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Kinetics of reactive absorption of carbon dioxide with solutions of aniline in carbon tetrachloride and chloroform

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Abstract

Kinetics of reactive absorption of carbon dioxide with solutions of aniline in commercially available chlorinated hydrocarbon solvents, namely, carbon tetrachloride and chloroform was studied in stirred cell and model stirred contactor at 303 ± 1 K, at atmospheric pressure. Carbon dioxide partial pressure was varied from 0.42 to 0.84 atm and concentration of liquid-phase reactant aniline was varied from 0.75 to 4.5 kmol/m^3. The reaction appeared to be first order with respect to carbon dioxide in the case of both the solvents used. The reaction order with respect to aniline was found to be zero in carbon tetrachloride and −0.4 in chloroform. The intrinsic kinetic rate constants at 303 ± 1 K were found to be 1.18×10^{-3} s^{-1} and 8.93×10^{-4} (kmol/m^3)$^{0.4}$ s^{-1}, in the case of carbon tetrachloride and chloroform, respectively, as solvents. These data are expected to be useful for the design and scale up of carbon dioxide absorbers in the process development for carbamates/isocyanates.

Keywords: Kinetics; Reactive absorption; Carbon dioxide; Aniline; Carbon tetrachloride; Chloroform

1. Introduction

The reactive absorption of carbon dioxide (CO_2) with aniline dissolved in commercially available chlorinated hydrocarbon solvents, namely, carbon tetrachloride and chloroform was studied. Industrially, the absorption of acid gases such as CO_2, hydrogen sulfide, and carbonyl sulphide, with aqueous amines and amine blends is very important in gas purification processes and has been studied extensively [1–3]. In recent years, 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 [4–14]. There are a large number of recent research publications [15–34] as well as patents in this area [35–52]. However, the commercial utilization of this process makes the systematic kinetic study necessary. In addition, the information available in the literature on the kinetics of reactive absorption of CO_2 with solutions of amines in nonaqueous chlorinated hydrocarbon 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 aniline in commercially available chlorinated hydrocarbon solvents such as carbon tetrachloride and chloroform.

2. Previous studies

Recently, Aresta et al. [6] 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 [53] has studied the homogeneous uncatalysed and hydroxide-catalyzed reactions of some secondary amines with CO_2. Second-order kinetics was observed. Crooks and Donnellan [54,55] 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

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Nomenclature

$\underline{a}$	surface area per unit volume (m^{-1})
A	solute gas component (CO_2)
AR	analytical reagent
B	liquid phase reactant (aniline)
c_{A0}	concentration of A in bulk liquid phase ($kmol/m^3$)
c_{Ai}	concentration of A at gas–liquid interface ($kmol/m^3$)
c_{B0}	bulk concentration of B in liquid phase ($kmol/m^3$)
D_A	diffusivity of A in liquid phase ($m^2\,s^{-1}$)
D_B	diffusivity of B in liquid phase ($m^2\,s^{-1}$)
$f_{gas\ 2}$	fugacity of gas 2, for Eq. (1) (kPa)
$f_{hyp.\ liq\ 2}$	fugacity of hypothetical liquid 2, for Eq. (1) (kPa)
k_1	pseudo first-order rate constant (s^{-1})
k_L	physical liquid side mass transfer coefficient ($m\,s^{-1}$)
$k_{m,n}$	intrinsic kinetic rate constants defined in Eq. (3) ($(kmol/m^3)^{1-(m+n)}\,s^{-1}$)
$k_{1,n}$	intrinsic kinetic rate constants defined in Eq. (A.6) ($(kmol/m^3)^{-n}\,s^{-1}$)
l	liquid hold-up
LR	laboratory reagent
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 ($kmol/(m^2\,s)$)
T	temperature (K)
v_2	molar liquid volume of the solute ($m^3/kmol$)
x_2	mole fraction of the solute gas in the liquid phase
z	stoichiometric factor for chemical reaction expressed by Eq. (3)

Greek letters

δ_1, δ_2	Hildebrand solubility parameter of solvent and solute gas respectively ($MPa^{1/2}$)
ε	relative dielectric constant of solvent,
φ_1	volume fraction of the solvent
μ	viscosity of the components ($kg/(m\,s)$)

the amine concentration. The rate and activation data are consistent with the Danckwerts' mechanism [53,56,57] 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. [58] have reported the 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 favor the zwitterion intermediate mechanism proposed by Caplow [53] and Danckwerts [56,57]. The reaction order was found to increase (ranging from 1 to 2) with the basicity of the amine. Very recently, Masuda et al. [59] 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, chloroform, 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 acetonitrile (protophobic, dipolar, aprotic solvent), in benzene or chloroform (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 CO_2 absorption studies have been conducted in aqueous media except in recent research work by Alvarez-Fuster et al. [60] and Sada et al. [61,62]. Alvarez-Fuster et al. [60] found that the reaction order with respect to cyclohexylamine in ethanediol to be 1. Sada et al. [61] 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. Sada et al. [62] studied the heterogeneous kinetics of reactive absorption of CO_2 with solutions of monoisopropanolamine and cyclohexylamine in solvents such as methanol, ethanol, 2-propanol, toluene, and water, using a semi batch stirred tank 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 with respect to monoisopropanolamine was 1 for aqueous solution and had a value between 1.46 and 1.93 for the other alcoholic solution systems. The order with respect to cyclohexylamine was almost 1 for aqueous and alcoholic solutions and 2 for toluene solution. Very recently, Dinda et al [63] 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 aniline 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 amines in chlorinated hydrocarbon solvents. These data will be essential for the potential utilisation of CO_2 in the commercial production of many commercially important carbamates/isocyanates. This work was, therefore, undertaken to study the kinetics of reactive absorption of CO_2 with solutions of aniline (as a model aromatic monoamine) in commercially available nonaqueous chlorinated hydrocarbon solvents such as carbon tetrachloride and chloroform. It is expected that the data obtained for aniline 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.

3. Experimental apparatus and procedure

3.1. Stirred cell

Pure CO_2 from a cylinder was used. CO_2 was stored in a balloon at atmospheric pressure. All the 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 [64,65]. 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 by using a cruciform stirrer. The stirrer speed was varied from 50 to 102 rev/min. The effective interfacial area was 31.2×10^{-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. The concentration of aniline was varied from 0.75 to 4.5 kmol/m^3. 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.

3.2. 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 aniline solutions in different solvents. The design features of this contactor were akin to those employed by Patwardhan and Sharma [64,65], and Yadav and Sharma [66]. This model stirred contactor was operated at a gas-side stirrer speed of 1500 rev/min and liquid-side stirrer speed of 110 rev/min. The mode of operation of contactor was semicontinuous. To assess the effect of gas-side resistance, the gas-side stirrer speed was varied from 720 to 1500 rev/min. All the 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 the basis of chemical analysis of carbamate formed in the liquid phase.

4. Physicochemical data

4.1. Solubility of CO_2 in solutions of aniline in carbon tetrachloride and chloroform

The equilibrium mole fraction (x_2) of CO_2 in the mixtures of aniline in carbon tetrachloride and chloroform was predicted using regular solution theory [67], using Eq. (1),

$$\frac{1}{x_2} = \frac{f_{\mathrm{hyp,liq}\,2}}{f_{\mathrm{gas}\,2}} \exp\left\{\frac{v_2(\delta_1 - \delta_2)^2 \varphi_1^2}{RT}\right\} \qquad (1)$$

The predicted values of equilibrium mole fraction of the CO_2 in pure carbon tetrachloride were crosschecked experimentally by measuring the dissolved CO_2 concentration in CO_2-saturated solutions of carbon tetrachloride and chloroform at 303 ± 1 K. The predicted as well as experimentally measured values for carbon tetrachloride and chloroform compared well with those reported in the literature [68]. Hence, the CO_2 solubility (c_{Ai}) values for the mixtures of aniline in carbon tetrachloride and chloroform were calculated from predicted mole fraction solubility value (Table 1, Fig. 1). As the concentration of aniline increases the solubility of CO_2 increases in both the solvents.

4.2. Diffusivity of CO_2 in solutions of aniline in carbon tetrachloride and chloroform

The values of diffusivity of CO_2 in carbon tetrachloride, chloroform and in the mixtures of aniline in carbon tetrachloride and chloroform were predicted using the Wilke–Chang formula [69]. Please refer to Table 2 and Fig. 2. The diffusivity of CO_2 decreases with aniline concentration due to an increase of viscosity. The variation of estimated combined physicochemical property ($c_{\mathrm{Ai}} D_{\mathrm{A}}^{1/2}$) of CO_2 in the liquid medium with different aniline concentrations is shown in Fig. 3.

4.3. Physical mass transfer coefficient

Values of the physical mass-transfer coefficient, k_{L}, are needed to check the conditions for different controlling regimes [70]. The k_{L} values at different speeds of stirring in the stirred cell were determined by absorbing pure CO_2 in deionized water. The

Table 1
Predicted solubility of CO_2 in pure and aniline solutions of carbon tetrachloride and chloroform solvents and in pure aniline at 303 K and 1 atm total pressure

[Aniline], c_{B0} (kmol/m^3)	[CCl_4] (kmol/m^3)	Predicted solubility of CO_2, $c_{\mathrm{Ai}} \times 10^2$ (kmol/m^3)	[$CHCl_3$] (kmol/m^3)	Predicted solubility of CO_2, $c_{\mathrm{Ai}} \times 10^2$ (kmol/m^3)
0.75	9.39	7.73	11.55	7.78
1.50	8.70	7.92	10.70	7.95
2.25	8.00	8.10	10.14	8.14
3.00	7.31	8.32	8.99	8.30
4.50	5.93	8.69	7.25	8.67

Predicted solubility of CO_2 in pure aniline = 1.06×10^{-1} kmol/m^3. Predicted solubility of CO_2 in pure CCl_4 = 7.56×10^{-2} kmol/m^3. Predicted solubility of CO_2 in pure $CHCl_3$ = 7.68×10^{-2} kmol/m^3.

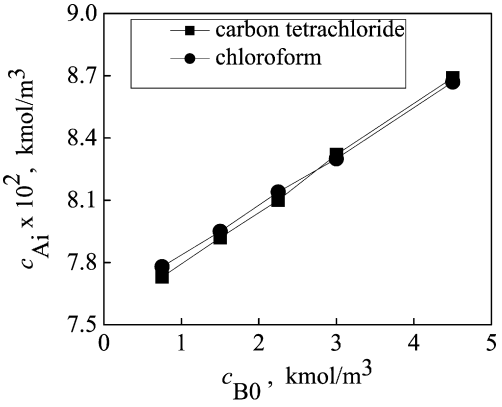

Fig. 1. Variation in predicted solubility of CO_2 in aniline solutions of carbon tetrachloride and chloroform at 303 K.

Table 2
Predicted diffusivity of CO_2 in aniline solutions of carbon tetrachloride and chloroform at 303 K

[Aniline], c_{B0} (kmol/m^3)	Predicted diffusivity of CO_2, $D_A \times 10^9$ (m^2 s^{-1})	
	Carbon tetrachloride	Chloroform
0.75	5.57	6.16
1.50	5.06	5.65
2.25	4.52	5.2
3.00	4.03	4.8
4.50	3.21	4.01

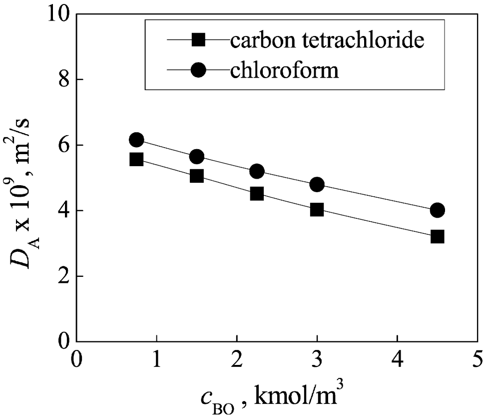

Fig. 2. Variation in predicted diffusivity of CO_2 in aniline solutions of carbon tetrachloride and chloroform at 303 K.

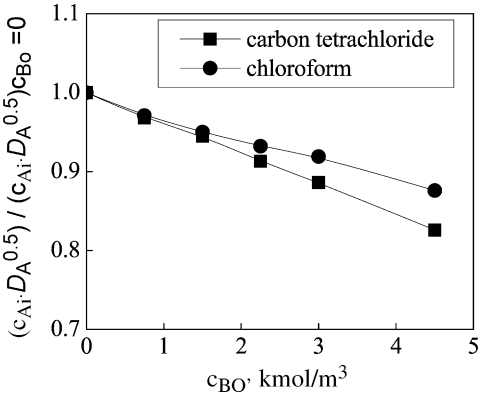

Fig. 3. Estimated variation of $c_{Ai}D_A^{1/2}/(c_{Ai}D_A^{1/2})_{c_{B0}=0}$ with aniline concentration in carbon tetrachloride and chloroform at 303 K.

k_L values at different speeds of stirring in the model stirred contactor were obtained from earlier work by Yadav [66], conducted on a model stirred contactor with identical configuration. The values of diffusivity of CO_2 in aniline solutions were estimated from Eq. (2),

$$\frac{D_A \mu}{T} = \text{constant} \quad (2)$$

5. Materials

Aniline of synthesis grade, and carbon tetrachloride and chloroform of LR grade were obtained from Merck Limited. CO_2 cylinder containing AR grade CO_2 was obtained from BOC (Special Gases) Limited, Mumbai. Nitrogen gas cylinder was obtained from a reputed firm.

6. Theory

The following chemical reaction was considered for the analysis of experimental results:

$$A_{(\text{dissolved gas})} + zB_{(\text{liquid-phase reactant})} \xrightarrow{k_{m,n}} \text{product} \quad (3)$$

where A = CO_2, B = aniline, product = carbamate, z = stoichiometric factor = 2, and $k_{m,n} = (m+n)$th order kinetic rate constant for the reaction between A and B

The theory of mass transfer accompanied by *irreversible* and *reversible* reactions of general order, and the methods of discerning the controlling mechanism has been discussed in detail by Doraiswamy and Sharma [70]. Please see Appendix A for relevant equations. A reaction belongs to very slow reaction regime if the rate of reaction between dissolved A and B is very much slower, than the rate of transfer of A into the B phase and at any moment B phase is saturated with solute A. Under this condition, the rate of formation of products will be determined by the kinetics of homogeneous chemical reaction. For the very slow reaction regime, the transfer rate of A is given by Eq. (A.1). The condition to be satisfied for the very slow reaction regime is given by Eq. (A.2). For slow reaction regime, the rate of reaction between A and B is faster than the rate at which A is transferred to the B phase and the rate is controlled by the transfer of A into the B phase. When the concentration of dissolved A in the bulk B phase is negligible, then the specific reaction rate can be given by Eq. (A.3). The conditions to be satisfied for the slow reaction regime, if the bulk concentration of A in liquid phase is negligible, are given by Eqs. (A.4) and (A.5). The dissolved gas undergoes a pseudo-first-order reaction when the concentration of the reactant in the neighborhood of the gas–liquid interface is not very different from that in the bulk and the concentration of the dissolved gas is very small compared to the reactant concentration. The conditions to be satisfied are given by Eqs. (A.6) and (A.7). The specific rate of reaction is given by Eq. (A.8). In some cases, the reaction of dissolved A may occur partly in the film and partly in the bulk and yet there may be a finite concentration of the dissolved solute A in the bulk liquid phase, then such a case may be considered as the overlapping case of very slow, slow and fast reaction regime.

The rate expression for that overlapping case is given by Eq. (A.9).

7. Results and discussion

Most of the experiments were conducted in the stirred cell. However, the solubility of CO_2 in solutions of aniline in both the solvents used is not very small ($\approx 8.09 \times 10^{-2}$ kmol/(m^3 atm) in carbon tetrachloride, $\approx 8.15 \times 10^{-2}$ kmol/(m^3 atm) in chloroform); hence, it is expected that the gas-side resistance may be present when CO_2 is absorbed from mixtures of CO_2 and nitrogen. Hence, in order to find out the order of reaction with respect to CO_2, some experiments were conducted in the model stirred contactor as well, wherein the gas-side resistance was eliminated by stirring the gas-phase independently at a very high stirring speed of about 1500 rev/min.

7.1. Absorption of CO_2 with solution of aniline in carbon tetrachloride

The influence of CO_2 partial pressure on the specific rate of absorption was investigated in the model stirred contactor, where the partial pressure of CO_2 was varied from 0.54 to 0.84 atm at the gas–liquid interface (Fig. 4). It was found from Fig. 4 and Eq. (A.8) that m, namely the order of reaction with respect to solute gas A (CO_2), is 1.06, which can be rounded off to 1.

Fig. 5 shows the variation of the specific absorption rate of pure CO_2 with stirring speed in the stirred cell, at different aniline concentrations. The specific rate appeared to be dependent on the hydrodynamic factors in the range of stirring speed from 50 to 102 rev/min, for the studied aniline concentrations. However, as the aniline concentration increases the slope of the lines decreases, which means the specific absorption rate was less dependent on the hydrodynamic factors at higher aniline concentration.

To find out the controlling regime (mechanism) of reaction, we have calculated the values of $R_A/(k_L\ c_{Ai})$. These values are tabulated in Table 3. From the foregoing analysis, the absorption of CO_2 with aniline dissolved in carbon tetrachloride, therefore, appears to conform to the intermediate regime between very slow, slow and fast reactions regime where the dissolved CO_2 reacts partly in the film and partly in the bulk and yet there may be a finite quantity of dissolved CO_2 in the bulk liquid.

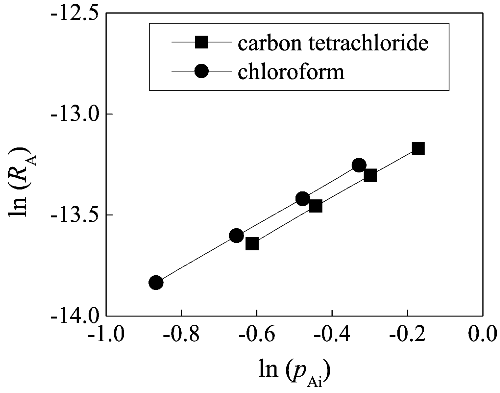

Fig. 4. Variation of specific absorption rate of CO_2 with partial pressure of CO_2 at 1.50 kmol/m^3 aniline concentration, in carbon tetrachloride and chloroform, at 303 ± 1 K, (liquid phase stirring speed = 110 rev/min, stirred contactor).

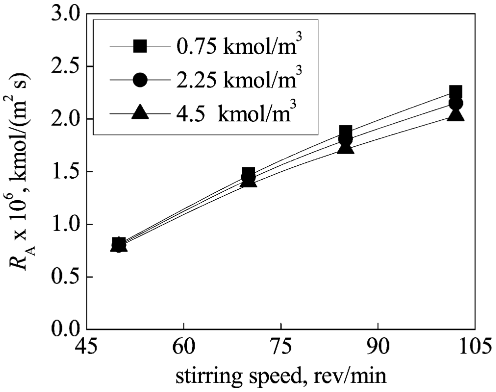

Fig. 5. Variation of specific absorption rate of CO_2 with stirring speed at different aniline concentrations in carbon tetrachloride (stirred cell) at 303 ± 1 K.

Therefore, considering the intermediate reaction regime, we have graphically found out the order of reaction with respect to aniline. Here, instead of plotting ln(R_A) versus ln(c_{Bo}), we have plotted ln(k_1) (k_1 was obtained using Eq. (A.9)) versus ln(c_{Bo}) in Fig. 7, owing to our observation that both c_{Ai} and liquid viscosity (and hence D_A) change with a change in c_{B0}. It was found from this graph that n, namely the order of reaction with respect to liquid phase reactant B (aniline), is −0.05, which

Table 3

Calculated values of $R_A/(k_L\ c_{Ai})$ and $(1 + (c_{B0}D_B^{0.5}/zc_{Ai}D_A^{0.5}))$ for the absorption of CO_2 with aniline dissolved in carbon tetrachloride at 303 K (Eqs. (A.7) and (A.8))

Contactor	Stirring speed (rev/min)	p_A[a] (atm)	c_{B0} (kmol/m^3)	$R_A/(k_Lc_{Ai})$	$1 + (c_{B0}D_B^{0.5}/zc_{Ai}D_A^{0.5})$
Stirred cell	102	0.83	0.75	0.630	3.68
Stirred cell	102	0.84	1.50	0.635	6.23
Stirred cell	102	0.86	2.25	0.642	8.68
Stirred cell	102	0.87	3.00	0.648	10.96
Stirred cell	102	0.90	4.50	0.667	15.29
Stirred contactor	110	0.84	1.50	0.691	6.25
Stirred contactor	110	0.74	1.50	0.687	6.96
Stirred contactor	110	0.64	1.50	0.683	7.89
Stirred contactor	110	0.54	1.50	0.672	9.17

[a] Values are corrected for the vapor pressure of carbon tetrachloride.

Table 4
Absorption of CO_2 with aniline dissolved in carbon tetrachloride at 303 ± 1 K with a stirring speed = 102 rev/min

Contactor	c_{B0} (kmol/m^3)	p_A[a] (atm)	Rate equation	$k_{1,-0.05} \times 10^3$ (kmol/m^3)$^{0.05}$ s^{-1}	Remarks
Stirred cell	0.75	0.83	(A.9)	1.20	Between very slow, slow and fast reaction regime
Stirred cell	1.50	0.84	(A.9)	1.16	Between very slow, slow and fast reaction regime
Stirred cell	2.25	0.86	(A.9)	1.14	Between very slow, slow and fast reaction regime
Stirred cell	3.00	0.87	(A.9)	1.12	Between very slow, slow and fast reaction regime
Stirred cell	4.50	0.90	(A.9)	1.10	Between very slow, slow and fast reaction regime
Stirred contactor	1.5	0.84	(A.9)	1.20	Between very slow, slow and fast reaction regime
Stirred contactor	1.50	0.74	(A.9)	1.18	Between very slow, slow and fast reaction regime
Stirred contactor	1.50	0.64	(A.9)	1.16	Between very slow, slow and fast reaction regime
Stirred contactor	1.50	0.54	(A.9)	1.10	Between very slow, slow and fast reaction regime

[a] Values are corrected for the vapor pressure of carbon tetrachloride.

can practically be rounded off to 0. Table 4 gives the pertinent details. The average value of the intrinsic kinetic rate constant ($k_{1,0}$), at 303 ± 1 K, was estimated at 1.18×10^{-3} s$^{-\mathbf{1}}$.

7.2. Absorption of CO_2 with solution of aniline in chloroform

The specific rate of absorption in the model stirred contactor was found to be directly proportional to the partial pressure of CO_2, which was varied from 0.42 to 0.72 atm, at the gas–liquid interface (Fig. 4). It was found from Fig. 4 and Eq. (A.9) that m, namely the order of reaction with respect to solute gas A (CO_2), is 1.08, which can be rounded off to 1.

It is apparent from Fig. 6 that the specific rate in the stirred cell is dependent on the hydrodynamic factors in the range of stirring speeds from 50 to 102 rev/min, for lower aniline concentrations. However, the specific rate was found to be almost independent of the hydrodynamic factors, for higher aniline concentrations.

From the foregoing analysis, and from the values of $R_A/(k_L c_{Ai})$ as given in Table 5, it appears that the absorption of CO_2 with aniline dissolved in carbon tetrachloride, conforms to the intermediate regime between very slow, slow and fast reactions regime. In this regime, the dissolved CO_2 reacts partly in the film and partly in the bulk and yet there may be a finite quantity of dissolved CO_2 in the bulk liquid.

k_1 was obtained using Eq. (A.9). From the plot of $\ln(k_1)$ versus $\ln(c_{Bo})$ as shown in Fig. 7, it was found that n, namely the order of reaction with respect to liquid phase reactant B (aniline), is −0.39, which can be rounded off to −0.4. Table 6

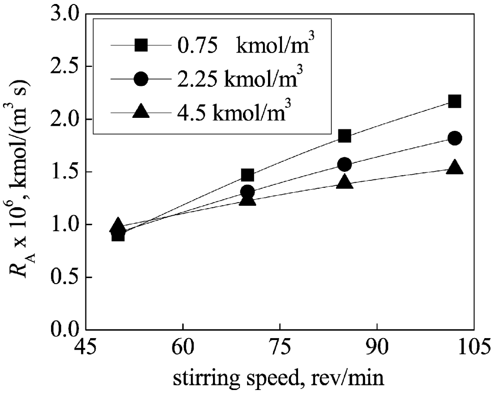

Fig. 6. Variation of specific absorption rate of CO_2 with stirring speed at different aniline concentrations in chloroform (stirred cell) 303 ± 1 K.

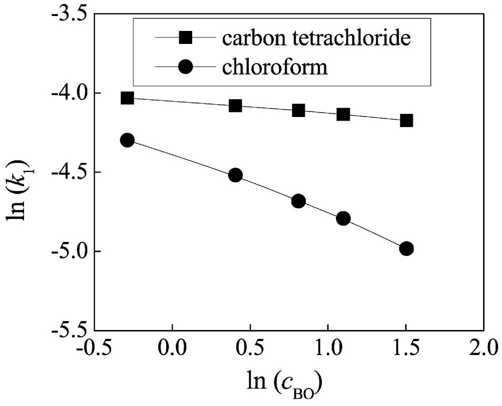

Fig. 7. Variation of k_1 with aniline concentration in carbon tetrachloride and chloroform, at 303 ± 1 K, (stirring speed = 102 rev/min, stirred cell).

Table 5
Calculated values of $R_A/(k_L\, c_{Ai})$ and $(1 + (c_{B0} D_B^{0.5}/z c_{Ai} D_A^{0.5}))$ for the absorption of CO_2 with aniline dissolved in chloroform at 303 K (Eqs. (A.7) and (A.8))

Contactor	Stirring speed (rev/min)	p_A[a] (atm)	c_{B0} (kmol/m^3)	$R_A/(k_L c_{Ai})$	$1 + (c_{B0} D_B^{0.5}/z c_{Ai} D_A^{0.5})$
Stirred cell	102	0.70	0.75	0.552	3.66
Stirred cell	102	0.72	1.50	0.506	6.21
Stirred cell	102	0.74	2.25	0.478	8.63
Stirred cell	102	0.76	3.00	0.454	10.97
Stirred cell	102	0.80	4.50	0.436	15.32
Stirred contactor	110	0.72	1.50	0.567	6.21
Stirred contactor	110	0.62	1.50	0.557	7.05
Stirred contactor	110	0.52	1.50	0.554	8.22
Stirred contactor	110	0.42	1.50	0.544	9.95

[a] Values are corrected for the vapor pressure of chloroform.

Table 6
Absorption of CO_2 with aniline dissolved in chloroform at 303 ± 1 K with a stirring speed = 102 rev/min

Contactor	c_{B0} (kmol/m^3)	p_A[a] (atm)	Rate equation	$k_{1,-0.4} \times 10^4$ (kmol/m^3)$^{0.4}$ s^{-1}	Remarks
Stirred cell	0.75	0.70	(A.9)	8.82	Between very slow, slow and fast reaction regime
Stirred cell	1.50	0.72	(A.9)	9.06	Between very slow, slow and fast reaction regime
Stirred cell	2.25	0.74	(A.9)	9.17	Between very slow, slow and fast reaction regime
Stirred cell	3.00	0.76	(A.9)	9.08	Between very slow, slow and fast reaction regime
Stirred cell	4.50	0.80	(A.9)	9.13	Between very slow, slow and fast reaction regime
Stirred contactor	1.5	0.72	(A.9)	9.29	Between very slow, slow and fast reaction regime
Stirred contactor	1.50	0.62	(A.9)	8.94	Between very slow, slow and fast reaction regime
Stirred contactor	1.50	0.52	(A.9)	8.82	Between very slow, slow and fast reaction regime
Stirred contactor	1.50	0.42	(A.9)	8.47	Between very slow, slow and fast reaction regime

[a] Values are corrected for the vapor pressure of chloroform.

Table 7
Values of intrinsic kinetic rate constants, solubility parameters, relative dielectric constants, for carbon tetrachloride, chloroform, acetonitrile, methyl ethyl ketone, toluene and xylene

Properties	Carbon tetrachloride	Chloroform	Acetonitrile[a]	Methyl ethyl ketone[a]	Toluene[a]	m-Xylene[a]
δ_1, MPa$^{1/2}$, at 298 K	18.0	18.70	24.60	19.05	18.30	18.06
ε, at 298 K	2.23	4.8	36.60	18.50	2.40	2.30
$k_{1,n}$, at 303 ± 1 K (kmol/m^3)$^{-n}$ s^{-1}	1.18×10^{-3}	8.93×10^{-4}	1.40×10^{2}	4.90×10^{-1}	2.02×10^{-1}	2.45×10^{-2}

[a] From Dinda et al. [64].

gives the pertinent details. The average value of the intrinsic kinetic rate constant ($k_{1,-0.4}$), at 303 ± 1 K, was estimated at 8.93×10^{-4} (kmol/m^3)$^{0.4}$ s^{-1}.

7.3. *Effect of solvent on intrinsic kinetic rate constants*

For the purpose of observing the effect of solvent on the intrinsic kinetic rate constant $k_{1,n}$, the relevant data of Dinda et al. [63] has also been considered here (Table 7, Figs. 8 and 9). With the exception of chloroform as the solvent, the intrinsic kinetic rate constant of $k_{1,n}$ appeared to increase with Hildebrand solubility parameter δ_1 as well as with the relative dielectric constant ε. The Hildebrand solubility parameter is the total van der Waals force, and is a numerical value that indicates the relative solvency behavior of a specific solvent. It is derived from the cohesive energy density of the solvent, which in turn is derived from the heat of vaporization.

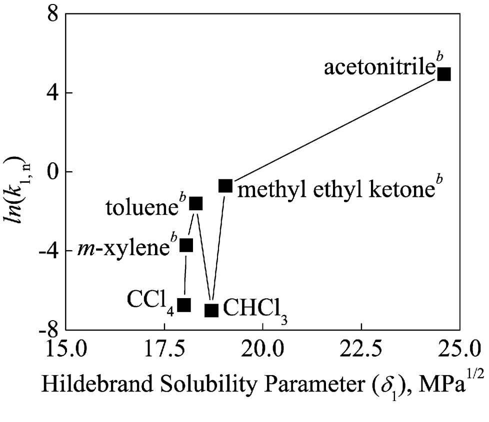

Fig. 8. Variation of $k_{1,n}$ with solubility parameter.

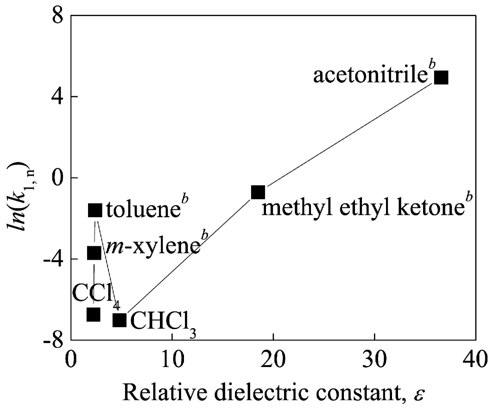

Fig. 9. Variation of $k_{1,n}$ with relative dielectric constant.

8. Conclusions

The absorption of CO_2 with solutions of aniline in commercially available chlorinated hydrocarbon solvents such as carbon tetrachloride and chloroform, within the aniline concentration range between 0.75 and 4.50 kmol/m^3, was found to conform to the intermediate regime between very slow, slow and fast reactions regime where the dissolved CO_2 reacts partly in the film and partly in the bulk and yet there may be a finite quantity of dissolved CO_2 in the bulk liquid. The reaction was found to be first order with respect to CO_2. The reaction order with respect to aniline was found to be 0, and −0.4 in the case of carbon tetrachloride and chloroform, respectively, as solvents. These findings will have a direct bearing on the design and scale up of absorber in the process development for carbamates/isocyanates. In addition, there appears to be a correlation between the intrinsic kinetic rate constant and the polarity of the solvent employed.

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Appendix A

$$R_A \underline{a} = l k_{m,n} (c_{Ai})^m (c_{B0})^n \tag{A.1}$$

$$k_L(c_{Ai}) \gg l k_{m,n} (c_{Ai})^m (c_{B0})^n \tag{A.2}$$

$$R_A = k_L(c_{Ai}) \tag{A.3}$$

$$k_L(c_{Ai}) \ll l k_{m,n} (c_{Ai})^m (c_{B0})^n \tag{A.4}$$

$$\frac{((2/m+1) D_A k_{m,n} (c_{Ai})^{m-1} (c_{B0})^n)^{1/2}}{k_L} \ll 1 \tag{A.5}$$

$$\frac{(D_A k_1)^{1/2}}{k_L} \gg 1 \tag{A.6}$$

$$\frac{(D_A k_1)^{1/2}}{k_L} \ll 1 + \frac{c_{B0}}{z c_{Ai}} \left(\frac{D_B}{D_A} \right)^{1/2} \tag{A.7}$$

$$R_A = c_{Ai} (D_A k_1)^{1/2} \tag{A.8}$$

$$R_A = \frac{c_{Ai} (D_A k_1)^{0.5}}{\tanh[(D_A k_1)^{0.5}/k_L]} \times \left\{ 1 - \left[\cosh^2 \left\langle \frac{(D_A k_1)^{0.5}}{k_L} \right\rangle \times \left\langle \frac{l k_1}{\underline{a}} \frac{\tanh[(D_A k_1)^{0.5}/k_L]}{(D_A k_1)^{0.5}} \right\rangle \right]^{-1} \right\} \tag{A.9}$$

References

[1] K. Bratzler, A. Doerges, Amisol process purifies gases, Hydrocarbon Process. 53 (1974) 78–80.

[2] J. Wall, Gas processing handbook, Hydrocarbon Process. 54 (1975) 79–138.

[3] M.M. Sharma, Kinetics of reactions of carbonyl sulphide and carbon dioxide with amines and catalysis by Brönsted bases of the hydrolysis of COS, Trans. Faraday Soc. 61 (1965) 681–688.

[4] M. Aresta, E. Quaranta, Role of the macrocyclic polyether in the synthesis of N-alkyl carbamate esters from primary amines, CO_2 and alkyl halides in the presence of crown-ethers, Tetrahedron 48 (1992) 1515–1530.

[5] M. Aresta, E. Quaranta, Reaction of alkali-metal tetraphenylborates with amines in the presence of CO_2: a new easy way to aliphatic and aromatic alkali-metal carbamates, J. Chem. Soc., Dalton Trans.: Inorg. Chem. 20 (1995) 3359–3363.

[6] M. Aresta, A. Dibenedetto, E. Quaranta, M. Boscolo, R. Larsson, The kinetics and mechanism of the reaction between carbon dioxide and a series of amines: observation and interpretation of an isokinetic effect, J. Mol. Catal. A: Chem. 174 (2001) 7–13.

[7] A. Belforte, F. Calderazzo, Formation of alkylurethanes from carbon dioxide by regioselective *O*-alkylation of alkali-metal *N*,*N*-diethylcarbamates in the presence of complexing agents, J. Chem. Soc., Dalton Transactions: Inorg. Chem. 5 (1989) 1007–1009.

[8] B.M. Bhanage, Shin-ichiro. Fujita, Y. Ikushima, A. Masahiko, Synthesis of cyclic ureas and urethanes from alkylene diamines and amino alcohols with pressurized carbon dioxide in the absence of catalysts, Green Chem. 5 (2003) 340–342.

[9] Z. Jiyan, Z. Xinqiang, W. Yanji, W. Shufang, Y. Hongjian, Synthesis of MDI from Dimethyl Carbonate over Solid Catalysts, Ind. Eng. Chem. Res. 41 (2002) 5139–5144.

[10] R. Mahé, Y. Sasaki, C. Bruneau, P.H. Dixneuf, Catalytic synthesis of vinyl carbamates from carbon dioxide and alkynes with ruthenium complexes, J. Org. Chem. 54 (1989) 1518–1523.

[11] W.D. McGhee, Y. Pan, D.P. Riley, Highly selective generation of urethanes from amines, carbon dioxide, and alkyl chlorides, J. Chem. Soc., Chem. Commun. 6 (1994) 699–700.

[12] W.D. McGhee, D.P. Riley, K. Christ, Y. Pan, B. Parnas, Carbon dioxide as a phosgene replacement: synthesis and mechanistic studies of urethanes from amines, CO_2, and alkyl chlorides, J. Org. Chem. 60 (1995) 2820–2830.

[13] T. Mitsudo, Y. Hori, Y. Yamakawa, Y. Watanabe, Ruthenium catalyzed selective synthesis of enol carbamates by fixation of carbon dioxide, Tetrahedron Lett. 28 (1987) 4417–4418.

[14] T.E. Waldman, W.D. McGhee, Isocyanates from primary amines and carbon dioxide: "dehydration" of carbamate anions, J. Chem. Soc., Chem. Commun. 8 (1994) 957–958.

[15] D. Chaturvedi, A. Kumar, S. Ray, A high yielding one-pot novel synthesis of carbamate esters from alcohols using Mitsunobu's reagent, Tetrahedron Lett. 44 (2003) 7637–7639.

[16] X.-B. Lu, X.-J. Feng, Ren. He, Catalytic formation of ethylene carbonate from supercritical carbon dioxide/ethylene oxide mixture with tetradentate Schiff-base complexes as catalysts, Appl. Catal. A: Gen. 234 (2002) 25–33.

[17] R. Srivastava, M.D. Manju, D. Srinivas, P. Ratnasamy, Phosgene-free synthesis of carbamates over zeolite-based catalysts, Catal. Lett. 97 (2004) 41–47.

[18] M.A. Casadei, A. Inesi, F.M. Moracci, L. Rossi, Electrochemical activation of carbon dioxide: synthesis of carbamates, Chem. Commun. (Cambridge) 22 (1996) 2575–2576.

[19] M. Yoshida, N. Hara, S. Okuyama, Catalytic production of urethanes from amines and alkyl halides in supercritical carbon dioxide, Chem. Commun. (Cambridge) 2 (2000) 151–152.

[20] M. Abla, J.-C. Choi, T. Sakakura, Halogen-free process for the conversion of carbon dioxide to urethanes by homogeneous catalysis, Chem. Commun. (Cambridge) 21 (2001) 2238–2239.

[21] D.B. Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti, G. Pampaloni, Converting carbon dioxide into carbamato derivatives, Chem. Rev. 103 (2003) 3857–3898.

[22] Y. Sasaki, P.H. Dixneuf, Ruthenium-catalyzed reaction of carbon dioxide, amine, and acetylenic alcohol, J. Org. Chem. 52 (1987) 4389–4391.

[23] Y. Sasaki, P.H. Dixneuf, Ruthenium-catalyzed synthesis of vinyl carbamates from carbon dioxide, acetylene, and secondary amines, J. Org. Chem. 52 (1987) 314–315.

[24] A.R. Katritzky, M. Black, W.Q. Fan, Carbon dioxide: a reagent for the simultaneous protection of nucleophilic centers and the activation of alternative locations to electrophilic attack. 17. Substitution of *N*-methyl-1- and *N*-methyl-2-naphthylamine and side-chain functionalization of *o*-toluidine, J. Org. Chem. 56 (1991) 5045–5048.

[25] R. Nomura, Y. Hasegawa, M. Ishimoto, T. Toyosaki, H. Matsuda, Carbonylation of amines by carbon dioxide in the presence of an organoantimony catalyst, J. Org. Chem. 57 (1992) 7339–7342.

[26] M.A. Casadei, F.M. Moracci, G. Zappia, A. Inesi, L. Rossi, Electrogenerated superoxide-activated carbon dioxide, a new mild and safe approach to organic carbamates, J. Org. Chem. 62 (1997) 6754–6759.

[27] D. Saylik, M.J. Horvath, P.S. Elmes, W.R. Jackson, C.G. Lovel, K. Moody, Preparation of isocyanates from primary amines and carbon dioxide using Mitsunobu chemistry, J. Org. Chem. 64 (1999) 3940–3946.

[28] R.N. Salvatore, Seung Il. Shin, A.S. Nagle, K.W. Jung, Efficient carbamate synthesis via a three-component coupling of an amine, CO_2, and alkyl halides in the presence of CS_2CO_3 and tetrabutylammonium iodide, J. Org. Chem. 66 (2001) 1035–1037.

[29] M.O. Bratt, P.C. Taylor, Synthesis of carbonates and related compounds from carbon dioxide via methanesulfonyl carbonates, J. Org. Chem. 68 (2003) 5439–5444.

[30] C.J. Dinsmore, P.S. Mercer, Carboxylation and Mitsunobu reaction of amines to give carbamates: retention versus inversion of configuration is substituent-dependent, Org. Lett. 6 (2004) 2885–2888.

[31] W.D. McGhee, D.P. Riley, Palladium-mediated synthesis of urethanes from amines, carbon dioxide, and cyclic diolefins, Organometallics 11 (1992) 900–907.

[32] W.D. McGhee, D.P. Riley, M.E. Christ, K.M. Christ, Palladium-catalyzed generation of *O*-allylic urethanes and carbonates from amines/alcohols, carbon dioxide, and allylic chlorides, Organometallics 12 (1993) 1429–1433.

[33] D.C. Dean, M.A. Wallace, T.M. Marks, D.G. Melillo, Efficient utilization of [^{14}C] carbon dioxide as a phosgene equivalent for labeled synthesis, Tetrahedron Lett. 38 (1997) 919–922.

[34] M.J. Horvath, D. Saylik, P.S. Elmes, W.R. Jackson, C.G. Lovel, K. Moody, A Mitsunobu-based procedure for the preparation of alkyl and hindered aryl isocyanates from primary amines and carbon dioxide under mild conditions, Tetrahedron Lett. 40 (1999) 363–366.

[35] Joon-Chul. Choi, A. Mahamdi, T. Sakakura, Preparation of carbamate esters from amines, alcohols, and carbon dioxide, Japanese Patent JP2004189728, 2004.

[36] T. Sakakura, A. Mahhumdy, Chun-Che. Tsui, Preparation of carbamate esters as intermediates for polyurethanes from amines, alcohols, and carbon dioxide, Japanese Patent JP2002212159, 2002.

[37] B. Lee, Phosgene-free process for preparing carbamates using dry ice under standard temperature and pressure, International Patent WO2002034698, 2002.

[38] H. Barth, H.J. Betche, K. Steiner, S. Schneider, U. Bayer, M. Westermayer, U. Wolfsperger, Preparation of carbamates from indoles and other nitrogen heterocycles using carbon dioxide, German Patent DE19913483, 2000.

[39] K.W. Jung, Efficient carbamate synthesis by reaction of amines, electrophiles and carbon dioxide in the presence of a cesium compound, International Patent WO2000050389, 2000.

[40] J.H. Orth, Preparation of aminocarbamates from diamines and carbon dioxide, International Patent WO9729083, 1997.

[41] W.D. McGhee, M.D. Paster, D.P. Riley, K.W. Ruettimann, A.J. Solodar, T.E. Waldman, Process for preparing isocyanates, International Patent WO9518098, 1995.

[42] L. Heuer, Preparation of carbamates, German Patent DE4318889, 1994.

[43] W.D. McGhee, Process for preparing isocyanates, International Patent WO9417032, 1994.

[44] W.D. McGhee, T.E. Waldman, Phosphazene induced preparation of isocyanates, US Patent US5298651, 1994.

[45] W.D. McGhee, J.J. Talley, Preparation of urethanes and carbonates, US Patent US5302717, 1994.

[46] W.D. McGhee, M.K. Stern, T.E. Waldman, Process for preparing isocyanate and carbamate ester products, US Patent US5233010, 1993.

[47] W.D. McGhee, T.E. Waldman, Process for preparing isocyanates from amines and carbon dioxide, US5189205, 1993.

[48] W.D. McGhee, B.L. Parnas, D.P. Riley, J.J Talley, Phosgene-free process for preparing urethane and carbonate monomers and polymers, European Patent EP511948, 1992.

[49] W.D. McGhee, D.P. Riley, Preparation of urethane and carbonate products, European Patent EP477159, 1992.

[50] D.P. Riley, W.D. McGhee, Preparation of urethane products, US Patent US5055577, 1991.

[51] H. Kawanami, Y. Ikushima, K. Hatakeda, K. Torii, Preparation of cyclic urethanes from amino alcohols and carbon dioxide under mild and environmentally friendly conditions, Japanese Patent JP2003064062, 2003.

[52] Y. Kubota, M. Odaka, T. Tomohiro, H. Okuno, Manufacture of cyclic urethanes, Japanese Patent JP06092945, 1994.

[53] M. Caplow, Kinetics of carbamate formation and breakdown, J. Am. Chem. Soc. 90 (1968) 6795–6803.

[54] J.E. Crooks, J.J.P. Donnellan, Kinetics of the reaction between carbon dioxide and tertiary amines, J. Org. Chem. 55 (1990) 1372–1374.

[55] J.E. Crooks, J.P. Donnellan, Kinetics of the formation of *N*,*N*-dialkylcarbamate from diethanolamine and carbon dioxide in anhydrous ethanol, J. Chem. Soc., Perkin Trans. 2 2 (1988) 191–194, Phys. Org. Chem.

[56] P.V. Danckwerts, Absorption accompanied by chemical reaction, AIChE J. 12 (1955) 456–463.

[57] P.V. Danckwerts, The reaction of carbon dioxide with ethanolamines, Chem. Eng. Sci. 34 (1979) 443–446.

[58] S.H. Ali, S.Q. Merchant, M.A. Fahim, Kinetic study of reactive absorption of some primary amines with carbon dioxide in ethanol solution, Sep. Purif. Technol. 18 (2000) 163–175.

[59] K. Masuda, Y. Ito, M. Horiguchi, H. Fujita, Studies on the solvent dependence of the carbamic acid formation from ω-(1-naphthyl)alkylamines and carbon dioxide, Tetrahedron 61 (2005) 213–229.

[60] C. Alvarez-Fuster, N. Midoux, A. Laurent, J.C. Charpentier, Chemical kinetics of the reaction of CO_2 with amines in pseudo $(m-n)$th order conditions in polar and viscous organic solutions, Chem. Eng. Sci. 36 (1981) 1513–1518.

[61] E. Sada, H. Kumazawa, Y. Osawa, M. Matsuura, Z.Q. Han, Chemical kinetics of the reaction of carbon dioxide with ethanolamines in nonaqueous solvents, AIChE J. 31 (1985) 1297–1303.

[62] E. Sada, H. Kumazawa, Y. Osawa, M. Matsuura, Z.Q. Han, Reaction kinetics of carbon dioxide with amines in nonaqueous solvents, The Chem. Eng. J. 33 (1985) 87–95.

[63] S. Dinda, A.V. Patwardhan, N.C. Pradhan, Kinetics of reactive absorption of carbon dioxide with solutions of aniline in nonaqueous aprotic solvents, Ind. Eng. Chem. Res. 45 (2006) 6632–6639.

[64] A.V. Patwardhan, Heterogeneous Reactions, Ph.D. (Technology) dissertation, Department of Chemical Technology, University of Mumbai, India, 1988.

[65] A.V. Patwardhan, M.M. Sharma, Kinetics of absorption of oxygen in aqueous alkaline solutions of polyhydroxybenzenes, Ind. Eng. Chem. Res. 27 (1988) 36–41.

[66] G.D. Yadav, M.M. Sharma, Effect of diffusivity on true gas-side mass transfer coefficient in a model stirred contactor with a plane liquid interface, Chem. Eng. Sci. 34 (1979) 1423–1424.

[67] M.R.J. Dack, Solution and Solubilities (Part 1), Wiley, New York, 1974.

[68] E. Wilhelmi, R. Battino, Thermodynamic functions of the solubilities of gases in liquids at 25 degrees, Chem. Rev. 73 (1973) 1–9.

[69] P.V. Danckwerts, Gas–Liquid Reactions, McGraw-Hill, New York, 1970.

[70] L.K. Doraiswamy, M.M. Sharma, Heterogeneous Reactions, Analysis, Design, and Examples, vol. II, Wiley, New York, 1984.