

PA5 Chemical Reaction of CO₂ with MDEA

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1. Introduction

A wetted-sphere absorber was used to obtain kinetic data for the aqueous phase reaction between CO₂ and N-methyldiethanolamine (MDEA). Data were obtained over the temperature range of 293 to 342 K for partial pressures of CO₂ near atmospheric and for 10 to 30 mass % MDEA. The data are consistent with a mechanism in which MDEA catalyzes the hydrolysis of CO₂.

The model discussed in which all significant liquid phase reactions were considered was used to estimate the forward rate constant of the MDEA catalyzed hydrolysis of CO₂ from the experimental absorption data. The forward rate constant was also estimated from approximate analytical expressions for absorption accompanied by pseudo first-order reaction (Wild and Potter, 1968) neglecting all reactions except the MDEA catalyzed hydrolysis of CO₂. A comparison of the numerical and approximate analytical results indicate that the effect of the reaction between hydroxide and CO₂ is significant. Neglecting the CO₂/OH⁻ reaction can result in significant errors in the rate constant for the MDEA catalyzed hydrolysis reaction at the higher temperatures.

2. Materials and methods

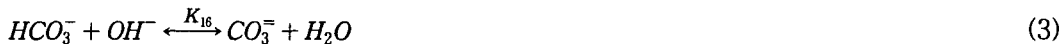
2.1. Mechanism

Donaldson and Nguyen (1980) proposed that the reaction mechanism for CO₂ with tertiary amines is a base-catalyzed hydration reaction:



This mechanism implies that tertiary amines (e.g. MDEA) do not react directly with CO₂. Versteeg and van Swaaij (1988), who studied CO₂ absorption into nonaqueous solutions of MDEA in ethanol, found that only physical absorption occurs in nonaqueous tertiary amine systems which supports the validity of reaction (1).

The following reactions may also occur in aqueous tertiary amine solutions:



Reactions (1) and (2) are considered to be reversible reactions with finite rates, while reactions (3) through (5) are considered to be reversible and instantaneous, since they involve only a proton transfer.

The kinetics of the reaction of CO₂ with aqueous MDEA has been studied by several researchers. Barth et al. (1984), Blauwhoff et al. (1984), and Crooks and Donnellan (1990) studied this system at 298 K. Estimates of the kinetic rate constants for reaction (1) at various temperatures have been reported by Yu et al. (1985), Haimour et al. (1987), Versteeg and van Swaaij (1988), Tomcej and Otto (1989), and Littel et al. (1990). However, there are still some significant discrepancies in the results presented by these authors. Littel et al. (1990) claim that Versteeg and van Swaaij (1988) overestimated the contribution of hydroxide in reaction (6.2) to the absorption rate of CO₂, and suggest that other authors (Yu et al., 1985; and Tomcej and Otto, 1989) may have done the same.

2.2. Experimental

A wetted-sphere absorber was used to measure absorption rates in this work. All experiments were done under atmospheric pressure and with partial pressures of CO₂ near atmospheric. The temperature was measured with type J thermocouples and the temperature was maintained to within ±0.2 K.

The MDEA was obtained from Aldrich with a lot purity of 99.9 mass%. The CO₂ was Bone Dry Grade and was obtained from Union Carbide Corp. The aqueous solutions of MDEA were prepared by weight with distilled-deionized water and were degassed at 80 K under vacuum. The CO₂ loading of the aqueous MDEA solutions after degassing, as determined by titration, was effectively zero. The concentration of MDEA in the solutions after degassing was determined by titration with HCl.

The experimental absorption rate data were interpreted to obtain estimates for the forward second-order rate constant of reaction (1), *k*₃, using two different models. Model I is based on the assumption that only reaction (1) significantly contributes to the absorption rate of CO₂ and that this reaction is pseudo-first-order and ir-

reversible. Model II is a more comprehensive model in which reactions (1) through (5) are included and are considered to be reversible.

Model I:

The absorption rate data from the wetted-sphere apparatus were interpreted using the equations developed by Wild and Potter (1968) for gas absorption accompanied by an irreversible pseudo-first-order chemical reaction into a laminar-liquid film on a sphere. According to Littel et al. (1990), the effect of reactions (2) through (5) on the absorption rate of CO₂ into aqueous MDEA can be neglected, and that the pseudo-first-order rate constant is given by the following expression:

$$k = k_3[\text{MDEA}] \quad (6)$$

where it is assumed in equation (6) that reaction (1) can be considered to be irreversible over the short experimental contact times.

The criterion under which a second-order reaction (e.g. reaction (1)) can be considered to have pseudo-first-order kinetics is given by Danckwerts (1970):

$$\sqrt{\pi k \tau} \ll 2 \left(\sqrt{\frac{D_A}{D_B}} + \frac{C_B^0}{C_A^*} \sqrt{\frac{D_B}{D_A}} \right) \quad (7)$$

where τ is the gas-liquid contact time, D_A is the liquid phase diffusivity of the absorbed gas, C_A^* is the interfacial concentration of the absorbed gas, D_B is the diffusivity of the liquid-phase reactant B, and C_B^0 is the initial concentration of species B. All of the data presented here satisfy this criterion.

Model II:

In the development of Model I, it was assumed that reactions (2) through (5) can be neglected. However, in Model II all reactions, (1) through (5), are included and are considered to be reversible. Reactions (1) and (2) have finite reaction rates. Whereas, reactions (3) through (5) involve only a proton transfer and are assumed to be instantaneous with respect to mass transfer and to be at equilibrium. Note that not all the reaction equilibrium constants for reactions (1) through (5) are independent. Only four equilibrium constants (K_2 , K_{16} , K_{14} and K_{20}) are independent. The remaining one can be obtained by an appropriate combination of the independent equilibrium constants so that $K_3 = K_2/K_{14}$.

The model was used to estimate the forward rate constant (k_3) of the MDEA catalyzed hydrolysis of CO₂ by adjusting the value of k_3 until the predicted rate of absorption of CO₂ was within 1% of the measured rate of absorption.

3. Results and discussion

The absorption experiments for CO₂ into aqueous MDEA solutions were carried out over the concentration range of 10 to 30 mass % at 313 K, and with 10 wt% over the temperature range of 293 to 342 K. All experiments were done under atmospheric pressure with partial pressures of CO₂ near atmospheric and with initial CO₂ loading of the solutions equal to zero.

The CO₂ absorption rate data for 10, 20 and 30 mass % MDEA at 313 K were interpreted according to Model I to obtain estimates for the pseudo-first-order rate constant (*k*) of reaction (1). These results revealed that *k* is a linear function of the MDEA concentration. Therefore, the rate expression for reaction (1) is first-order in both CO₂ and MDEA concentration. The estimates of *k*₃ from Model I for 10, 20 and 30 mass % MDEA at 313 K and 10 mass % MDEA from 293 to 342 K are listed in Table 6.1. These estimates were fitted by the Arrhenius equation and the activation energy of reaction (1) was determined to be 11.0 kcal/mol which is in good agreement with the value of 11.5 kcal/mol reported by Littel et al. (1990) from the reinterpreted results of Versteeg and van Swaaij (1988). This result is expected since Littel et al. (1990) made similar assumptions to those made in Model I.

A comparison of the estimates of *k*₃ from Model II and Model II with *k*₂=0 shows that the effect of neglecting only reaction (2) is significant. Therefore, reaction (2) has a significant effect and cannot be neglected when estimating kinetic rate constants from experimental absorption rate data for CO₂ into aqueous MDEA, which is contrary to the suggestion of Littel et al. (1990). In addition, since reactions (3) through (5) involve OH⁻, their equilibrium expressions cannot be neglected when reaction (2) is included. It is concluded that the estimates of *k*₃ obtained by interpreting the experimental absorption rate data with Model II are more realistic than those obtained from Model I and Model II with *k*₂=0. The estimates of *k*₃ for 10 wt% MDEA from Model II are plotted in Figure 6.1 and are fitted by the following Arrhenius equation:

$$k_3 = 2.22 \times 10^7 \exp\left(\frac{-4547}{T}\right) \quad (8)$$

where *T* is in units of K, and *k*₃ is in units of m³/kmol s. The activation energy, as determined from Model II, is 9.0 kcal/mol which can be compared to the reported values of 11.5 kcal/mol by Littel et al. (1990), 10.2 kcal/mol by Versteeg and van Swaaij (1988), 9.2 kcal/mol by Yu et al. (1985), 17.1 kcal/mol by Haimour et al. (1987), and 10.2 kcal/mol by Tomcej and Otto (1989).

4. Conclusions

As mentioned earlier, the aqueous MDEA solutions used in the absorption experiments were not initially loaded with CO₂ ($L_{CO_2}=0$). For solutions which have an initial CO₂ loading ($L_{CO_2}>0$), the CO₂ would consume part of the OH⁻. This would result in lowering the liquid bulk OH⁻ concentration before the absorption experiments began. Hence, the contribution of reaction (2) to the rate of absorption of CO₂ would probably decrease with increasing initial CO₂ loading, and the effect of reaction (2) on the estimation of k_3 would probably diminish accordingly. This may explain why some authors have concluded that the effect of reaction (2) is negligible.

The estimates of k_3 for 10, 20 and 30 mass% MDEA at 313 K determined from Model II show a slight dependence on the MDEA concentration. This is not surprising since it is known that the reaction rate constant may vary with composition especially in nonideal systems (Froment and Bischoff, 1979). This phenomenon was also observed by Glasscock et al. (1991) for aqueous DEA and DEA/MDEA solutions. The estimates of k_3 at 313 K can be approximated over the concentration range of 0.82 kmol/m³ to 2.56 kmol/m³ by the following equation:

$$k_3 = 9.37 + 2.34[MDEA], \quad T = 313K$$

where [MDEA] is in units of kmol/m³ and k_3 is in units of m³/kmol s.

It is clear from this figure that as the interfacial concentration of CO₂ decreases, the contribution of reaction (2) to the enhancement factor (and the rate of absorption) of CO₂ increases.

References

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