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ON THE KINETICS BETWEEN CO₂ AND ALKANOLAMINES BOTH IN AQUEOUS AND NON-AQUEOUS SOLUTIONS—II. TERTIARY AMINES

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Abstract—The reaction between CO₂ and tertiary alkanolamines (MDEA, DMMEA, TREA) has been studied in aqueous solutions at various temperatures. Also the absorption of CO₂ in a solution of MDEA in ethanol has been studied. Reaction kinetics have been established by chemically enhanced mass transfer of CO₂ into the various solutions. The experiments were performed in a stirred vessel with a horizontal interface which appeared to the eye to be completely smooth. The reaction of CO₂ with tertiary amines can be described satisfactorily with the base-catalysis mechanism proposed by Donaldson and Nguyen (1980). Also attention has been paid to the influence of reversibility and small amounts of impurities (primary and secondary amines) on the measured mass transfer rate. For the reaction rate constant, \( k_2 \), of the reaction between carbon dioxide and tertiary amines exists a Brønsted relation. There is a linear relation between the logarithm of \( k_2 \) and \( pK_a \) at 293 K.

1. INTRODUCTION

Selective absorption of H₂S from sour gas streams may lower the capital and operating costs of the treating process drastically (Blauwhoff et al., 1985). Aqueous tertiary alkanolamine solutions have been found to be very effective solvents for the selective removal of H₂S, especially methyldiethanolamine (MDEA) and triethanolamine (TEA) are frequently used (Kohl and Riesenfeld, 1979).

The absorption rate of H₂S into aqueous tertiary amine solutions can be calculated accurately because the reaction rate between H₂S and alkanolamines can be regarded as instantaneous with respect to mass transfer for all amines. In order to estimate the amount of coabsorption of CO₂ the kinetics of the reaction between carbon dioxide and tertiary amines are needed.

For aqueous tertiary amine solutions a good agreement among various investigations is reported for triethanolamine (TEA) at 298 K (Donaldson and Nguyen, 1980; Barth et al., 1981; Blauwhoff et al., 1984). Discrepancies remain with the high values for the reaction rate constant measured by Sada et al. (1976) and Hikita et al. (1977). The study of Jørgensen and Faurholt (1954) introduced another important aspect, the formation of monoalkylcarbonate at pH > 13. For the reaction between MDEA and CO₂ in aqueous solutions at 298 K good agreement exists on the reaction rate constant and reaction order between the results of Blauwhoff et al. (1984) and Barth et al. (1984).

In order to check the reaction mechanism proposed for tertiary amines [base catalysis of the CO₂ hydration (Donaldson and Nguyen, 1980)], additional experimental work has been carried out.

2. THE REACTION MECHANISM

Tertiary amines can not react with CO₂ directly, although a limited number of authors reported that a reaction occurred at extremely high pH. Jørgensen and Faurholt (1954) studied the reaction for TEA at high pH-values (pH ≈ 13) and concluded that the formation of monoalkylcarbonate occurred (see eq. 1):

\[
\text{H} \quad \text{R}_2
\]

\[
\text{CO}_2 + \text{R}_1 \text{C}-\text{C}-\text{N}-\text{R}_3 + \text{OH}^- \quad \text{OH}
\]

\[
\text{H} \quad \text{R}_2
\]

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 (3)
\]

\[
\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^- (4)
\]

At low pH-values (pH < 11) the rate of this reaction can be neglected. However, another reaction between CO₂ and tertiary amines in aqueous solutions is also observed. Donaldson and Nguyen (1980) proposed that the reaction may be described with a kind of base catalysis of the CO₂ hydration according to:

\[
\text{CO}_2 + \text{R}_1 \text{R}_2 \text{R}_3 \text{N} + \text{H}_2\text{O} \rightarrow \text{R}_1 \text{R}_2 \text{R}_3 \text{NH}^+ + \text{HCO}_3^-.
\]

In aqueous solutions the following reactions also occur:

\[
\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3.
\]

\[
\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-.
\]

For aqueous TEA solutions at 298 K there is a good
agreement between the results of the various authors (Donaldson and Nguyen, 1980; Barth et al., 1981; Blauwhoff et al., 1984). Compared to Sada et al. (1976) and Hikita et al. (1977), however, the observed reaction rates are substantially lower. This discrepancy is likely due to small amounts of primary and secondary amine impurities. As is shown by Versteeg et al. (1988b) these impurities can have an overruling effect even in very low concentrations on the reaction rate measured experimentally. Also at 298 K good agreement is found for MDEA by Barth et al. (1984) and Blauwhoff et al. (1984).

In order to check the proposed reaction mechanism, additional experiments have been carried out in the present investigations. Therefore the reaction between CO₂ and an aqueous solution of triethylamine (TREA) at 292 K has been studied in order to investigate the reaction of CO₂ with tertiary amines in the absence of the formation of monoalkylcarbonate (see reaction 1). To investigate the influence of alkalinity of the various tertiary amines on the reaction rate constant CO₂ has been absorbed in an aqueous solution of dimethylmethanolamine (DMMEA) at 293 K. Furthermore, CO₂ has been absorbed into a MDEA-ethanol mixture where no reaction should occur according to the proposed mechanism. Additional data are presented on the influence of temperature on the reaction between CO₂ and aqueous solutions of the industrially important amine MDEA.

### 3. EXPERIMENTAL

The experimental set-up and experimental procedure has been described in detail elsewhere (Blauwhoff et al., 1984; Versteeg, 1986; Versteeg and van Swaaij, 1988). The purity of all amines was > 98% wt and were used as supplied. However, in case of MDEA an attempt was made to purify the amine by means of a vacuum distillation. The results of the distillation are presented in Table 1. As can be concluded from Table 1 no real improvement of the purity of MDEA was reached and therefore all experiments were carried out with the amines as supplied. In order to check the influence of primary and secondary amines on the reaction rate of tertiary amines, the measured mol-fluxes were compared with calculated mol-fluxes according to the numerical multi-component model (Versteeg et al., 1988b).

| Table 1. Primary and secondary amine contaminants in MDEA before and after vacuum distillation |
|-----------------------------------------------|------------------|------------------|------------------|
| Contaminant                     | Vacuum distillation before | Vacuum distillation after |
| Monoethanolamine               | <10 mg/kg         | <10 mg/kg         |
| Diethanolamine                 | 350 mg/kg         | 310 mg/kg         |
| Methylmonoethanolamine         | 360 mg/kg         | 220 mg/kg         |

### 4. RESULTS

#### 4.1. TREA–H₂O

When CO₂ is absorbed in aqueous tertiary alkanoamine solutions at high pH values at least a part of the reaction may be accounted to the formation of monoalkylcarbonate. However, in the case of triethylamine the formation of this species is not possible. The only reaction that can occur is the base catalysis of the CO₂ hydration as proposed by (Donaldson and Nguyen, 1980). In the present investigation the absorption of CO₂ in aqueous triethylamine solutions has been studied at 292 K in order to verify the proposed reaction mechanism (see eq. 2) for the reaction between CO₂ and tertiary amines.

For the interpretation of the results the solubility of N₂O is given in Table 2 and the diffusivity was calculated by means of the Stokes–Einstein relation (Versteeg and van Swaaij, 1987). From Fig. 1 it can be concluded that a reaction occurs with an order in amine equal to 1 and a second order reaction rate constant k₃ = 0.029 m³ mol⁻¹ s⁻¹. The accuracy is not very high due to the fact that the contribution of reaction (4) (Versteeg and van Swaaij, 1988) to the overall reaction rate varies from 30% up to 60%. This result indicates that the observed reaction is in good agreement with the proposed reaction mechanism and that for tertiary alkanolamines another reaction besides the monoalkylcarbonate formation takes place.

| Table 2. The solubility of N₂O in aqueous TREA solutions at 292 K |
|----------------|------------------|
| [TREA] (mol. m⁻³) | Solubility (mol. mol⁻¹) |
| 136            | 0.675            |
| 342            | 0.638            |
| 464            | 0.622            |
| 487            | 0.600            |
| 608            | 0.600            |
| 876            | 0.592            |

Fig. 1. Experimental results for TREA–H₂O at 292 K.
4.2. **MDEA–ethanol**

The absorption of CO₂ in a solution of MDEA and ethanol was studied in order to check the reactivity of this solution which should be equal to zero according to the proposed reaction mechanism. The absorption rate of CO₂ into this solution could be described completely with the non-stationary mass balance for physical absorption and was almost identical to the absorption rate of N₂O, corrected for the differences in physical constants, in the same solution. The total amount of CO₂ absorbed was nearly the same as the amount which can be physically solved in this solution and the difference can be completely accounted to the presence of primary and secondary amine impurities (see Table 1). From this result it is easy to conclude that in non-aqueous solutions no reaction, even no alkylcarbonate formation, occurs between CO₂ and tertiary (alkanol)amines. This is in good agreement with the proposed reaction mechanism. Moreover, in view of the selective removal of H₂S this result makes it possible to suppress the coabsorption of CO₂ to the lowest level possible, i.e. to that of the physical absorption.

4.3. **MDEA–H₂O**

The kinetics of the reaction between CO₂ and aqueous MDEA solutions has been studied at 293, 298, 308, 318 and 333 K. Hardly any data are yet available on the temperature influence on the reaction rate for this industrially important amine. In Fig. 2 the results of the kinetic experiments are presented. From Fig. 2 it can be concluded that the reaction order for all temperatures investigated is about equal to 1 and therefore is in good agreement with the proposed reaction mechanism. In Table 3 the reaction rate constants obtained by means of linear regression are presented. The reaction rate constant can be calculated with the following equation:

\[ k_2 = 1.19 \times 10^5 \cdot \exp \left( \frac{T_a}{T} \right) \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \]  

in which \( T_a = 5103 \text{ K} \). Yu et al. (1985) reported an activation temperature of 4632 K which is well in line with the present results.

The assumption of pseudo first order irreversible reaction was valid for all experimental conditions studied as was verified with the absorption model (Versteeg et al., 1988a).

However, the influence of primary and secondary amine contaminants on the absorption rate measured may have an overruling effect, in particular for tertiary amines. This effect has been evaluated with the absorption model for MDEA with the composition before the vacuum distillation (see Table 1). From Fig. 3 it can be

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**Table 3. Fitted values of kinetic constants for the system MDEA–water**

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( k_2 ) (m²·mol⁻¹·s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>0.0033</td>
</tr>
<tr>
<td>298</td>
<td>0.0043</td>
</tr>
<tr>
<td>308</td>
<td>0.0077</td>
</tr>
<tr>
<td>318</td>
<td>0.0124</td>
</tr>
<tr>
<td>333</td>
<td>0.0268</td>
</tr>
</tbody>
</table>

---

![Fig. 2. Experimental results for MDEA–H₂O at various temperatures.](image2)

![Fig. 3. Influence of contaminants on the enhancement factor for CO₂–2500 mol·m⁻³ amine–H₂O at 293 K.](image3)
Conclusion. The reaction between CO$_2$ and tertiary amines can be described with the base catalysis of the CO$_2$ hydration as proposed by (Donaldson and Nguyen, 1980). The formation of monoalkylcarbonate is not responsible for the reactivity measured in aqueous tertiary amine solutions at low pH as can be concluded from the experiments with TREA. In non-aqueous solvents no reaction occurs. This conclusion is relevant

5. CONCLUSIONS

The reaction between CO$_2$ and tertiary amines can be described with the base catalysis of the CO$_2$ hydration as proposed by (Donaldson and Nguyen, 1980). The formation of monoalkylcarbonate is not responsible for the reactivity measured in aqueous tertiary amine solutions at low pH as can be concluded from the experiments with TREA. In non-aqueous solvents no reaction occurs. This conclusion is relevant.
to the development of gas treating processes for the selective removal of H$_2$S.

The determination of reaction mechanism and reaction rate constants from mass transfer experiments can be substantially affected by effects of reversibility or contaminants.

A Brønsted relation exists between the reaction rate constant, $k_2$, and the alkalinity of the tertiary amines.

Due to the small variation in H$_2$O concentration during the experiments it was not possible to investigate the influence of H$_2$O on the reaction rate. In order to obtain a complete description of the mechanism of the reaction between CO$_2$ and tertiary amines it is necessary to study this influence. In the near future results of absorption experiments for the system CO$_2$–H$_2$O–ethanol will be published.

**NOTATION**

- $k_2$: second order reaction rate constant, m$^3$.mol$^{-3}$.s$^{-1}$
- $K_a$: acid dissociation constant.
- $T_a$: activation temperature, K

**REFERENCES**


