Effect of non-aqueous solvents on kinetics of carbon dioxide absorption by $^tBu_3P/B(C_6F_5)_3$ frustrated Lewis pairs

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ABSTRACT

Frustrated Lewis pairs (FLPs), combinations of sterically hindered Lewis acids and bases, are known for their ability to capture CO_2. Although there have been several theoretical studies on the mechanisms of the reactions between CO_2 and some FLP systems, experimental studies on the reaction kinetics have been inconclusive. In this study, the mechanism and kinetics of CO_2 absorption by an FLP system consisting of tri-*tert*-butylphosphine ($^tBu_3P$) and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) in bromobenzene, cyclopentyl methyl ether (CPME), and *tert*-butyl methyl ether (MTBE) were investigated using the stopped-flow method. The pseudo-first-order reaction rate constants, k_o (s^{-1}), were measured for a concentration range of 0.02–0.035 M and over a temperature range of 298–323 K. The experimental data were fitted according to modified termolecular mechanisms with average absolute relative deviations of 4.34%, 4.63%, and 3.51% for the CO_2–FLP:bromobenzene, CO_2–FLP:CPME, and CO_2–FLP:MTBE systems, respectively. The forward reaction rate constants, k (m^3 $kmol^{-1}$ s^{-1}), were calculated based on the proposed reaction mechanism. The forward reaction rate constants were higher than those for various aqueous tertiary amine systems but lower than those for aqueous monoethanolamine and piperazine systems. Moreover, the activation energies were estimated from Arrhenius plots. They were calculated to be 22.0, 19.7, and 21.8 kJ mol^{-1} for the CO_2–FLP:bromobenzene, CO_2–FLP:CPME, and CO_2–FLP:MTBE systems, respectively. This study promotes the development of novel efficient solvent formulations for CO_2 capture.

1. Introduction

Carbon dioxide is one of the significant greenhouse gases responsible for global warming; its concentration in the atmosphere has reached remarkable levels in the last 20 years owing to increase in industrial activities and the human population [1]. CO_2 emission reached 410 ppm in 2020; hence, appropriate action must be undertaken to address global warming, which is a worldwide threat to life on Earth. Although many alternative energy sources have been recommended, especially for industrial processes, fossil fuels continue to be the preferred energy source because of their high energy output, easy accessibility, and high combustion capacity [2]. Iron–steel, plastic, paper, packaging, cement, and especially power generation plants have primarily contributed to the increasing CO_2 emission in the atmosphere. Considering the increase in the production capacity of these industries, CO_2 emission must be

reduced by 50% by 2050 [3]. In order to develop new energy sources and propose cost-efficient long-term solutions for life-threatening CO_2 emission, studies on CO_2 capture and storage have gained increasingly significant importance in recent years [4–6].

It is accepted that the chemical absorption of CO_2 into aqueous amine solutions followed by regeneration of the CO_2-loaded solutions through temperature swing desorption is the most convenient method for CO_2 capture [7,8]. The CO_2 absorption solvent must have low vapor pressure, viscosity, and corrosiveness. The solvent must also highly selectively dissolve CO_2, be relatively easy to regenerate, and have high CO_2 absorption rate and loading capacity [9,10]. However, conventional aqueous-amine-based solvents are corrosive, have high reboiler duty during regeneration, and cause high solvent loss during acid gas stripping [11–17]. Therefore, the development of novel solvent formulations, especially those that include organics, has gained importance.

Fig. 1. Molecular structures of (a) $B(C_6F_5)_3$ and (b) $^tBu_3P$.

Fig. 2. Molecular structures of (a) bromobenzene, (b) CPME, and (c) MTBE.

Fig. 3. The reaction between $^tBu_3P/B(C_6F_5)_3$ and CO_2.

Non-aqueous absorbents are promising solvents because of their low energy requirement for regeneration, low degradation, and low corrosiveness [18]. CO_2 binding organic liquids (CO_2-BOLs) and ionic liquids (ILs) have been proposed to be used as phase-changing non-aqueous solvents for the capture of CO_2 [19–22]. CO_2-BOLs, which are switchable solvents, are liquid mixtures of strong organic bases and alcohols that can reversibly react with CO_2 and have high volumetric and gravimetric CO_2 capacities [23–26]. However, a drawback of CO_2-BOLs is the relatively high volatility of the individual constituents, which can result in solvent loss during regeneration. Heldebrandt and co-workers proposed polarity-assisted regeneration with lower regeneration temperatures around 75 °C to reduce solvent loss and reboiler duty cost [27]. On the other hand, ILs are molten salts formed through the combination of cations and anions; they have gained attention because of their tunable physicochemical properties and less energy-intensive nature [28–30]. ILs exhibit high thermal stability and CO_2 solubility; they are in the liquid state over a wide temperature range [31]. ILs have CO_2 absorption capacity of around one mole per mole of IL, higher than those of traditional aqueous-amine-based solvents [32]. Nevertheless, ILs have disadvantages such as high viscosity and high cost over conventional amine solvents. Moreover, their effects on human health and the environment have not been clearly identified [33,34].

Recently, frustrated Lewis pairs (FLPs) was developed and has been investigated for the activation of CO_2 and other small molecules. FLPs are simple combinations of Lewis acids and Lewis bases that cannot undergo a neutralization reaction owing to steric and/or electronic hindrance [35,36]. FLP molecules can be activated from their unstable intermediates through interaction with a third molecule such as CO_2, N_2O, or H_2 [37]. Since 2006, the interactions between Lewis acids and bases and their reactivity and usage have been extensively studied [37–40]. Stephan and Erker stated that blends of bulky phosphines and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) exhibit high activity toward H_2 activation [35]. Thermodynamic and kinetic studies on H_2 activation through the catalytic reduction effect of FLPs have been reported by Whittemore et al. [41]. Voicu et al. determined the thermodynamic properties of systems involving the reversible reaction between CO_2 and the FLP of $^tBu_3P$ and $ClB(C_6F_5)_2$ in bromobenzene using a microfluidic (MF) approach [42]. The thermodynamic parameters, Gibbs free energy, enthalpy, entropy, for CO_2 binding in the reactions of three different Lewis acid/base combinations have been determined by using an MF gas/liquid device [43]. The pathway for the reaction between CO_2 and a P/B-based FLP composed of $^tBu_3P$ and $B(C_6F_5)_3$ in bromobenzene has been determined through density functional theory calculations [44]. Zhuang et al. conducted a theoretical study on the capture of CO_2 by P/N-based FLPs and reported the thermodynamic and kinetic results, with activation energy ranging from 22.4 to 32.3 kJ mol^{-1} [45]. The ability of FLPs to activate small molecules, in particular, CO_2, has been reviewed and supported computationally [46,47]. Therefore, a broad range of FLPs have been considered to be capable of CO_2 capture. Although there have been theoretical studies and thermodynamic calculations for the reversible reactions between FLPs and CO_2, the reaction kinetics related
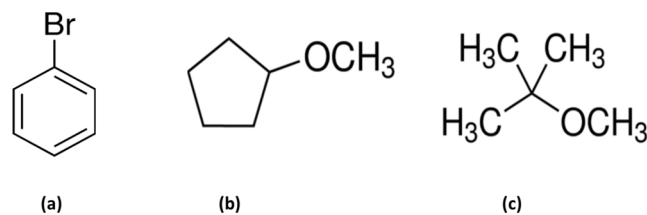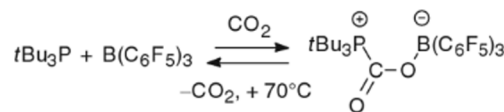
to FLP–CO_2 species has not been investigated so far.

This paper describes the reaction mechanism and kinetics of CO_2 and a P/B-based FLP system formed by the combination of Lewis acid tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) and Lewis base tri-*tert*-butyl-phosphine ($^tBu_3P$) in three different solvents: bromobenzene, cyclopentyl methyl ether (CPME), and *tert*-butyl methyl ether (MTBE). The molecular structures of the selected Lewis base and acid are shown in Fig. 1.

First, bromobenzene was selected as the solvent for CO_2 absorption by $B(C_6F_5)_3/^tBu_3P$ because of its low volatility and high solubility of FLP and CO_2 [43]. Because of the toxicity of bromobenzene, environmentally friendly green solvent alternatives CPME and MTBE were also used in experimental studies. There are no literature reports on the effects of solvents on the reaction kinetics of CO_2 absorption through FLP systems. The molecular structures of these solvents are presented in Fig. 2.

In this study, the reaction kinetics for FLP systems and CO_2 are examined in detail for the first time. As a novel approach, this study calculates the observed pseudo-first-order reaction rate constants (k_o, s^{-1}), forward reaction rate constants (k, m^3 kmol^{-1} s^{-1}), reaction orders, and activation energies for a CO_2–FLP system in three different solvents by using the stopped-flow method.

2. Theory

The reaction kinetics for FLP systems, consisting of combinations of sterically hindered acids and bases, and CO_2 were examined in detail for the first time. First, a $^tBu_3P/B(C_6F_5)_3$ FLP system was prepared, and their reaction kinetics in three different solvents (bromobenzene, CPME, and MTBE) were investigated experimentally using a "stopped-flow" method. The reaction between $^tBu_3P/B(C_6F_5)_3$ and CO_2 to form $^tBu_3P$-$CO_2B(C_6F_5)_3$ is shown in Fig. 3 [44].

The mechanisms for reactions involving primary amines are mentioned briefly, because of their possible similarities with FLP systems. A zwitterion reaction mechanism, termolecular reaction mechanism, or base-catalyzed hydration mechanism is typically used to describe the reaction pathway for CO_2 and amine systems [48–50].

The termolecular reaction mechanism was first proposed by Crooks and Donnellan and then reintroduced by Da Silva, while Svendsen claimed that an amine molecule reacts with both CO_2 and a base molecule in a single step by forming a weakly bound intermediate product [49,51].

The observed CO_2 absorption rate can be defined through Eq. (2.2) using pseudo-first-order reaction kinetics.

$$r_{obs} = k_o[CO_2] \qquad (2.2)$$

The reaction mechanism for CO_2 and an FLP system dissolved in a solvent (S; bromobenzene, MTBE, or CPME) can be explained on the basis of a modified termolecular reaction mechanism (Eq. (2.3)).
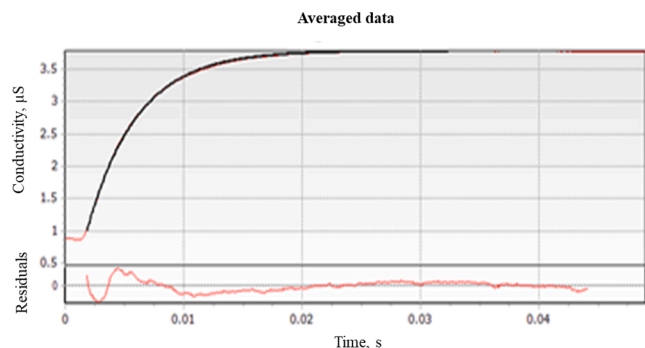
Averaged data

Fig. 4. Sample data for 0.035 M FLP in bromobenzene at 323 K.

$$r_{obs} = \{k_{FLP}[FLP][FLP] + k_s[S][FLP]\}[CO_2] \qquad (2.3)$$

The observed pseudo-first-order reaction rate constant, k_o (s^{-1}), can be expressed by Eq. (2.4).

$$k_o = \{k_{FLP}[FLP] + k_S[S]\}[FLP] \qquad (2.4)$$

For each set of experiments, the concentration of the CO_2 solution was 20 times lower than the concentration of the FLP solution in order to attain pseudo-first-order conditions. Therefore, the solvent concentration can be assumed to be constant and a new rate constant, k (m^3 $kmol^{-1}$ s^{-1}), can be defined.

$$k = k_S[S] \qquad (2.5)$$

$$k_o = \{k_{FLP}[FLP] + k\}[FLP] \qquad (2.6)$$

For this mechanism, the fractional reaction order, which can vary between 1 and 2 relative to the reaction rate, is reportedly considered to be suitable [52–54]. Furthermore, if the system displays first-order reaction kinetics, then Eq. (2.6) simplifies to the following equation:

$$k_o = k[FLP] \qquad (2.7)$$

3. Materials and methods

3.1. Reagents

$B(C_6F_5)_3$ (95% purity; CAS no. 1109–15-5) and $^tBu_3P$ (98%; CAS no. 13716–12-6) were obtained from Sigma-Aldrich. CO_2 gas (99.99%) was obtained from Linde (Germany). Bromobenzene (99%; CAS no. 108–86-1), CPME (≥99.90%; CAS no. 5614–37-9) and MTBE (≥99.90%; CAS no. 1634-04-4) were obtained from Sigma-Aldrich.

3.2. Stopped-flow experiments

The stopped-flow method was used for the determination of the pseudo-first-order reaction rate constants of the homogeneous reactions between dissolved CO_2 and FLP systems. The stopped-flow equipment (model SF-61SX2, manufactured by Hi-Tech Scientific, UK) was designed for the investigation of the intrinsic rate by measuring the change in conductivity during a rapid reaction. An external water bath (Labo B100-D23, Labo Inc., Turkey) was used to control the temperature of the sample-flow circuits to within ± 0.1 K. During an experimental run, a syringe loaded with a fresh saturated CO_2 solution and another loaded with an FLP solution were pushed pneumatically to inject the reacting solutions into a mixer. Equal volumes of the two mixtures were mixed in the conductivity cell, and the reaction was monitored by measuring the change in conductivity as a function of time. The k_o (s^{-1}) values were obtained from fitted exponential equations by using the software accompanying the equipment. Experiments were repeated at least ten times to obtain consistent k_o values. A typical graph for the reaction between CO_2 and 0.035 M FLP in bromobenzene at 323 K is

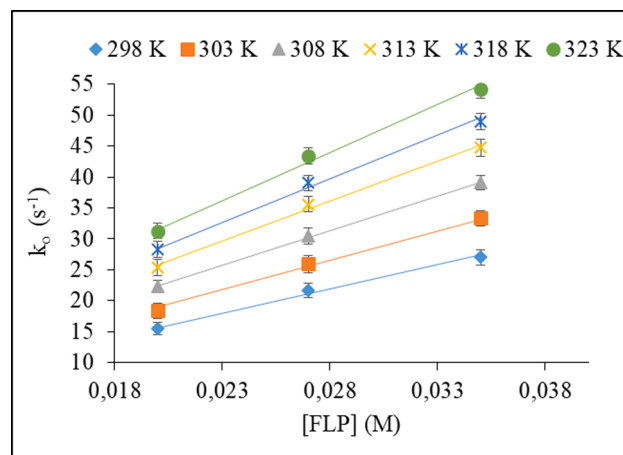**Fig. 5.** Pseudo-first-order rate constants as functions of FLP concentration for CO_2_FLP:bromobenzene system at various temperatures. All data are the averages of ten replicate experiments and error bars indicate the standard deviation of the mean.

Table 1
Forward reaction rate constants for FLP:bromobenzene system at various temperatures.

Temperature (K)	k (m^3 $kmol^{-1}$ s^{-1})
298	782.6 ± 6.8
303	949.5 ± 4.3
308	1119.1 ± 1.2
313	1288.4 ± 6.1
318	1416.6 ± 10.4
323	1569.7 ± 10.9

presented in Fig. 4. Additional details regarding the experimental procedure were based on previous literature [52,55,56].

4. Results and discussion

FLP systems consisting of mixtures of Lewis acid $B(C_6F_5)_3$ and Lewis base $^tBu_3P$ dissolved in three different solvents, namely, bromobenzene, CPME, and MTBE, were developed in this study. The observed pseudo-first-order reaction rate constants (k_o, s^{-1}) were measured directly using the stopped-flow method at concentrations ranging from 0.02 to 0.035 M and temperatures ranging from 298 to 323 K. The influences of the selected solvents on the rates of CO_2 absorption by FLPs were investigated in detail for the first time.

The k_o values for the reaction between CO_2 and the FLP in bromobenzene were measured at six different temperatures and three different concentrations (Fig. 5).

As expected, the k_o values increased with both increasing FLP concentration and temperature over the measured ranges. The forward reaction rate constants (k, m^3 $kmol^{-1}$ s^{-1}) for the CO_2–FLP:bromobenzene system were determined by fitting the lines from the plots of k_o versus FLP concentration. As can be seen in Fig. 5, the values are very consistent with the pseudo-first-order plot. The second-order reaction rate constants for the CO_2–FLP:bromobenzene system are summarized in Table 1.

Previously, the kinetic parameters for the homogenous reaction between CO_2 and FLP (tBu_3P/$B(C_6F_5)_2Cl$) dissolved in bromobenzene were analyzed over the range of 0.02 M- 0.035 M and for a temperature range of 298–313 K [57]. In this study, the effect of sterically hindered Lewis acid on reaction rate kinetics were investigated for the reaction between CO_2 and FLP (tBu_3P/$B(C_6F_5)_3$) dissolved in bromobenzene and it was observed that tBu_3P/$B(C_6F_5)_3$ has higher rate of reaction than tBu_3P/B
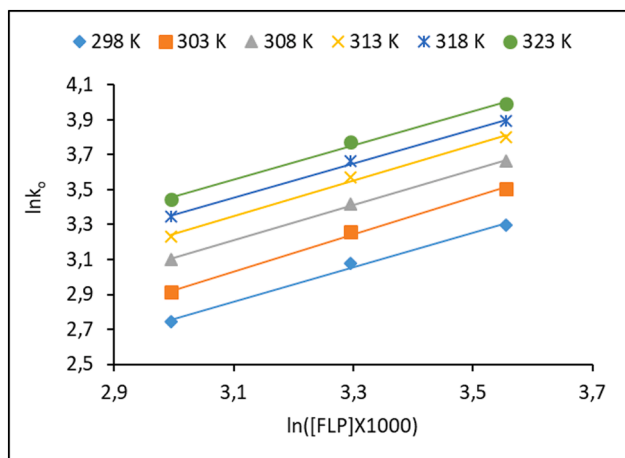
Fig. 6. Apparent reaction order plot for CO_2–FLP:bromobenzene system at various temperatures.
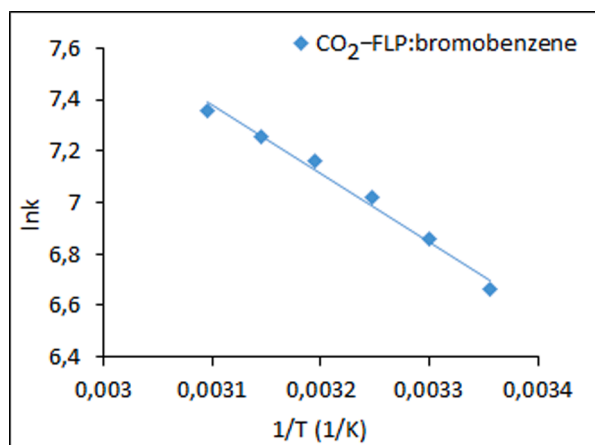

Fig. 7. Arrhenius plots for CO_2–FLP system in bromobenzene.

$(C_6F_5)_2Cl$.

In order to verify the reaction orders, the natural logarithms of the k_o values were plotted against the FLP concentrations (Fig. 6). Empirical power law kinetics were determined by the least squares method. The slopes of the fitted lines correspond to the reaction order. The reaction orders with respect to the FLPs were determined to be very close to 1.00

with high correlation coefficients (R^2) of 0.99 and were consistent with the modified termolecular mechanism suggested in Eq. (2.7).

Arrhenius plots based on the Arrhenius equation (Eq. (4.1)) were used to calculate the activation energy of the reactions between CO_2 and the FLP in bromobenzene.

$$k = A\exp(-E_a/RT) \tag{4.1}$$

where A is the frequency factor (m^3 mol^{-1} s^{-1}) and E_a is the activation energy (kJ mol^{-1}).

Arrhenius plots for the CO_2–FLP system in bromobenzene are presented in Fig. 7. According to these plots, the average activation energy for this system was 22.0 kJ mol^{-1}.

The effect of FLP concentration (0.02–0.035 M) on the k_o values was also investigated for the CO_2–FLP:CPME and CO_2–FLP:MTBE systems over a temperature range of 298–323 K; the results are shown in Fig. 8.

It can be seen that both temperature and FLP concentration had significant effects on the k_o values for the CO_2–FLP:CPME and CO_2–FLP:MTBE systems, as expected.

From the slopes of the lines in Fig. 8, the second-order forward reaction rate constants for the CO_2–FLP:CPME and CO_2–FLP:MTBE systems were determined; these constants are summarized in Table 2.

The apparent reaction orders for the CO_2–FLP:CPME and CO_2–FLP:MTBE systems were determined according to power law kinetics. Based on the slopes of the lines in Fig. 9, the reaction orders for these systems at various temperatures were approximately 1, which indicates that the suggested modified termolecular mechanism is suitable for these chemical reactions.

Moreover, Arrhenius plots, shown in Fig. 10, were constructed and the activation energies for the CO_2–FLP:CPME and CO_2–FLP:MTBE systems were determined using the Arrhenius equation.

The average activation energies for the CO_2–FLP:CPME and CO_2–FLP:MTBE systems were found to be 19.7 and 21.8 kJ mol^{-1}, respectively. The rank of the FLP systems in ascending order based on

Table 2
Forward reaction rate constants for the CO_2–FLP:CPME and CO_2–FLP:MTBE systems at various temperatures.

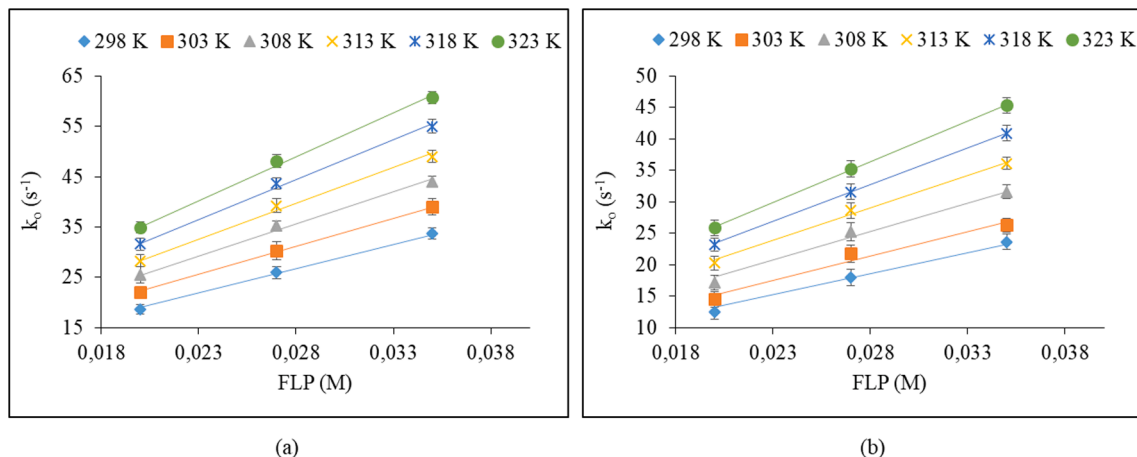| Temperature (K)	$k_{CO2–FLP:CPME}$ (m^3 $kmol^{-1}$ s^{-1})	$k_{CO2–FLP:MTBE}$ (m^3 $kmol^{-1}$ s^{-1})
298	957.3 ± 5.5	664.8 ± 9.2
303	1113.4 ± 0.2	764.2 ± 7.1
308	1273.7 ± 10.5	904.7 ± 4.7
313	1419.3 ± 11.3	1037.6 ± 3.2
318	1586.9 ± 9.9	1168.1 ± 1.2
323	1750.3 ± 9.8	1297.7 ± 1.8

(a)

(b)

Fig. 8. Pseudo-first-order rate constants as functions of FLP concentration for the (a) CO_2–FLP:CPME and (b) CO_2–FLP:MTBE systems at various temperatures. All data are the averages of ten replicate experiments and error bars indicate the standard deviation of the mean.
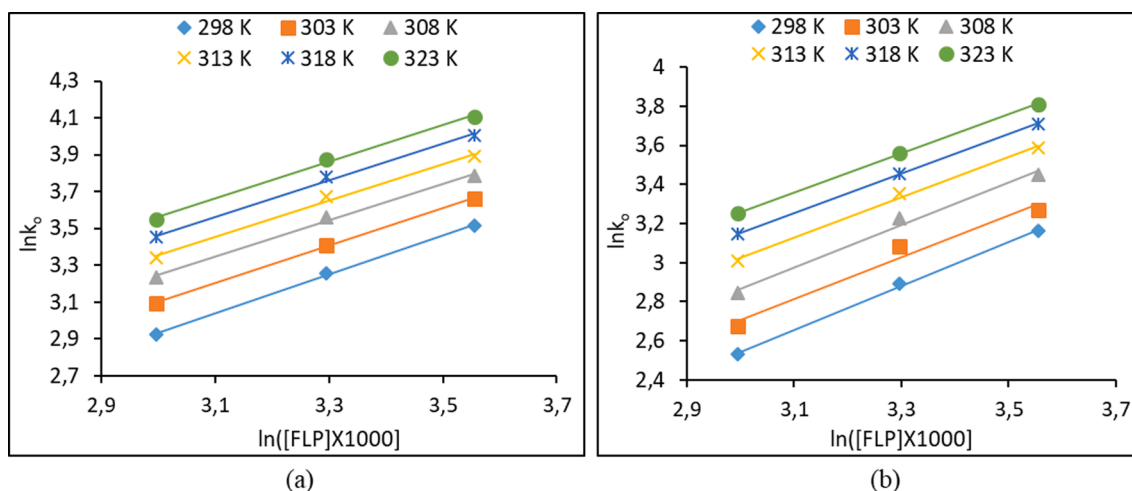
Fig. 9. Apparent reaction order plots for the (a) CO_2–FLP:CPME and (b) CO_2–FLP:MTBE systems at various temperatures.
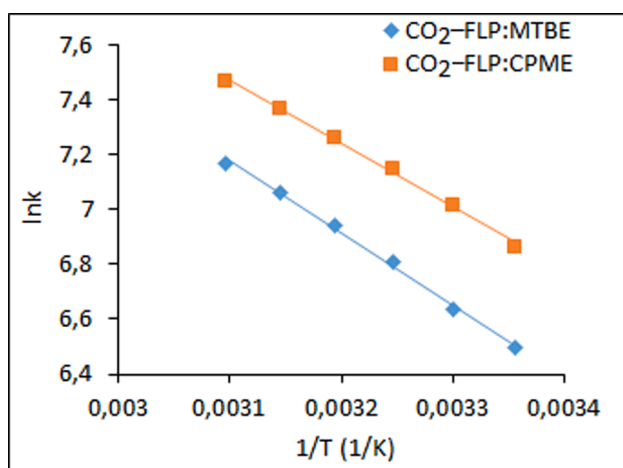

Fig. 10. Arrhenius plots for the CO_2–FLP:CPME and CO_2–FLP:MTBE systems.

the activation energy is as follows: CO_2–FLP:CPME (19.7 kJ mol^{-1}) < CO_2–FLP:MTBE (21.8 kJ mol^{-1}) < CO_2–FLP:bromobenzene (22.0 kJ mol^{-1}). The slight difference in activation energies is due to the molecular structures, molecular size and steric hindrances of the proposed solvents. The steric and inductive effects of the alkyl groups remarkably affect the activation energy of the reaction [58].

The graphically calculated forward reaction rate constants were substituted in Equation (2.7) to obtain the corresponding calculated k_o values for the three systems over the 298–323 K temperature range. Then, the calculated and experimental k_o values for these FLP systems were compared in a parity plot, shown in Fig. 11.

It is apparent that the calculated and experimental k_o values are in good agreement, with average absolute relative deviation (AARD%) values of 4.34%, 4.63%, and 3.51% for the CO_2–FLP:bromobenzene, CO_2–FLP:CPME, and CO_2–FLP:MTBE systems, respectively. They are in acceptable ranges of less than 10%. These results show that the suggested kinetic model in the present study is acceptable and provides accurate results.

Finally, the experimentally obtained results for the selected FLP systems were compared with previously reported results (Table 3). Primary amine monoethanolamine (MEA); secondary amines diethanolamine (DEA), methylaminoethanol (MAE), and 1-amino-2-propanol (1A2P); and tertiary amines *N*-methyldiethanolamine (MDEA), diethylmonoethanolamine (DEMEA), dimethylmonoethanolamine (DMMEA), and 4-diethylamino-2-butanol (DEAB) were selected. In

addition, the forward reaction rate constants for a sterically hindered amine, 2-amino-2-methyl-1-propanol (AMP), and a cyclic diamine, piperazine (PZ), were calculated.

The forward reaction rate constants for the CO_2–FLP:bromobenzene, CO_2–FLP:CPME, and CO_2–FLP:MTBE systems were calculated to be 782.6, 957.3, and 664.8 m^3 $kmol^{-1}$ s^{-1}, respectively, at 298 K. Therefore, our results show that the forward reaction rate constants for these FLP systems are higher than those for various aqueous tertiary and sterically hindered amine systems, but much lower than those for aqueous MEA and PZ systems. Previous work by our group examined the reaction kinetics of the FLP (tBu$_3$PB(C$_6$F$_5$)$_2$Cl): bromobenzene system with CO_2. The relatively low reaction rate constants of FLP: bromobenzene system were enhanced significantly by blending constant amounts of promoters, such as amino ethyl piperazine (AEPZ), carbonic anhydrase (CA) and 1-ethyl-3-methyl imidazolium bis (trifluoromethyl sulfonyl) imide ([emim][Tf$_2$N]) [57]. The non-aqueous CO_2–FLP:bromobenzene, CO_2–FLP:CPME, and CO_2–FLP:MTBE systems can be considered as potential absorbents because they have lower specific heat capacity than aqueous systems. The reboiler duty required for solvent regeneration for these solvent systems is lower than those for conventional aqueous amine systems.

5. Conclusion

The reaction kinetics for dissolved CO_2 and FLP:bromobenzene, FLP:CPME, and FLP:MTBE systems were determined experimentally by using stopped-flow method. The k_o values of the reactions between CO_2 and these non-aqueous FLP systems were measured over different concentrations and at temperatures of 298–323 K. It could be concluded that both FLP concentration and temperature have significant effects on the k_o values for FLP systems. The reaction mechanism for CO_2 and the FLP systems was modelled according to a modified termolecular mechanism, which was consistent with the experimental k_o values. The AARD% values of < 5.0%, fitted using Eq. (2.7), indicated good agreement between the experimental and calculated data, indicating the applicability of the termolecular mechanism. The forward reaction rates and activation energies for selected solvent systems were reported here for the first time. The obtained results were compared with reaction rate constants and activation energies of widely used aqueous amine systems. The results showed that these non-aqueous FLP systems led to relatively high reaction rates and can be accessed by adding small amounts of promoters. The major advantage of using all-organic solvent systems for CO_2 capture is the potentially lower heat requirement for regeneration than those required with aqueous solvents. This study suggests that applicability of the FLP systems as alternatives to traditional solvent
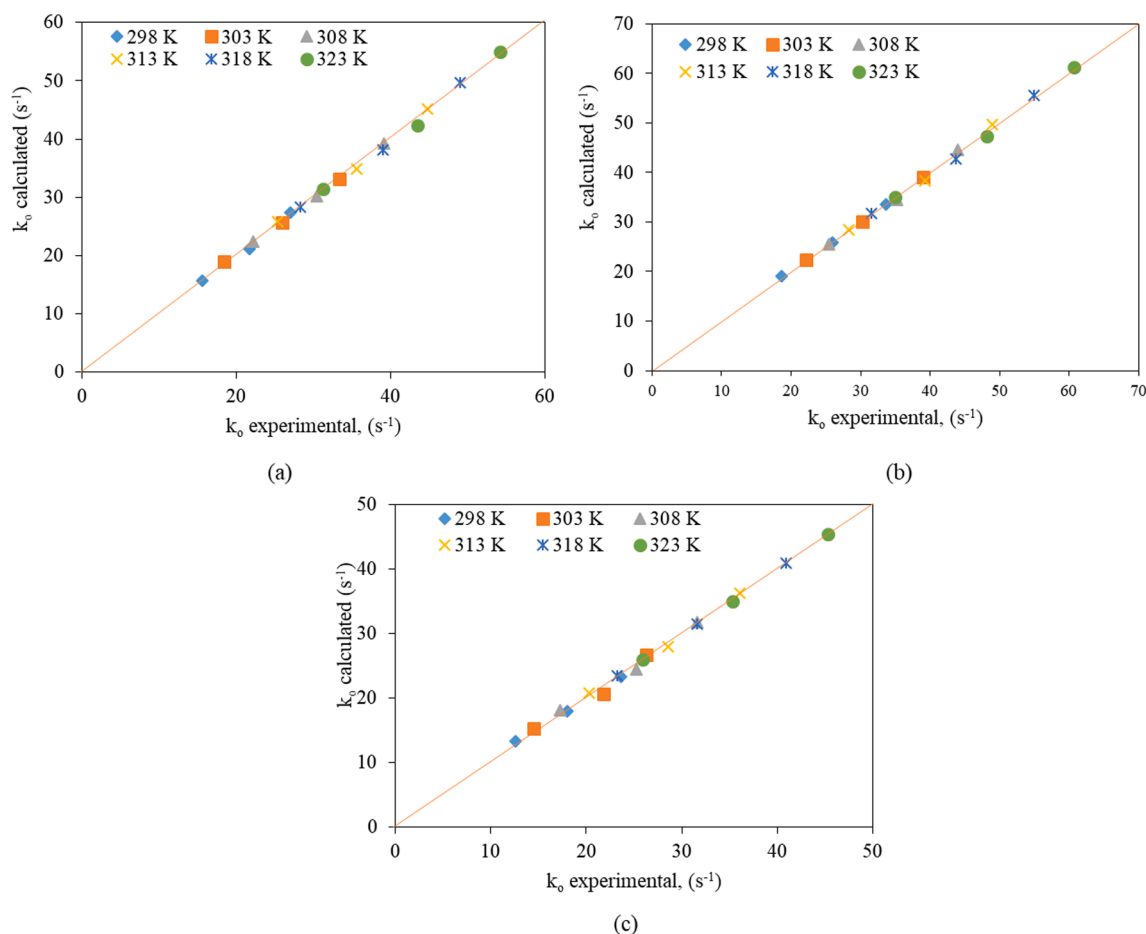
Fig. 11. Comparison of calculated and experimental k_o values for the (a) CO_2–FLP:bromobenzene, (b) CO_2–FLP:CPME, and (c) CO_2–FLP:MTBE systems.

Table 3
Forward reaction rate constants and activation energies for CO_2 absorption into various aqueous amine solutions at 298 K.

Amine	k (m^3 $kmol^{-1}$ s^{-1})	Activation energy (kJ mol^{-1})
MEA	5939.0 [59]	40.3 [60]
DEA	412.0 [61]	53.1 [62]
MAE	5381.0 [63]	37.3 [60]
1A2P	4314.0 [64]	39.6 [60]
MDEA	6.7 [65]	40.0 [66]
DEMEA	43.2 [67]	51.9 [67]
DMMEA	27.2 [67]	53.6 [67]
DEAB	64.0 [67]	62.6 [67]
AMP	473.0 [68]	41.7 [69]
PZ	65460.0 [70]	33.6 [71]

systems for post-combustion CO_2 removal.

CRediT authorship contribution statement

Neslisah Cihan: Formal analysis, Investigation. **Ozge Yuksel Orhan:** Conceptualization, Methodology, Formal analysis, Writing - review & editing, Project administration. **Hulya Yavuz Ersan:** Conceptualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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