1974a, b) concluded that surface adsorption and diffusion significantly increased the absorption rate if the tracer in the liquid adsorbs on the internal surface of the particles. Prasher and Ma (1977) supposed that a dynamic equilibrium existed between the adsorbed molecules and the liquid in the pore. However, according to Prasher and Ma (1977), surface diffusion was not likely to occur in liquid filled porous particles because the adsorbed molecule usually is surrounded by a large number of solvent molecules. Therefore, the so-called “hopping mechanism” necessary for the surface transport cannot occur. By assuming immobilized adsorbed molecules, a dynamic equilibrium and a linear adsorption isotherm, they found that the diffusivity of (relatively large) tracer molecules in the liquid in the pores was sterically hindered and decreased with the ratio of the average pore radius to the solute molecular radius. Unfortunately, theoretical approximations were used to estimate important parameters like the molecular diffusivity of the tracer in the liquid and the tortuosity of the porous material.

The present contribution verifies whether the model proposed by Hogendoorn et al. (1993) can be used to describe the experimentally observed absorption rates of CO₂ and H₂S in porous particles impregnated with reactive alkanolamine solutions. Contrary to the absorption rate experiments presented in literature the absorbed component in the present study was not a liquid but a gas. Absorption rate experiments were carried out with large \( \gamma \)- and \( \gamma \)-alumina particles. The \( \alpha \)-alumina material was chosen because in many situations it can be considered as chemically inert, while \( \gamma \)-alumina was chosen because of the frequent application in fluidization processes. The alkanolamines used were, with increasing reaction rate towards CO₂, respectively, MethylDiEthanolAmine (MDEA), DiEthylMonoEthanolAmine (DEMEA) and MonoEthanolAmine (MEA). The reaction rate of H₂S with all three alkanolamines can be considered instantaneous with respect to mass transport.

Physical absorption experiments of CO₂ and N₂O in particles impregnated with non-reactive liquids were carried out to obtain the tortuosity of the porous particles. N₂O is often used to estimate the diffusivity and solubility of CO₂ in reactive liquids by means of the well accepted “N₂O–CO₂” analogy (Laddha et al., 1981).

Also equilibrium experiments were carried out and compared with the data from literature for the homogeneous liquid system. In this way the interaction of the gases with the liquid support could be investigated.

2. THEORY

2.1. Model description

If a gaseous reactant A absorbs in a liquid filled porous sphere, where it reacts with component B according to the reaction

\[ A + \gamma_B B \rightarrow [\gamma_a C + \gamma_d D] \quad \gamma_B > 0; \gamma_a \text{ and } \gamma_d \leq 0 \]  

with the kinetics

\[ R_A = k_{n,m}[A]^n[B]^m - k_{p,A}[C]^p[D]^q \]  

the mass balance for each component can be described by (Hogendoorn et al., 1993):

\[ \frac{\partial \Gamma_i}{\partial t} + \frac{\partial \Gamma_i}{\partial r} \left( r^2 \frac{\partial \Gamma_i}{\partial r} \right) = e_{p,i} R_A, \quad i = A, B, C \text{ or } D. \]  

If the gas A adsors on the internal surface of the particle and forms \( \Gamma_{ads} \), this component must be incorporated in the model. If it is assumed that the adsorption rate is instantaneously fast and that A is reversibly adsorbed, the adsorption isotherm describes the relation between A and \( \Gamma_{ads} \) at any point and time inside the particle. Usually, the adsorption isotherm can be represented by a Langmuir adsorption isotherm, which is given by

\[ [A]_{ads} = \frac{c_2 [A]}{1 + c_1 [A] c_2}. \]  

The dimension of \([A]_{ads}\) is generally mol m⁻² surface, but in the present model it seemed more convenient to define \([A]_{ads}\) as the number of moles adsorbed per unit pore volume. Herewith the dimensions of all components are identical which results in a straightforward interpretation of the equilibrium experiments. Component \( \Gamma_{ads} \) is incorporated in the mass balance for A which is now described by eq. (5):

\[ \frac{\partial [A]}{\partial t} + \frac{\partial [A]_{ads}}{\partial t} - \frac{D_a}{q r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial [A]}{\partial r} \right) + \frac{D_{a,ads}}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial [A]_{ads}}{\partial r} \right) = R_A. \]  

The boundary and initial conditions for the liquid filled particle are given by relations (4) and (6)–(9).

\[ [i]_{r=0} = \text{constant}, \quad 0 < r < r_1, \quad i = A, B, C \text{ or } D \]  

\[ [A]_{r=1} = \text{m}[A]_o \]  

\[ \frac{\partial [i]}{\partial r} \bigg|_{r=r_1} = 0, \quad \text{non-volatile components B, C and D} \]  

\[ \frac{\partial [i]}{\partial r} \bigg|_{r=0} = 0, \quad i = A, B, C \text{ or } D. \]  

If the reaction rate is infinitely fast in comparison with the diffusion in the particle, the balance for component A is, for all stoichiometric coefficients equal to 1, given by

\[ \frac{\partial [A]}{\partial t} + \frac{\partial [A]_{ads}}{\partial t} + \frac{\partial [C]}{\partial t} = \frac{D_a}{q r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial [A]}{\partial r} \right) + \frac{D_{a,ads}}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial [A]_{ads}}{\partial r} \right) + \frac{D_c}{q r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial [C]_{ads}}{\partial r} \right) \]
and for component D and B by
\[
\frac{\partial[D]}{\partial t} - \frac{\partial[C]}{\partial t} = \frac{D_d}{q r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial[D]}{\partial r} \right) - \frac{D_c}{q r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial[C]}{\partial r} \right)
\tag{11}
\]
\[
\frac{\partial[B]}{\partial t} + \frac{\partial[C]}{\partial t} = \frac{D_b}{q r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial[B]}{\partial r} \right) + \frac{D_c}{q r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial[C]}{\partial r} \right).
\tag{12}
\]

Because equilibrium is established at any time and place within the liquid in the particle the concentration of component C is calculated according to relation (13):
\[
K = \frac{[C][D]}{[A][B]}. \tag{13}
\]
The boundary conditions for components B and D become
\[
D_b \frac{\partial[B]}{\partial r} \bigg|_{r_1} + D_c \frac{\partial[C]}{\partial r} \bigg|_{r_1} = 0 \tag{14}
\]
and
\[
D_b \frac{\partial[D]}{\partial r} \bigg|_{r_1} - D_c \frac{\partial[C]}{\partial r} \bigg|_{r_1} = 0. \tag{15}
\]

During the experiments the particles are present in a closed reactor which is initially evacuated. Next the vapour pressure of the liquid in the particles is allowed to establish. At \( t = 0 \) s pure gas is added instantaneously to a partial pressure \( P_0 \). If it is assumed that the ideal gas law is applicable, the pressure decrease is calculated with the following mass balance:
\[
\frac{V_s \partial P}{RT \partial t} = -J \partial a_s V_{\text{tot}}, \tag{16}
\]

in which the specific contact area for spheres is expressed by
\[
a_s = \frac{3r_s}{r_1} \tag{17}
\]
and the flux \( J \) is for a finite rate reaction given by
\[
J = D_s \frac{\varepsilon_p \partial[A]}{\partial r} \bigg|_{r_1} + \varepsilon_p D_{a,ads} \frac{\partial[A]_{ads}}{\partial r} \bigg|_{r_1} \tag{18}
\]
while for an infinitely fast reaction the flux \( J \) is given by relation (19):
\[
J = D_s \frac{\varepsilon_p \partial[A]}{\partial r} \bigg|_{r_1} + \varepsilon_p D_{a,ads} \frac{\partial[A]_{ads}}{\partial r} \bigg|_{r_1} + D_c \frac{\partial[C]}{\partial r} \bigg|_{r_1} \tag{19}
\]
The initial condition of eq. (16) is given by
\[
P_{t=0} = P_0. \tag{16a}
\]
Equation (16) can be solved simultaneously with the micro balances for the components in the particle to obtain the theoretical time–pressure curve (see Hogendoorn et al., 1993).

### 2.2. Particle geometry

In the model description of Section 2.1 it is assumed that the particles are spherical. However, the particles used in the experimental study of the gas absorption rate were cylindrical with a length to diameter ratio of about 1.

Ma and Evans (1968) presented theoretically calculated dimensionless time–accumulation curves for physical absorption in particles of various shapes. From their work it can be concluded that particles with the same volume to surface ratio show, especially at low dimensionless accumulations, practically the same absorption rate. The curves for cylinders, with a length to diameter ratio of 1, and spheres nearly coincide over the entire absorption period. The same phenomenon is known for catalytic first-order irreversible reactions. The analytical degree of utilization for particles with the same volume to surface ratio is, especially at high Thiele moduli, nearly identical (Aris, 1957).

Therefore, in the present study the cylindrical particles were approximated by a sphere with the same volume to surface ratio. For cylinders with a length to diameter ratio of 1 this means that the cylinder can be approximated by a sphere with an identical radius. Possible discrepancies between the theoretical time-pressure curves for the cylindrical and spherical geometry are expected to be small and will probably occur only at intermediate to high dimensionless accumulations.

### 2.3. Reaction scheme

If CO₂ absorbs in an aqueous tertiary alkanolamine solution multiple reactions occur. The reactions of importance for CO₂ with aqueous MDEA are:
\[
\text{CO}_2 + \text{H}_2\text{O} + \text{MDEA} \leftrightarrow \text{MDEAH}^\ddagger + \text{HCO}_3^- \tag{20}
\]
\[
K_{\text{CO}_2} = \frac{[\text{MDEAH}^\ddagger][\text{HCO}_3^-]}{[\text{MDEA}][\text{CO}_2]} \tag{21}
\]
\[
\text{CO}_2 + \text{OH}^- \leftrightarrow \text{HCO}_3^-, \quad K_1 = \frac{[\text{HCO}_3^-]}{[\text{OH}^-][\text{CO}_2]} \tag{22}
\]
\[
\text{HCO}_3^- + \text{OH}^- \leftrightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}, \quad K_2 = \frac{[\text{CO}_3^{2-}][\text{H}_2\text{O}]}{[\text{HCO}_3^-][\text{OH}^-]} \tag{23}
\]
\[
\text{MDEAH}^\ddagger + \text{H}_2\text{O} \leftrightarrow \text{MDEA} + \text{H}_3\text{O}^+, \quad K_a = \frac{[\text{MDEA}][\text{H}_3\text{O}^+]}{[\text{MDEAH}^\ddagger][\text{H}_2\text{O}]} \tag{24}
\]
\[
2\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^- \tag{24}
\]

The reactions of CO₂ occurring in an aqueous tertiary alkanolamine DEMEA solution are similar to that of MDEA. The first two reactions are reactions of...
finite rate, while the following three only involve a proton transfer and are considered instantaneous with respect to mass transfer. In a model based on the Higbie penetration theory, Glasscock and Rochelle (1989) and Littel et al. (1991a) showed that the influence of reactions (21)–(24) was for tertiary amines negligible for the conditions the authors applied.

Primary or secondary amines react directly with CO$_2$ and for e.g. an aqueous MEA solution the main reaction is now given by

$$\text{CO}_2 + 2\text{MEA} \leftrightarrow \text{MEACOO}^- + \text{MEAH}^+,$$

(25)

The contribution of reaction (21) to the reaction rate can be neglected for primary and secondary amines compared to reaction (25). The overall equilibrium value $K_{\text{CO}_2}$ is calculated according to

$$K_{\text{CO}_2} = \frac{[\text{MEACOO}^-][\text{MEAH}^+]}{[\text{MEA}][\text{CO}_2]},$$

(26)

in which $K_1$, $K_w$ and $K_\text{s}$ are defined in accordance with the equations given in the reaction scheme for the tertiary amines, and $K_\text{s}$ is the equilibrium constant for the reaction

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

(27)

$$K_\text{s} = \frac{[\text{MEA}][\text{HCO}_3^-]}{[\text{MEACOO}^-][\text{H}_2\text{O}]}.$$

The values for the equilibrium constants were obtained from literature and are summarized in Table 1. For all three alkanolamines the forward reaction is first order with respect to both CO$_2$ and the alkanolamines. The rate expression for the reverse reaction and the corresponding reaction rate constant were derived from the equilibrium expression and the assumption that at equilibrium $R_\text{s} = 0$ (Bosch, 1989a).

If H$_2$S absorbs in an aqueous alkanolamine solution (primary, secondary or tertiary) the most important reaction is

$$\text{H}_2\text{S} + \text{Amine} \leftrightarrow \text{HS}^- + \text{AmineH}^+, $$

(28)

$$K_{\text{H}_2\text{S}} = \frac{[\text{AmineH}^+][\text{HS}^-]}{[\text{Amine}][\text{H}_2\text{S}]}.$$

For all alkanolamines this reaction can be considered instantaneous with respect to mass transfer. The overall equilibrium value, $K_{\text{H}_2\text{S}}$, is again comprised of various basis equilibria and calculated according to

$$K_{\text{H}_2\text{S}} = \frac{K_3}{K_\text{s}}.$$  

(29)

In which $K_3$ represents the equilibrium value of the reaction

$$\text{H}_2\text{S} + \text{H}_2\text{O} \leftrightarrow \text{HS}^- + \text{H}_3\text{O}^+.$$  

(30)

$$K_3 = \frac{[\text{HS}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{S}][\text{H}_2\text{O}]}.$$

In the model calculations the following three additional assumptions were made:

—All components in the liquid show ideal behaviour, which means that no activity coefficients were introduced in the equilibrium equations.

—The temperature in the reactor was constant. Although the reaction of CO$_2$ with alkanolamines is exothermic, the number of moles which was absorbed in the experiments was very small, so the temperature rise in the particles could be neglected.

—The diffusivities of the ionic species were taken equal to assure electroneutrality in the liquid phase (Littel, 1991a).

### 3. EXPERIMENTAL

#### 3.1. Materials

Some preliminary calculations and experiments showed that the absorption period for particles with a diameter of less than 1 mm was too short to obtain accurate experimental data. Therefore, the absorption rate experiments were carried out with large particles, whose properties are listed in Table 2. Because the length of the cylindrical particles varied slightly, the value given in Table 2 is the average of the length of 10 randomly chosen pellets. To study the effect of the basicity of the porous carriers, γ-alumina powders obtained from Aldrich were also used for the equilibrium experiments. When suspended in water these powders produce a slightly acidic, neutral or basic suspension. The pH of the aqueous suspensions of the materials is also listed in Table 2. The amines were obtained from Janssen Chimica (MEA and MDEA) and Aldrich (DEMEA) while ethanol and toluene were obtained from Merck. All chemicals were used as received.

#### 3.2. Impregnation of the particles

Before impregnation, the particles or powder were dried at 200°C for one night in order to remove water. For the particles a "wet" impregnation method was used, while for the powder "dry" impregnation appeared to be necessary.

The wet impregnation consisted of the following steps. The particles were brought in a flask and the desired solution was added until the particles were completely submerged. Subsequently, the flask was evacuated to the vapour pressure. After this the particles
Absorption of acid gases in porous particles

Table 2. Properties of the materials used

<table>
<thead>
<tr>
<th>Material</th>
<th>Name</th>
<th>Manufacturer</th>
<th>Shape</th>
<th>Size</th>
<th>Porosity (-)</th>
<th>pH of aqueous suspension</th>
<th>BET surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al₂O₃</td>
<td>Al104T</td>
<td>Engelhard</td>
<td>Cylinders</td>
<td>l = 5.0</td>
<td>0.58</td>
<td>9.8</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>1/8 in</td>
<td></td>
<td></td>
<td>d = 6.46 mm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
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<td>Engelhard</td>
<td>Cylinders</td>
<td>l = 3.60</td>
<td>0.58</td>
<td>9.8</td>
<td>94</td>
</tr>
<tr>
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<td>1/8 in</td>
<td></td>
<td></td>
<td>d = 3.22 mm</td>
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<tr>
<td>α-Al₂O₃</td>
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<td>Engelhard</td>
<td>Cylinders</td>
<td>l = 3.24</td>
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<td>4</td>
</tr>
<tr>
<td></td>
<td>1/8 in</td>
<td></td>
<td></td>
<td>d = 3.21 mm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>Weakly acidic</td>
<td>Aldrich</td>
<td>Powder</td>
<td>d ~ 70 μm</td>
<td>0.50</td>
<td>4.6</td>
<td>161</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>Neutral</td>
<td>Aldrich</td>
<td>Powder</td>
<td>d ~ 70 μm</td>
<td>0.50</td>
<td>7.5</td>
<td>177</td>
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<tr>
<td>γ-Al₂O₃</td>
<td>Weakly basic</td>
<td>Aldrich</td>
<td>Powder</td>
<td>d ~ 70 μm</td>
<td>0.50</td>
<td>9.9</td>
<td>156</td>
</tr>
</tbody>
</table>

Fig. 1. Schematic representation of experimental set-up.

were stored overnight to ensure total impregnation and removal of entrapped gas. The excess of impregnation liquid was removed and the particles were ready to use.

The γ-alumina powder of Aldrich had a small pore diameter (5.8 nm) and hence very strong capillary forces can occur. These forces made it possible to impregnate the powder with the dry impregnation method. The desired solution was slowly added to the stirred powder until the powder became clotty. The impregnated powder was exposed to vacuum and stored overnight for removal of remaining entrapped gas. Thereafter the powder was impregnated a second time with the desired liquid. The amount which could be added the second time was negligible in comparison to the volume which could be impregnated the first time.

To compare the different impregnation methods for the γ-alumina, the 1/8 in γ-alumina pellets (pore diameter ± 5 nm) were impregnated both wet and dry (the large particles were, in contrast to the powder, not stirred but shaken). The total amount of liquid which could be impregnated in the 1/8 in γ-alumina particles was identical for both impregnation methods.

Analysis of the excess of a MDEA solution, used to impregnate γ-alumina particles with the wet impregnation method, indicated that the concentration of the amine in and outside the particles was identical to the initial concentration in the solution, which meant that no noticeable surface adsorption of the amine occurred.

3.3. Experimental set-up and procedure

A schematic representation of the experimental set-up is given in Fig. 1. Two double walled temperature controlled reactor cells with a calibrated volume of about 1 × 10⁻³ m³ were connected via a valve. Both cells were equipped with a pressure transducer. Impregnated particles were brought in one of the cells and evacuated to the vapour pressure of the liquid in the particles. Pure gas was admitted to the other cell. At t = 0 the valve was opened for a short time (typically less than 3 s), and gas was allowed to flow in the
absorption vessel. The theoretical initial pressure in the absorption vessel could be calculated with the pressure drop in the gas supply vessel. In all the experiments with \( \text{H}_2\text{S} \) and also with the fast reacting \( \text{CO}_2-\text{MEA} \) system a slightly different procedure was followed. At \( t = 0 \) the valve was opened and kept open during the entire absorption period. To avoid a vapour stream from the absorption vessel to the gas supply vessel, a small amount of water \(( \pm 2 \text{ ml}) \) was added to the gas supply vessel in order to saturate the gas.

The pressure decrease in the absorption vessel was recorded with a pressure transducer, which had been connected to a computer. This method made it possible to measure the pressure with very short time intervals. To determine the equilibrium compositions, gas was, after reaching equilibrium in the absorption vessel, fed to the reactor several times up to a partial pressure of about 1 bar. All experiments were carried out with fresh unloaded porous materials at a temperature of 298 \( \pm 1 \text{ K} \).

4. RESULTS AND DISCUSSION: EQUILIBRIUM EXPERIMENTS

4.1. Particles impregnated with non-reacting liquids

4.1.1. Physical solubilities of \( \text{CO}_2 \) and \( \text{N}_2\text{O} \) in \( \alpha \)-alumina pellets. In the experiments with \( \alpha \)-alumina the solubilities found for \( \text{N}_2\text{O} \) in the non-reacting solvents water, ethanol and toluene were within \( \pm 10\% \) equal to the dimensionless solubilities given in literature for the homogeneous liquid systems. The dimensionless solubility of \( \text{CO}_2 \) in with ethanol and toluene impregnated \( \alpha \)-alumina particles agreed also satisfactorily with the literature data (see Table 3). However, the solubility of \( \text{CO}_2 \) in \( \alpha \)-alumina impregnated with water, turned out to be substantially higher than expected. This contribution could be due to the slightly basic properties of the \( \alpha \)-alumina. Therefore, the \( \alpha \)-alumina was impregnated with a 0.01 M HCl solution and the measured solubility of \( \text{CO}_2 \) was nearly identical to the one found for homogeneous liquid systems.

4.1.2. Absorption capacity of \( \text{N}_2\text{O}, \text{CO}_2 \) and \( \text{H}_2\text{S} \) in \( \gamma \)-alumina impregnated with non-reacting solvents. Again the experimentally determined solubility of \( \text{N}_2\text{O} \) in \( \gamma \)-alumina particles impregnated with various solvents agree reasonably with the data found in literature (see Table 3). However, the absorption of \( \text{CO}_2 \) in porous \( \gamma \)-aluminas impregnated with non-reacting liquids was substantially higher than expected on the basis of the physical solubility. In Fig. 2 the extra "absorption" in the \( \gamma \)-alumina particles of Engelhard is plotted as a function of the concentration physically dissolved \( \text{CO}_2 \) in the liquid. This extra absorption in ethanol and toluene had to be caused by surface adsorption of \( \text{CO}_2 \) on \( \gamma \)-alumina. This is a well known phenomenon in gas–solid systems (e.g. Rosyniek, 1975), but from the present experiments it can be concluded that surface adsorption of \( \text{CO}_2 \) is also of importance in \( \gamma \)-alumina particles impregnated with

<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier</th>
<th>Name</th>
<th>Gas</th>
<th>Source</th>
<th>Literature value (m)</th>
<th>Experimental value (m)</th>
<th>Number of measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-alumina</td>
<td>Engelhard</td>
<td>AI900T</td>
<td>\text{N}_2\text{O}</td>
<td>UPAC</td>
<td>2.61</td>
<td>3.07</td>
<td>4</td>
</tr>
<tr>
<td>( \alpha )-alumina</td>
<td>Engelhard</td>
<td>AI900T</td>
<td>\text{N}_2\text{O}</td>
<td>Lille (1996)</td>
<td>2.19</td>
<td>2.61</td>
<td>4</td>
</tr>
<tr>
<td>( \alpha )-alumina</td>
<td>Engelhard</td>
<td>AI980T</td>
<td>\text{CO}_2</td>
<td>UPAC</td>
<td>2.17</td>
<td>2.60</td>
<td>4</td>
</tr>
<tr>
<td>( \alpha )-alumina</td>
<td>Engelhard</td>
<td>AI980T</td>
<td>\text{CO}_2</td>
<td>Lille (1996)</td>
<td>2.18</td>
<td>2.62</td>
<td>4</td>
</tr>
<tr>
<td>( \alpha )-alumina</td>
<td>Engelhard</td>
<td>AI980T</td>
<td>\text{H}_2\text{S}</td>
<td>UPAC</td>
<td>2.88</td>
<td>2.88</td>
<td>4</td>
</tr>
<tr>
<td>( \gamma )-alumina</td>
<td>Engelhard</td>
<td>AI980T</td>
<td>\text{N}_2\text{O}</td>
<td>Lille (1996)</td>
<td>3.00</td>
<td>3.00</td>
<td>4</td>
</tr>
<tr>
<td>( \gamma )-alumina</td>
<td>Engelhard</td>
<td>AI980T</td>
<td>\text{CO}_2</td>
<td>Lille (1996)</td>
<td>2.41</td>
<td>2.41</td>
<td>4</td>
</tr>
<tr>
<td>( \gamma )-alumina</td>
<td>Engelhard</td>
<td>AI980T</td>
<td>\text{H}_2\text{S}</td>
<td>Lille (1996)</td>
<td>0.82</td>
<td>0.82</td>
<td>4</td>
</tr>
</tbody>
</table>
Absorption of acid gases in porous particles

Fig. 2. CO₂ adsorption isotherm at 298 K for γ-alumina particles impregnated with non-reactive liquids.

Absorption of acid gases in porous particles

Fig. 3. CO₂ adsorption isotherm at 298 K for Aldrich powders impregnated with water.

Fig. 4. H₂S adsorption isotherm at 298 K for γ-alumina particles.

The results of the experiments with the Aldrich powders with various surface properties support this view. The γ-alumina powders of Aldrich have similar internal surface areas and porosities and corresponding surface to porous volume ratios. The CO₂ absorption capacity for the basic and neutral aluminas of Aldrich impregnated with water arc, within the experimental error, identical (see Fig. 3). If the extra absorption could be completely attributed to the OH⁻ formation in the liquid, the amount of absorbed CO₂ for the neutral and acidic alumina should correspond to the solubility data found for homogeneous liquid systems, while the basic material would have a higher CO₂ absorption capacity. However, not only the CO₂ absorption capacity for the basic, but also for the neutral and acidic alumina is considerably higher than the solubility data for homogeneous water systems. It is of course possible that a small amount of the extra absorption in basic aluminas is due to the reaction with OH⁻ in the liquid but the main contribution to the extra absorption is most likely caused by surface adsorption of CO₂.

The equilibrium isotherm of H₂S in γ-alumina particles impregnated with water shows that this gas also adsorbs on the internal surface of this material (Fig. 4). However, in comparison with CO₂, the adsorption capacity is lower, which is probably due to the somewhat lower acidity of H₂S in relation to that of CO₂.

4.2. Absorption capacity of CO₂ and H₂S in particles impregnated with reactive liquids

Absorption equilibrium data of CO₂ in α-alumina impregnated with a 2 M MDEA solution were compared with experimental data for the homogeneous liquid system (Jou et al., 1982; Bhairi, 1984). As can be seen in Fig. 5 the agreement between the present data for the impregnated solution and the data obtained by Jou et al. (1982) and Bhairi (1984) is satisfactory. Probably, as a consequence of the difference in purity of the alkanolamines, the discrepancy between literature data is, especially at lower CO₂ concentrations, considerable. However, these adsorption equilibrium data, in α-alumina particles impregnated with reacting, as well as non-reacting liquids, indicate that no noticeable surface adsorption of one of the components involved in the CO₂-alkanolamine reaction considered inert.

The absorption equilibrium of CO₂ in γ-alumina pellets impregnated with a 2 M MDEA solution is given in Fig. 6. The continuous line presents the summation of the CO₂ adsorption in γ-alumina pellets impregnated with water according to the Langmuir isotherm (Fig. 2) and the (interpolated) absorption data of Jou et al. (1982) for a 2 M MDEA solution. The same was done for the absorption of CO₂ in Aldrich powders impregnated with a 2 M
MDEA solution (Fig. 7). Again the continuous lines present the summation of the Langmuir adsorption isotherms (Fig. 3) and the (interpolated) data obtained by Jou et al. (1982) for a 2 M MDEA solution. As can be seen in Figs 6 and 7 the summation of the Langmuir adsorption isotherm and the data measured by Jou et al. (1982) agree reasonably well with the absorption data of CO₂ in γ-alumina particles impregnated with MDEA solutions. From these data it can be concluded that the presence of MDEA does not substantially influence the surface adsorption of CO₂.

The absorption of H₂S in α-alumina impregnated with a MDEA solution is given in Fig. 8. The absorption data can be described reasonably well, but not exactly, with an equilibrium value of $K_{H_2S} = 18$. This equilibrium value is based on ideal behaviour of all components and is not directly comparable to the value taken from literature (see Table 1, $K_{H_2S,\text{infinite dilution}} = 38.4$). If the activities of the ions are for this situation taken into account ($\gamma \leq 1$ for ions, $\gamma \geq 1$ for molecules), the concentration independent equilibrium value [see relation (31)] will even be smaller than 18.

\[
K_{H_2S} = \frac{[HS^-][MDEAH^+]}{[H_2S][MDEA]}
\]

This equilibrium value ($K_{H_2S,\text{independent}} \approx 18$) is lower as expected on the basis of the data from literature at infinite dilution ($K_{H_2S,\text{infinite dilution}} = 38.4$), but in the available data in literature a substantial scatter can be observed which gives rise to differences in equilibrium values. This smaller equilibrium value as found in this work is therefore plausible, and was used as input parameter in the simulations of the absorption rate experiments (see Section 6.2.3).

5. EXPERIMENTAL ABSORPTION RATES IN NON-REACTING LIQUIDS

5.1. Absorption rate experiments with non-reacting liquids

Physical absorption rate experiments with non-reacting liquids were carried out to obtain the tortuositites of the porous supports and the surface diffusion coefficient of CO₂ in γ-alumina.

5.2. α-alumina pellets

The tortuosity of the α-alumina was obtained by fitting the theoretically calculated absorption rate curves to the experimental curves for CO₂ and N₂O in non-reacting liquids like water, ethanol and toluene.
Absorption of acid gases in porous particles

The tortuosity of the material was determined at \( q = 2.0 \pm 0.3 \). With this value all physical absorption rate experiments could be simulated satisfactorily.

5.3. \( \gamma \)-alumina pellets

Physical absorption rate experiments of \( \text{N}_2\text{O} \) in toluene, ethanol and a 2 M MDEA solution were used to estimate the tortuosity of \( \gamma \)-alumina (see Table 4 for diffusivity data). Fitting the theoretical curves to the experimental curves resulted for the \( \frac{1}{4} \) and \( \frac{1}{8} \) in \( \gamma \)-alumina pellets in a tortuosity of \( q = 2.4 \pm 0.3 \).

Subsequently, the surface diffusion coefficient of \( \text{CO}_2 \) could be determined by fitting the theoretically calculated curves to experimentally obtained time-pressure data for the absorption of \( \text{CO}_2 \) in \( \gamma \)-alumina impregnated with non-reacting liquids. In the simulation the surface absorption of \( \text{CO}_2 \) according to the Langmuir isotherm [see eq. (4) where \( c_1 \) and \( c_2 \) as given in Fig. 2] was taken into account. The best results for all non-reacting liquids were obtained with a surface diffusion coefficient of \( D_{\text{s,ads}} = 0 \), indicating that the adsorbed molecules were immobile. A few examples for the various fluids and particle sizes are given in Fig. 9. The continuous line represents the numerically calculated partial pressures, while the points are the experimentally determined partial pressures. In all experiments the experimental \( \text{CO}_2 \) absorption rate was slightly lower than theoretically predicted. This could either be due to an inaccuracy in the fitted Langmuir isotherm or to the fact that the rate of the adsorption step was not instantaneous. The conclusion of immobile adsorbed \( \text{CO}_2 \) molecules is based on the assumption of an instantaneous adsorption rate and supports the opinion of Prasher and Ma (1977), who concluded that surface diffusion is an unlikely transport mechanism in liquid filled pores. However, a finite adsorption rate of \( \text{CO}_2 \) and a surface diffusion coefficient larger than zero could probably also result in the same agreement between theory and experiment. Nevertheless, the present model is able to describe the absorption behaviour of \( \text{CO}_2 \) in liquid impregnated \( \gamma \)-alumina particles sufficiently accurate.

Table 4. Diffusivity of gases in liquids at 298 K

<table>
<thead>
<tr>
<th>Gas</th>
<th>Solvent</th>
<th>( D \times (10^{-9} \text{m}^2 \text{s}^{-1}) )</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_2 )</td>
<td>Ethanol</td>
<td>4.07</td>
<td>Snijder (1994)</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>Toluene</td>
<td>4.89</td>
<td>Snijder (1994)</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>Water</td>
<td>1.91</td>
<td>Versteeg (1988)</td>
</tr>
<tr>
<td>( \text{N}_2\text{O} )</td>
<td>Ethanol</td>
<td>4.25</td>
<td>Snijder (1994)</td>
</tr>
<tr>
<td>( \text{N}_2\text{O} )</td>
<td>Toluene</td>
<td>5.08</td>
<td>Snijder (1994)</td>
</tr>
<tr>
<td>( \text{N}_2\text{O} )</td>
<td>Water</td>
<td>1.78</td>
<td>Versteeg (1988)</td>
</tr>
<tr>
<td>( \text{N}_2\text{O} )</td>
<td>2M MDEA</td>
<td>1.00</td>
<td>Versteeg (1988)</td>
</tr>
</tbody>
</table>

Fig. 9. \( \text{CO}_2 \) absorption rate at 298 K in \( \gamma \)-alumina particles impregnated with non-reacting liquids.
6. Absorption rate experiments in reactive solutions

6.1. Introduction
First the absorption of CO$_2$ in various alkanolamine solutions will be treated (Section 6.2) whereafter the absorption of H$_2$S in the tertiary alkanolamine MDEA (Section 6.3) will be dealt with. In Section 6.4 some qualitative remarks will be made about the possibility and influence of surface adsorption of the reaction products on the absorption rate.

6.2. Absorption rate of CO$_2$ in particles impregnated with alkanolamine solutions

6.2.1. Introduction. Before discussing the experimental results of the absorption rates of CO$_2$ in particles impregnated with various alkanolamine solutions (Section 6.2.3), some theoretical absorption rates and concentration profiles in the particles will be given in Section 6.2.2.

6.2.2. Influence of surface adsorption and parallel reactions. In Section 6.2.2.1 the influence of immobile surface adsorption of CO$_2$ on the absorption rate of CO$_2$ in particles filled with the primary alkanolamine MEA is discussed, while in Section 6.2.2.2 the influence of reaction (21)–(24) on the absorption rate for CO$_2$ in particles impregnated with tertiary alkanolamines will be dealt with. Also, in Section 6.2.2.2 the influence of the surface adsorption of CO$_2$ in particles impregnated with tertiary alkanolamines is discussed. Finally, in Section 6.2.2.3 it will be demonstrated that the influence of surface adsorption and parallel reaction on the present absorption rate experiments is small.

6.2.2.1. Primary alkanolamines
Absorption rate experiments of CO$_2$ in γ-alumina particles indicated that the adsorbed CO$_2$ molecules were immobile. The effect of CO$_2$ adsorption on the absorption rate in particles impregnated with a MEA solution at a constant pressure is given in Table 5. The required input parameters were taken from literature and summarized in Tables 1 and 8. In Table 5 the dimensionless accumulation is the amount of gas which is absorbed at a particular time divided by the maximum amount which is absorbed at equilibrium. From this table it can be concluded that surface adsorption has for the CO$_2$–MEA system a decreasing influence with increase in time and diameter of the particles. For short times and small particles the flux is substantially higher as a consequence of the instantaneous nature of the adsorption reaction and the small diffusion distances which have to be travelled through the liquid. Although the fluxes for the situations with surface adsorption are always higher than without surface adsorption, the dimensionless accumulation at comparable times is, except for very small dimensionless accumulations, always lower. This is due to the fact that the CO$_2$ molecules which adsorb on the surface have to be transported through the liquid phase. This increases the CO$_2$ gradient and thereby the flux, but the saturation time is increased. It should be noted however, that the total absorption capacity is about 45% higher for the situation with surface adsorption.

6.2.2.2. Tertiary alkanolamine solutions
As mentioned earlier (Section 2.3) the influence of the reaction (21)–(24) on the CO$_2$ absorption rate for tertiary alkanolamines sometimes may be negligible.

Table 5. Influence of surface adsorption on the absorption rate of CO$_2$ for particles of 70 μm and 6 mm impregnated with a 2 M MEA solution at 298 K and a constant partial pressure of CO$_2$ of 10 mol m$^{-3}$ (no gas phase resistance)

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Flux ($\times 10^{-3}$ mol m$^{-2}$ s$^{-1}$)</th>
<th>Accumulation (–)</th>
<th>Flux ($\times 10^{-3}$ mol m$^{-2}$ s$^{-1}$)</th>
<th>Accumulation (–)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>3.38 x 10$^{-5}$</td>
<td>15.6</td>
<td>48.0</td>
<td>1.46 x 10$^{-4}$</td>
<td>2.22 x 10$^{-4}$</td>
</tr>
<tr>
<td>1.56 x 10$^{-5}$</td>
<td>12.7</td>
<td>42.4</td>
<td>4.00 x 10$^{-4}$</td>
<td>8.02 x 10$^{-4}$</td>
</tr>
<tr>
<td>6.40 x 10$^{-4}$</td>
<td>12.5</td>
<td>28.6</td>
<td>1.32 x 10$^{-3}$</td>
<td>2.50 x 10$^{-3}$</td>
</tr>
<tr>
<td>2.16 x 10$^{-3}$</td>
<td>12.4</td>
<td>16.9</td>
<td>4.14 x 10$^{-3}$</td>
<td>5.76 x 10$^{-3}$</td>
</tr>
<tr>
<td>0.0100</td>
<td>11.9</td>
<td>12.5</td>
<td>0.0183</td>
<td>0.0168</td>
</tr>
<tr>
<td>0.0536</td>
<td>10.8</td>
<td>10.9</td>
<td>0.0913</td>
<td>0.0682</td>
</tr>
<tr>
<td>0.0926</td>
<td>10.1</td>
<td>10.2</td>
<td>0.1516</td>
<td>0.1104</td>
</tr>
<tr>
<td>0.2080</td>
<td>8.54</td>
<td>8.68</td>
<td>0.3105</td>
<td>0.2216</td>
</tr>
<tr>
<td>0.7147</td>
<td>3.98</td>
<td>4.35</td>
<td>0.7705</td>
<td>0.5501</td>
</tr>
<tr>
<td>1.406</td>
<td>0.63</td>
<td>1.67</td>
<td>0.9702</td>
<td>0.7440</td>
</tr>
<tr>
<td>2.307</td>
<td>0.02</td>
<td>0.66</td>
<td>0.9993</td>
<td>0.8612</td>
</tr>
<tr>
<td>4.477</td>
<td>0.24</td>
<td>0.49</td>
<td>0.9423</td>
<td>0.9423</td>
</tr>
<tr>
<td>7.049</td>
<td>0.08</td>
<td>0.08</td>
<td>0.9802</td>
<td>0.9802</td>
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<tr>
<td>10</td>
<td>0.02</td>
<td>0.02</td>
<td>0.9945</td>
<td>0.9945</td>
</tr>
</tbody>
</table>

$q = 2.4 \, \epsilon_p = 0.38$; for simulations with surface adsorption: $c_1 = 0.25$, $c_2 = 650$. 1 = without surface adsorption; 2 = surface adsorption included. The time for the 6 mm particles has to be multiplied by 100.

Maximum absorption capacity for the particles with surface adsorption (situation 2) is 45% larger than particles where no surface adsorption occurs (situation 1).
However, for small contact times, low CO$_2$ concentrations or high mass transfer coefficients some influence of reaction (21)-(24) can be observed (Glasscock and Rochelle, 1989). Therefore, for small particles, which are physically rapidly saturated, it may be possible that reaction (21)-(24) also influences the absorption rate. As can be seen for situations 1 and 2 in Table 6 [notice the plateau flux for situation 1, see Hogendoorn et al. (1993)] the influence of reaction (21)-(24) is especially observed for low CO$_2$ concentrations, whereas at higher CO$_2$ concentrations the effect of the extended reaction scheme is minor. The effect of surface adsorption is again most pronounced for short contact times. For a low CO$_2$ concentration the effect of reaction (21)-(24) can be observed even if surface adsorption occurs, while for high CO$_2$ concentrations this effect is much smaller (Table 6, situation 4). The dimensionless accumulation for the particles where surface adsorption occurs is comparable with the particles where no surface adsorption takes place for both reaction schemes. This is in contrast with the situation for MEA, and due to the low reaction rate constant of the CO$_2$-MDEA system: the rate of the CO$_2$ liquid transport necessary for the adsorption can, for small particles, keep pace with the reaction rate.

In case the diffusion lengths, i.e. particle diameter increases, the influence of surface adsorption decreases which can be seen in Table 7. For short times the flux for the situation with surface adsorption is still substantially higher than for the situation without surface adsorption, but with increasing time and thus diffusion lengths, the differences between the fluxes for situations 1 and 3 are, in comparison to the situation for small particles (Table 6), small. This can also be seen from the dimensionless accumulation, which was, for small particles for the situation with and without surface adsorption, comparable, while for the large particles the dimensionless accumulation for the situation with surface adsorption is always smaller. Also, for large particles the influence of reaction (21)-(24) diminishes strongly (situations 1 and 2, Table 7). The

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Flux</th>
<th>Accumulation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6. Influence of reaction (21)-(24) and surface adsorption on the absorption rate of CO$_2$ for particles of 70 µm impregnated with a 2 M MDEA solution at 298 K and a constant partial pressure of CO$_2$ (no gas phase resistance)

<table>
<thead>
<tr>
<th>CO$_2$</th>
<th>Flux</th>
<th>Accumulation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 Flux in units of 10$^{-7}$ mol m$^{-2}$ s$^{-1}$.

If surface adsorption occurs (situations 3 and 4) the maximum capacity is increased by 3% in comparison with situations 1 and 2.

For simulations with surface adsorption: $c_1 = 0.25$, $c_2 = 650$. 1 = only reaction (20); 2 = reactions (20)-(24); 3 = only reaction (20) with surface adsorption; 4 = reactions (20)-(24) and surface adsorption.

$g = 2.4$, $\varepsilon_p = 0.58$; for simulations with surface adsorption: $c_1 = 0.25$, $c_2 = 650$. 1 = only reaction (20); 2 = reactions (20)-(24); 3 = only reaction (20) with surface adsorption; 4 = reactions (20)-(24) and surface adsorption.
Table 7. Influence of reaction (21)–(24) and surface adsorption on the absorption rate of CO₂ for particles of 6 mm impregnated with a 2 M MDEA solution at 298 K and a constant partial pressure of CO₂ of 10 mol m⁻³ (no gas phase resistance)

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Flux ( \times 10^{-4} \text{mol m}^{-2} \text{s}^{-1} )</th>
<th>Accumulation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>([\text{CO}_2]) = 0.01 mol m⁻³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.375 x 10⁻³</td>
<td>7.98</td>
<td>8.43</td>
</tr>
<tr>
<td>0.01563</td>
<td>4.26</td>
<td>4.89</td>
</tr>
<tr>
<td>0.0640</td>
<td>2.91</td>
<td>3.48</td>
</tr>
<tr>
<td>0.216</td>
<td>2.64</td>
<td>2.99</td>
</tr>
<tr>
<td>1.00</td>
<td>2.62</td>
<td>2.75</td>
</tr>
<tr>
<td>5.36</td>
<td>2.58</td>
<td>2.62</td>
</tr>
<tr>
<td>9.26</td>
<td>2.55</td>
<td>2.58</td>
</tr>
<tr>
<td>20.80</td>
<td>2.50</td>
<td>2.51</td>
</tr>
<tr>
<td>71.47</td>
<td>2.31</td>
<td>2.31</td>
</tr>
<tr>
<td>140.6</td>
<td>2.11</td>
<td>2.10</td>
</tr>
<tr>
<td>250.0</td>
<td>1.87</td>
<td>1.86</td>
</tr>
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<td>447.7</td>
<td>1.56</td>
<td>1.55</td>
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<tr>
<td>704.9</td>
<td>1.29</td>
<td>1.28</td>
</tr>
<tr>
<td>1000</td>
<td>1.07</td>
<td>1.07</td>
</tr>
</tbody>
</table>

If surface adsorption occurs (situations 3 and 4) the maximum capacity is increased with 44% in comparison with situations 1 and 2.

\( q = 2.4 \ E_1 = 0.58; \) for simulations with surface adsorption: \( c_1 = 0.25, c_2 = 650.1 = \) only reaction (20); 2 = reactions (20)–(24); 3 = only reaction (20) with surface adsorption; 4 = reactions (20)–(24) with surface adsorption.

6.2.2.3. Influence of parallel reactions and surface adsorption on the time-pressure curves

The present absorption rate experiments were carried out with large alumina particles, initially high CO₂ concentrations and large contact times in the reactor. Under these circumstances the influence of both reaction (21)–(24) for tertiary alkanolamines and surface adsorption in γ-alumina particles is relatively small as was demonstrated in Sections 6.2.2.1 and 6.2.2.2. To verify whether either reaction (21)–(24) or the surface adsorption reaction had any noticeable effect on the time-pressure curves some comparative simulations were carried out for typical experimental conditions.

The absorption of CO₂ in porous α-alumina particles impregnated with a 2 M aqueous MDEA solution at 298 is given in Fig. 11. Both the simplified [only reaction (20)] and the extended reaction scheme [reaction (20)–(24)] were used in these calculations. From the results presented in Fig. 11 it can be seen that neglecting reaction (21)–(24) have very little influence on the time-pressure curve. Therefore, it was concluded that the actual experiments with tertiary alkanolamines could be interpreted on the basis of reaction (20). The equilibrium value of this reaction, \( K_{\text{CO}_2} \), was comprised of the equilibrium values of reactions (21), (23) and (24) and defined as

\[
K_{\text{CO}_2} = \frac{K_1 K}_w [\text{H}_2\text{O}].
\]

The influence of surface adsorption of CO₂ on the time-pressure curve for typical experimental conditions with γ-alumina particles is for both 2 M MEA as well as 2 M MDEA given in Fig. 12. In this figure it can be observed that the influence of surface adsorp-
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Fig. 11. Comparison for the absorption of CO$_2$ in a 2 M MDEA solution at 298 K for the extended and simplified reaction scheme.

Fig. 12. Influence of surface adsorption on the CO$_2$ absorption rate at 298 K for $\gamma$-alumina particles impregnated with 2 M aqueous alkanolamine solutions.

Fig. 13. CO$_2$ absorption rate at 298 K in $\alpha$-alumina particles impregnated with aqueous 2 M aqueous alkanolamine solutions.

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6.2.3. Experimental absorption rate experiments of CO$_2$ in alkanolamine solutions. Typical results for the absorption rate experiments of CO$_2$ in $\alpha$-alumina pellets impregnated with alkanolamine solutions are given in Fig. 13. The continuous line represents the numerically calculated partial pressures, while the points are the experimentally determined partial pressures. It should be emphasized that the parameters required for the calculations were taken from liter-
Table 8. Physical constants in 2 M aqueous alkanolamine solutions at 298 K

<table>
<thead>
<tr>
<th>Physical constant</th>
<th>MDEA</th>
<th>DEMEA</th>
<th>MEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_{W,0} )</td>
<td>0.54 (Littel, 1991b)</td>
<td>0.54 (Littel, 1991b)</td>
<td>0.63 (Versteeg, 1988)</td>
</tr>
<tr>
<td>Viscosity (Pa s)</td>
<td>2.20 ( \times 10^{-3} ) (Littel, 1991b)</td>
<td>2.71 ( \times 10^{-3} ) (Littel, 1991b)</td>
<td>1.3 ( \times 10^{-3} ) (Versteeg, 1988)</td>
</tr>
<tr>
<td>( D_{alumina} )</td>
<td>4.56 ( \times 10^{-10} ) (Snijder, 1990b)</td>
<td>1</td>
<td>9.07 ( \times 10^{-10} ) (Versteeg, 1988)</td>
</tr>
<tr>
<td>( k_{1,1} )</td>
<td>5.2 ( \times 10^{-3} ) (Littel, 1990b)</td>
<td>4.34 ( \times 10^{-2} ) (Littel, 1990b)</td>
<td>5.70 (Blauwhoff, 1984)</td>
</tr>
</tbody>
</table>


For the comparison of the experiments with the simulations for the \( \gamma \)-alumina particles, the adsorption of CO₂ in \( \gamma \)-alumina particles impregnated with aqueous alkanolamine solutions was taken into account. It was assumed that the Langmuir adsorption isotherm was not affected by the presence of the alkanolamines and could be described by the constants given in Fig. 2. This assumption is based on the experimental observation that the summation of the Langmuir adsorption isotherm and the absorption data of CO₂ in a homogeneous aqueous MDEA solution agree reasonably well with the adsorption data of CO₂ in \( \gamma \)-alumina particles impregnated with a MDEA solution (see Fig. 6). In Fig. 14 typical examples of the absorption rate of CO₂ in \( \gamma \)-alumina particles of \( \frac{1}{2} \) in impregnated with alkanolamine solutions are presented. In Fig. 15 results are given for the particles of \( \frac{1}{4} \) in. The agreement between theory and experiment for all alkanolamines is satisfactory in the range from the initial pressure to about 100 mbar. However, below 100 mbar the solvent becomes substantially converted and equilibrium is approached. The liquid composition increasingly influences the adsorption rate in this area. For all amines, but especially for MEA, substantial deviations between theoretical and experimental absorption behaviour were obtained in this area. Three possible causes for these deviations can be presented:

— The neglect of the influence of non-idealities on the equilibrium composition. Although the total liquid loading remains low, the assumption of ideal behaviour of all components may be incorrect.

— The value of the equilibrium constant used in the simulations could be inaccurate. If the overall equilibrium constant for the CO₂-MEA reaction [eq (25)] in the simulation was lowered from 39.4 (according to Table 1) to 5, the agreement between experiment and simulation was lowered from 39.4 (according to Table 1) to 5, the agreement between experiment and simulation was lowered from 39.4 to 5, the agreement between experiment and simulation was lowered from 39.4 to 5, the agreement between experiment and simulation was lowered from 39.4 to 5.

6.2.4. Absorption rate experiments of H₂S in a MDEA solution. The results for the absorption rate experiments of H₂S in particles impregnated with MDEA solutions are given in Fig. 16. Because the reaction of H₂S with MDEA is infinitely fast in comparison with the mass transport, the reaction can be considered at equilibrium at any place within the particle. This means that the equilibrium value has a great impact on the absorption rate. Therefore, it was preferred to use the own experimentally found equilibrium value \( K_{H₂S} = 18 \), see Fig. 8) in the simulations instead of the data from literature (see Section 4.1.2). In the simulations of the experiments with \( \gamma \)-alumina the immobile surface adsorption was also taken into account. It was assumed that the surface...
Adsorption isotherm of $\text{H}_2\text{S}$ in $\gamma$-alumina particles impregnated with MDEA solutions could be described by the isotherm found for water impregnated $\gamma$-alumina particles (see Fig. 4). Contrary to the absorption rate experiments for the $\text{CO}_2$ in $\gamma$-alumina pellets, the simulations indicate that surface adsorption has a slight influence on the time–pressure curves. The cause for this influence of surface adsorption is due to the relatively low equilibrium constant for the $\text{H}_2\text{S}$–MDEA system. The tortuosity used in the simulations was adopted from the physical absorption rate experiments as described in Sections 5.2 and 5.3. This means that these experiments were also simulated without the introduction of any additional fit parameters. The data required for the simulation are given in Table 9. The experimental absorption rates of $\text{H}_2\text{S}$
Fig. 16. H$_2$S absorption rate at 298 K in 2 M MDEA solutions in various aluminia carriers.

Table 9. Parameters for the H$_2$S and 2 M MDEA system at 298 K

<table>
<thead>
<tr>
<th>Parameters</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_{H_2S}$ = 2.17</td>
<td>Versteeg et al., 1989</td>
</tr>
<tr>
<td>$k_{H_2S}$ = 18</td>
<td>This work</td>
</tr>
<tr>
<td>$D_{H_2S}$ = $9.27 \times 10^{-10}$</td>
<td>Versteeg et al., 1989</td>
</tr>
<tr>
<td>$D_{MDEA}$ = $4.37 \times 10^{-10}$</td>
<td>Versteeg et al., 1988</td>
</tr>
</tbody>
</table>

Diffusivity and solubility of H$_2$S were estimated analogous to the “CO$_2$-N$_2$O” analogy (Versteeg et al., 1989).

Nevertheless, the agreement between theory and experiments is reasonable.

6.3. Influence of surface adsorption of the reaction products on the absorption rate

Analysis of the composition of the aqueous MDEA solution before and after the impregnation of the γ-alumina particles resulted in identical concentrations of MDEA. This means that adsorption of MDEA on the internal surface of γ-alumina is very small. No experimental data are known for the adsorption of the products of the reaction between CO$_2$ or H$_2$S and the various alkanolamines on the internal surface. Because the absorption data of CO$_2$ in γ-alumina impregnated with MDEA correspond reasonably well with the sum of the absorption data of CO$_2$ in γ-alumina impregnated with water and the absorption data of Jou et al. (1982), it can be assumed that the products do not strongly adsorb on the surface. However, it cannot be excluded that the surface adsorption of CO$_2$ decreases in the presence of the products of the CO$_2$-alkanolamine reaction.

The influence of surface adsorption of the products on the absorption rate of the gas will increase with the ratio of the amount adsorbed products on the surface to the equilibrium constant. Due to possible surface adsorption of the products the equilibrium constant can apparently be increased. For reactions of finite rate the equilibrium value only influences the absorption rate of the gas at longer times (see Hogendoorn et al., 1993). However, for reactions instantaneous with respect to mass transfer, possible adsorption of the reaction products will influence the absorption behaviour from the start of the experiment. Because the surface adsorption of the reaction products is expected to be low, it will probably have, just like the surface adsorption of CO$_2$ and H$_2$S, a limited effect on the time–pressure curve for the absorption of CO$_2$ in alkanolamine solutions.

7. CONCLUSIONS

An experimental study of the absorption behaviour of CO$_2$ and H$_2$S in α-alumina and γ-alumina particles impregnated with non-reactive and reactive solvents is presented. Physical absorption rate experiments of CO$_2$ and N$_2$O were carried out to obtain the tortuosity of the porous materials. The tortuosity of the pores of the α-alumina particles and γ-alumina particles in various particles show the same type of deviation. For short times the theory predicts absorption rates which are too low, while for longer times the absorption rates for all pellets is somewhat faster as measured experimentally. This systematic deviation is probably still due to equilibrium value (see Fig. 8) which is not able to predict the equilibrium data accurately over the whole H$_2$S concentration range.
were, respectively, 2.0 ± 0.3 and 2.4 ± 0.3. All additional parameters required for the simulation of the absorption of CO₂ and H₂S in alkanolamine solutions were taken from literature. The absorption of CO₂ and H₂S in α-alumina particles impregnated with these solutions could be described satisfactorily. Differences between experiments and simulations for CO₂ mainly occurred at approaching equilibrium and seemed to be primarily caused by the inaccuracy of the equilibrium composition of the CO₂-alkanolamine system. An unexpected immobile surface adsorption of CO₂ and H₂S in γ-alumina particles was observed in γ-alumina particles impregnated with reactive as well as non-reactive solvents. However, this surface adsorption did not influence the absorption rate of CO₂ and H₂S absorption in γ-alumina particles impregnated with alkanolamine solutions significantly. The rate of CO₂ and H₂S absorption in γ-alumina particles impregnated with alkanolamine solutions could, like the experiments with α-alumina, also be described within a reasonable accuracy.

NOTATION

\( a_c \) specific contact area between gas and solid, \( m^2 \cdot m^{-3} \)

\([A]\) concentration of absorbed component, \( \text{mol} \cdot m^{-3} \) liquid

\([A]_{ads}\) concentration of adsorbed component, \( \text{mol} \cdot m^{-3} \) liquid

\([B], [C]\) concentration of non-volatile reactants and products, \( \text{mol} \cdot m^{-3} \) liquid

\( c_1 \) constant in eq. (4), \( m^3 \cdot \text{mol}^{-1} \)

\( c_2 \) constant in eq. (4), \( \text{mol} \cdot m^{-3} \) liquid

\( D \) diffusion coefficient, \( m^2 \cdot s^{-1} \)

\( d \) diameter particle, \( m \)

\( J_\phi \) flux of absorbed component A, \( \text{mol} \cdot m^{-2} \cdot s^{-1} \)

\( K \) equilibrium constant, \( \text{mol} \cdot m^{-3} \cdot m^{-p+q} \)

\( k_{n,m} \) forward reaction rate constant, \( \text{mol} \cdot m^{-3} \cdot m^{-p+q} \cdot s^{-1} \)

\( k_{p,q} \) reverse reaction rate constant, \( \text{mol} \cdot m^{-3} \cdot m^{-p+q} \cdot s^{-1} \)

\( l \) length cylindrical particles m

\( m_a \) partition coefficient of A

\( P \) pressure, bar

\( q \) tortuosity

\( r_1 \) radius of particle, m

\( r \) radial coordinate, m

\( R_A \) reaction rate related to component A, \( \text{mol} \cdot m^{-3} \cdot \text{liquid} \cdot s^{-1} \)

\( R \) gas constant, \( J \cdot \text{mol}^{-1} \cdot K^{-1} \)

\( T \) temperature, K

\( t \) time, s

\( V_{gas} \) volume occupied by gas in absorption vessel, \( m^3 \)

\( V_{abs} \) total volume of absorption vessel, \( m^3 \)

\( V_c \) volume occupied by liquid impregnated particles, \( m^3 \)

\( \epsilon_p \) porosity

\( \gamma_l \) stoichiometric coefficient in relation (1)

Superscripts

\( n, m, p, q \) reaction orders in reaction rate expression

\( R_1 \)

0 initial

REFERENCES


Littelf, R. J., Filmer, B., Versteeg, G. F. and Swaaij van, W. P. M., 1991a, Modelling of the simultaneous absorp-


