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# Kinetics of reactive absorption of carbon dioxide with solutions of 1,6-hexamethylenediamine in polar protic solvents

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ABSTRACT

Reactive absorption of carbon dioxide with solutions of 1,6-hexamethylenediamine (HMDA) in methanol and water was studied in stirred cell and model stirred contactor at 303 ± 1 K. The volumetric rate of absorption of pure $CO_2$, at atmospheric pressure, was measured using a soap-film meter of appropriate size. Carbon dioxide partial pressure was varied from 0.41 to 0.96 atm and concentration of liquid phase reactant HMDA was varied from 0.5 to 3.0 kmol $m^{-3}$. The specific absorption rates were analysed using mass transfer with chemical reaction theory. The reaction order was found to be 0.85 with respect to $CO_2$ and HMDA each in water as solvent. The intrinsic kinetic rate constants ($k_{m,n}$) at 303 ± 1 K were found to be in the range of $(1.1–1.5) \times 10^2$ (kmol $m^{-3})^{-0.7}$ $s^{-1}$. In the case methanol as solvent, the reaction appeared to be the instantaneous reaction regime. These data are expected to be useful for the design and scale up of carbon dioxide absorbers in the process development for carbamates/isocyanates synthesis.

## 1. Introduction

The reactive absorption of carbon dioxide ($CO_2$) with 1,6-hexamethylenediamine (HMDA) dissolved in methanol and water was studied. Industrially, aqueous solutions of alkanolamines and various types of amine blends are widely used in gas purification processes for the absorption of acid gases such as $CO_2$, hydrogen sulfide, and carbonyl sulphide, etc. [1,2]. Particularly, the removal of $CO_2$ from the gas produced by burning fossil fuel has been of great interest owing to the global warming caused by the increase in the concentration of $CO_2$ in the atmosphere. Recently, the potential of $CO_2$ as a source of carbonyl (in place of phosgene) in the synthesis of high value industrial chemicals and intermediates, such as carbamates, isocyanates, and urethanes is being evaluated extensively. The traditional manufacturing route for organic isocyanates is by reaction of an amine with phosgene ($COCl_2$), the intermediate of this reaction is converted to the corresponding isocyanate in the presence of a nonaqueous aprotic solvent [3–8]. There is a large number of recent publications [9–21] in which phosgene have been replaced by a benign substitute. Use of carbon dioxide as a reagent in place of phosgene has the potential for cheaper, greener, inherently safer, and more selective route to produce carbamates, isocyanates, and polyurethanes. However, the commercial utilisation of the process requires systematic kinetic study. In addition, the information available in the literature on the kinetics of reactive absorption of $CO_2$ with solution of diamines in polar solvents is not very comprehensive. It is, however, apparent that these reactions are fast and mass transfer may be accompanied by chemical reaction in the diffusion film. It was, therefore, thought desirable to study the kinetics of reactive absorption of $CO_2$ with solutions of HMDA in methanol and water.

### 1.1. Previous studies

Recently, Aresta et al. [3] have reported the kinetics and mechanism of the homogeneous reaction of some organic amines with dimethyl carbonate (DMC) in the presence of dissolved $CO_2$. Second-order kinetics was used in the analysis. Caplow [22] has studied the homogeneous uncatalysed and hydroxide-catalysed reactions of some secondary amines with $CO_2$. Second-order kinetics was observed. Crooks and Donnellan [23,24] have reported the formation of N,N-dialkylcarbamate from diethanolamine and $CO_2$ in anhydrous ethanol. The rate of formation of N,N-dialkylcarbamate from diethanolamine and $CO_2$ in anhydrous ethanol was found to depend on the square of the amine concentration. The rate and activation data are consistent with the Danckwerts' mechanism [25,26] in which a zwitterion intermediate is present at very low concentration and reacts with a second molecule of amine at the diffusion-controlled limit to give a final salt in the rate-determining step. Ali et al. [27] have reported the

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**Nomenclature**

| | |
|---|---|
| A | solute gas component ($CO_2$) |
| AR | analytical reagent |
| $\underset{\sim}{a}$ | surface area per unit volume ($m^{-1}$) |
| B | liquid phase reactant (HMDA) |
| $c_{Ao}$ | concentration of A in bulk liquid phase ($kmol\,m^{-3}$) |
| $c_{Ai}$ | concentration of A at gas–liquid interface ($kmol\,m^{-3}$) |
| $c_{Bo}$ | bulk concentration of B in liquid phase ($kmol\,m^{-3}$) |
| $c_{Bi}$ | concentration of B at gas–liquid interface ($kmol\,m^{-3}$) |
| $D_A$ | diffusivity of A in liquid phase ($m^2\,s^{-1}$) |
| $D_B$ | diffusivity of B in liquid phase ($m^2\,s^{-1}$) |
| $f_{hyp.\,liq\,2}$ | fugacity of hypothetical liquid 2, for Eq. (1) ($kP_a$) |
| $f_{gas\,2}$ | fugacity of gas 2, for Eq. (1) ($kP_a$) |
| $k_m$ | pseudo m-order rate constant, $k_m = k_{m,n} c_{Bo}{}^n$ or $k_m = k_{m,n} c_{Bi}{}^n$ |
| $k_{m,n}$ | intrinsic kinetic rate constants defined in Eq. (3) ($(kmol\,m^{-3})^{1-(m+n)}\,s^{-1}$) |
| $k_L$ | physical liquid side mass transfer coefficient of the solute gas ($m\,s^{-1}$) |
| $l$ | liquid hold-up |
| $m$, $n$ | order with respect to solute gas A and liquid-phase reactant B, respectively |
| $p_A$ | partial pressure of A in gas phase (atm) |
| $R$ | universal gas constant |
| $R_A$ | specific absorption rate of solute gas ($kmol\,m^{-2}\,s^{-1}$) |
| $T$ | temperature (K) |
| $v_2$ | molar liquid volume of the solute ($m^3\,kmol^{-1}$) |
| $x_2$ | mole fraction of the solute gas in the liquid phase |
| $z$ | stoichiometric factor for chemical reaction expressed by Eq. (3) |

*Greek symbols*

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|---|---|
| $\delta_1, \delta_2$ | Hildebrand solubility parameter of solvent and solute gas respectively ($MPa^{1/2}$) |
| $\varepsilon$ | relative dielectric constant of solvent |
| $\mu$ | viscosity of the components ($kg\,m^{-1}\,s^{-1}$) |
| $\varphi_1$ | volume fraction of the solvent |

homogeneous kinetics of reaction of some primary amines with $CO_2$ in ethanol solution, using the stopped flow technique. The highest conversion to carbamate ion was detected with hexamine. The results favour the zwitterion intermediate mechanism proposed by Danckwerts [25,26]. The reaction order was found to increase (ranging from 1 to 2) with the basicity of the amine. Very recently, Masuda et al. [28] have studied the solvent dependence of the carbamic acid formation from ω-(1-naphthyl) alkyl-amines and dissolved $CO_2$, in a variety of solvents such as dimethyl sulphoxide (DMSO), dimethyl formamide (DMF), pyridine, dioxane, acetonitrile, benzene, water, 2-propanol, methanol, and water. Bubbling of $CO_2$ through solutions of naphthyl alkyl amines in DMSO, DMF or pyridine (protophilic, highly dipolar, aprotic solvent) resulted in complete conversion of the amines to the corresponding carbamic acids. In dioxane (protophilic, dipolar, aprotic solvent), the carbamic acid and a small amount of the ammonium carbamates were formed. By contrast, in (protophobic, dipolar, aprotic solvent), in benzene or water (polar, aprotic solvent), or in 2-propanol or methanol (dipolar, amphiprotic solvent), ammonium carbamates were formed, although the ammonium bicarbonates/carbonates were competitively formed in methanol.

Most of the reactive absorptions of $CO_2$ studies have been conducted in aqueous media except in recent research work by Alvarez-Fuster et al. [29] and Sada et al. [30]. Alvarez-Fuster et al. [29] found that the reaction order with respect to cyclohexylamine in ethanediol to be 1. Sada et al. [30] studied the heterogeneous kinetics of reactive absorption of $CO_2$ with mono- and diethanolamine in solvents such as methanol, ethanol, 2-propanol, and water, using a stirred tank absorber with a plane gas–liquid interface at 303 K. The reaction was found to be first order with respect to $CO_2$ for every solvent. The order of reaction with respect to ethanolamine was found to be 1 only for an aqueous solution of monoethanolamine; for the other solutions, the order ranged from 1.4 to 2, depending on the solvent species. Very recently, Dinda et al. [31] have studied the kinetics of reactive absorption of $CO_2$ with solutions of aniline in nonaqueous aprotic solvents, namely, acetonitrile, methyl ethyl ketone, toluene, and *m*-xylene. The reaction was found to be first order with respect to $CO_2$ for all the solvents studied. The order of reaction with respect to HMDA was found to be −0.5 in acetonitrile, 1 in methyl ethyl ketone, 2 in toluene, and 2.5 in *m*-xylene.

From the foregoing discussion, it is clear that very limited data are available on the kinetics of reactive absorption of $CO_2$ with solutions of simple aliphatic diamines in aqueous or nonaqueous solvents. These data will be essential for the potential utilisation of $CO_2$ in the commercial production of many commercially important carbamates/isocyantes. This work was, therefore, undertaken to study the kinetics of reactive absorption of $CO_2$ with solutions of HMDA (as a model aliphatic diamine) in methanol and water. It is expected that the data obtained for HMDA will be useful for many more commercially important aromatic and aliphatic mono- and di-amines, which are used in the industrial manufacture of carbamates and isocyanates.

## 2. Experimental details and materials

### *2.1. Stirred cell*

Pure $CO_2$ was stored in a balloon at atmospheric pressure. Experiments were carried out in a 64 mm, i.d. glass stirred cell. The design of the stirred cell was similar to that used by Patwardhan and Sharma [32]. A glass stirrer with four blades, which was set just into the liquid, was used. The gas phase in the stirred cell was also agitated using a cruciform stirrer. The stirrer speed was varied from 45 to 102 rev/min. The effective interfacial area was $31.2 \times 10^{-4}\,m^2$. A known amount of a solution was taken, and the volumetric rate of absorption of pure $CO_2$, stored in a balloon at essentially atmospheric pressure, was noted, using a soap-film meter of appropriate size. Prior to the measurement of the volumetric rate of absorption, the stirred cell was purged with pure $CO_2$ for a sufficient time. The purging was stopped, and the unit was connected to a balloon containing pure $CO_2$ at essentially atmospheric pressure. After about 100 s, the volumetric rate of uptake of $CO_2$ was noted.

### *2.2. Stirred contactor with a flat gas–liquid interface*

This type of contactor, which has independent stirrers for gas and liquid phases and where the interface is kept flat and no gas dispersion is allowed, was employed to study the effect of $CO_2$ partial pressure on the specific rate of $CO_2$ absorption with HMDA solutions in different solvents. The design features of this contactor were akin to those employed by Patwardhan and Sharma [32], and Yadav and Sharma [33]. This model stirred contactor was operated at a gas-side stirrer speed of about 1200 rev/min and liquid-side stirrer speed of 110 rev/min. The mode of operation of contactor was semicontinuous. Experiments were conducted at 303 ± 1 K and essentially at atmospheric pressure by employing mixtures of $CO_2$ and nitrogen. The specific rates of absorption were calculated on