

FTIR and NMR spectra of polymeric ionic liquids – Products of reaction between hydroxycontaining amidines and carbon dioxide

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ABSTRACT

Two hydroxy-containing amidine derivatives have been synthesized by condensation of amino-alcohols such as monoethanolamine (MEA) and *tris*(hydroxymethyl)aminomethane (TRIS) with *N,N*-dimethylformamide dimethyl acetal. Their interaction with carbon dioxide, leading to the formation of polymeric ionic liquids, was studied by FTIR and NMR spectroscopy. Dilute solutions of polymeric ionic liquids are also investigated by measuring the relative viscosity during the reaction. It has been found that during interaction of MEA-based amidine with CO₂ within first 60 min of reaction the intensities ratio of absorbance bands at 1644 and 1705 cm⁻¹ dropped from 2.84 to 1.33. The linear relationship between the time of reaction and the mentioned ratio of intensities has been established. In the similar manner the changes in the intensities ratio of absorbance bands at 1696 and 1629 cm⁻¹ can be used for monitoring the reaction between TRIS-based amidine and CO₂. Solution of polymeric ionic liquid prepared by reaction of TRIS-based amidine with CO₂ in *i*-propanol has been used for measuring molecular weight (M_w = 637, M_n = 349; M_w/M_n = 1.828) by gel-permeation chromatography.

1. Introduction

Carbon dioxide (CO₂) emissions are seen as one of the most significant problems from both an environmental and scientific point of view [1]. The scientific community pays much attention to the problem of reducing CO₂ emissions and reducing the impact of global warming. Numerous studies on CO₂ liquefaction problems have been undertaken with a view to achieving a positive solution to curb this problem [2]. In addition to environmental concerns, CO₂ attracts substantial attention because it is also considered an environmentally friendly source of C1 due to its low toxicity, as well as its usefulness in production of various organic products [3]. Therefore, several industrial processes have been developed that capture CO₂ from exhaust gases generated by burning fossil fuels. Extensive research has explored light-driven processes, particularly photocatalytic systems, to harness solar energy for chemical energy conversion [4]. Among the various methods developed for CO₂ transformation, sunlight-activated photocatalytic conversion stands out

as a renewable and user-friendly approach. Achieving this requires suitable materials to act as catalysts and light-absorbing substances to harness solar energy. Combining these components with an electron carrier efficiently allows for sustainable CO₂ conversion into desired fuels via photocatalysis. As well as the use of nanomaterials for converting CO₂ into various types of fuel, including formic acid, carbon monoxide, methanol and ethanol, the review is discussed [5]. CO₂ also serves as an excellent stimulus for switchable or stimulus-responsive materials due to its favorable properties: it is environmentally friendly, cost-effective, sustainable, widely available and does not lead to accumulation in the system. A variety of CO₂-sensitive materials have been developed, including polymers, latexes, solvents, solutes, gels, surfactants, and catalysts [6]. Some processes involve the use of aqueous solutions of amines that effectively interact with CO₂ at low temperature [7–9].

However, desorption of CO₂ occurs after consumption of a significant amount of energy in form of heating. Therefore, it is necessary to

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develop CO₂ absorption systems that can reversibly and efficiently capture and release CO₂. Numerous CO₂ absorbers with this mode of action have been described in literature, including silicon dioxide bound with amine, organometallic frameworks, mesoporous silica with amine addition, mesoporous phenolic networks, porous polymer networks bound with amine, polystyrene derivatives [10,11] or copolymers of dodecyl methacrylate/styrene containing an amidine functional groups [12]. Alternatively, other types of absorption systems that can capture CO₂ irreversibly with formation of useful materials are of interest [13].

There is also growing interest in developing innovative methods and materials to improve CO₂ capture capabilities. Supported ionic liquid membranes (SILMs), which are a type of ionic liquid (IL), have shown significant potential for efficient and cost-effective separation of CO₂ from gas streams. The review [14] examines the mechanisms, advantages, challenges and disadvantages of CO₂ capture using SILM, comparing them with traditional methods.

A number of investigations were based on using ionic liquids (ILs) as media for separation of CO₂ from the mixture of gases [10,15–20]. The high solubility of CO₂ in ILs is related to existence of weak Lewis acid–base interactions between the CO₂ electron-pair acceptor and electron-pair donor anion of the ILs [21,22]. The strength of the ILs–CO₂ interaction is usually affected by modifying the chemical structure of the ionic liquid structure, leading to improved capacity and selectivity of CO₂ [23,24]. However, it was noticed that those studies encountered numerous challenges in applying ILs to meet the different requirements in CO₂ separation processes. Therefore, the authors of paper [20] provided the retrosynthetic analysis of structural variables and properties of ILs that are especially important for proposed application. As a result, the new amine solvents and polymer materials have been developed that are capable to better address the efficient CO₂ capture and other demanding process parameters.

Several new types of switchable ILs have been reported in prof. Jessop group [25], that can be easily synthesized from a non-ionic mixture of molecular organic compounds such as amidine/alcohol [25], guanidine/alcohol [26,27] and amidine/amine [28] upon bubbling of an acid gas (CO₂, SO₂). The attractive property of prepared ILs is that they were switched back to the original molecular solvents by flushing out the acid gas by heating and/or bubbling an inert gas such as N₂ through it. Later similar studies were performed with using 1,8-diazabicyclo-[5.4.0]-undec-7-ene and its compositions with glycerol [29] and methanol [30].

Similar investigations [31,32] have been performed on using switchable cationic surfactants which are able to form switchable emulsion. Particularly the authors of paper [31] used the reaction of CO₂ with cationic surfactant containing amidine fragment to stabilize light crude oil emulsion. After purging nitrogen CO₂ was removed from the system, and the surfactant switched back to a non-ionic demulsifier. Subsequently, the stable emulsion was separated into two layers within 30 min

A number of publications [33–35] considered using reaction of CO₂ with different epoxy-derivatives, such as propylene oxide, vinylcyclohexene dioxide and other for formation of polycarbonates. Numerous selected examples of studies devoted to CO₂ capture are outlined in Table 1.

FTIR spectra of various amidines and their derivatives were investigated in number of publications [36,37]. Several studies [27,38–40] considered using FTIR method for monitoring reaction of CO₂ with amidine and guanidine derivatives. In particular, the authors of study [38] indicated that the formation of bicarbonate during the reaction of CO₂ with amidine was confirmed by appearance of band at 1651 cm⁻¹ which is associated with stretching vibrations of the protonated group C=N and band at 1602 cm⁻¹ which corresponded to the stretching vibrations of the bicarbonate.

It is also worth to mention latest research endeavors in CO₂ capturing using biomimetic technologies through the sunlight-activated photocatalytic conversion. Within this technique, two main roles play i)

Table 1Selected examples of studies devoted to CO₂ capture.

CO ₂ absorption systems	Products of reaction after CO ₂ capture	Reaction conditions	Ref.
Primary and secondary alkanolamines	Carbamates and cyclic oxazolidinones	CO ₂ is absorbed by alkanolamines at ambient temperature	[7]
Monoethanolamine (MEA), 2-(ethylamino) ethanol (EAE)	Carbamates and cyclic ureas (imidazolidinones)	CO ₂ is absorbed by MEA + EAE + sulfolane in aqueous solutions at 313 K	[9]
Ionic liquid-based phase change absorbents; Monoethanolamine and glycerol	Carbamates	The CO ₂ absorption was performed at three different temperatures (303, 318, and 333 K) at normal atmospheric pressure, while CO ₂ partial pressure was varied from 1 to 15 kPa, and the gas flow rate in the mixture was changed from 350 to 700 ml/min.	[12,18]
Aqueous solutions of Imidazole-amine species	Carbamate and bicarbonate formation promoted by the imidazole ring	All of the various 1-(3-aminopropyl)-imidazole -containing solvents behave in largely the same manner up to ~100 torr where each solvent achieves ~0.5 mol CO ₂ per mol –NH ₂ .	[20]
Amine-functionalized ionic liquids	Carbamate dianions and carbamic acid	CO ₂ absorption by the amine-functionalized IL at 310 K.	[16,17, 22–24]
Chilled ammonia	Ammonium carbonate	Temperature range of 0–10 °C by aqueous ammonia solution with a 28 wt% ammonia concentration	[8]
2-aminobenzonitriles in the presence of a polystyrene derivative with amidine moiety [poly(amidine)]	1H-Quinazoline-2,4-diones	Poly(amidine) (66.0 mg, 0.330 mmol of the repeat unit), 2-aminobenzonitrile (40.0 mg, 0.330 mmol), Na ₂ CO ₃ (17 mg, 0.165 mmol), and DMSO (1.00 ml) were added in a glass tube under a CO ₂ atmosphere. The mixture was vigorously stirred at 100 °C for 24 h under 1 atm of CO ₂ .	[10]
Copolymers of styrene and dodecyl methacrylate containing the amidine group	A copolymer of dodecyl methacrylate/styrene (DMA/St) containing bicarbonate and amidine cations	Copolymerization of DMA and St (3.64 g, 0.035 mol), DMA (17.8 g, 0.070 mol), a mixed solvent [dimethyl sulfoxide, toluene, 300 ml]. The mixture was stirred at 60 °C. The temperature was increased to 98–100 °C for 24 h.	[11]
Alkanolamidines, alkanolguanidines and diamines	Reversible zwitterionic liquids and cyclic carbonates	Carbon dioxide was bubbled in solution of alkanolamidine in DMSO (1:1) at ambient temperature	[27]
Switchable surfactants based on:	Amidinium bicarbonates and	Bubbling nitrogen, argon, or air through	[28,31, 32]

(continued on next page)

Table 1 (continued)

CO ₂ absorption systems	Products of reaction after CO ₂ capture	Reaction conditions	Ref.
a) the long-chain alkyl amidine compounds b) aryl amidine and tertiary amine as surfactant for polymerization of methyl methacrylate	ammonium bicarbonates	the amidinium bicarbonate solutions at 65 °C reverses the reaction, releasing carbon dioxide and breaking the emulsion.	
Switchable solvents consisting of alcohols and amines-based derivatives; and either an amidine or a guanidine	High-polarity ionic liquids	Dried 1,8-diazabicyclo-[5.4.0]-undec-7-ene and 1-hexanol (0.8 mmol each) were placed in a dry flask in a glove box under N ₂ . A narrow-gauge steel tube was inserted and CO ₂ was bubbled through the liquid at a rate of 2 bubbles per second for 1 h.	[25,26]
Solutions of 1,8-diazabicyclo-[5.4.0]-undec-7-ene in glycerol and methanol	Ionic liquids with switchable polarity	The DBU/CH ₃ OH/CO ₂ via bubbling CO ₂ through a 1:3 molar ratio solution of dried DBU and CH ₃ OH constant rate for two hours. The temperature and absolute pressure of vacuum distillation was 39 °C and 0.08 MPa, respectively.	[29,30]
Ionic liquid (1-ethyl-3-methylimidazolium tetrafluoroborate) (EMIMBF ₄) + fluorescent dye 1-hydroxy-3,6,8-pyrenetrisulfonate (HPTS) in ethyl cellulose (EC) matrix.	Changes in fluorescence intensity of EC film containing EMIMBF ₄ and HPTS after absorption of CO ₂	EC matrix containing EMIMBF ₄ and HPTS changes its fluorescence properties after absorption of CO ₂ (linear decreasing intensity of fluorescence up to 20% content of CO ₂).	[21]
Hydroxy-containing amidines based on monoethanolamine, (MEA) and tris (hydroxymethyl) aminomethane (TRIS)	Polymeric ionic liquids	Hydroxy-containing amidines were prepared at equimolar ratio between N,N-dimethylformamide dimethyl acetal and MEA or TRIS at 50°C. CO ₂ was bubbled into liquid amidines at ambient temperature.	[13, Current Paper]

photocatalysts, that can be bio-based, and ii) light absorbers, responsible for the sun energy harvesting. The precise combination of these components with an electron carrier may result an efficient system of photocatalytic CO₂ conversion. More detailed and well-summarized reviews on this direction can be found here [4,5].

Previously we reported the use of fluorescent method for control of capturing CO₂ by alifatic amines such as dipropylamine [41]. In another previous study [13] we investigated the synthesis of hydroxyl-containing amidines and their interaction with CO₂. However, that preliminary study did not include using NMR spectroscopy for confirmation of the structure of formed polymeric ionic liquids. In present study we investigated the reaction between N,N-dimethylformamide dimethyl acetal and two alifatic amine containing hydroxy-groups such as monoethanolamine, MEA (1) and tris (hydroxymethyl)aminomethane, TRIS (2). Products of this reaction are

two hydroxy-containing amidine derivatives (3) and (4), respectively (Fig. 1). Their reaction with carbon dioxide leading to formation of polymeric ionic liquids (5) and (6) has been investigated by using FTIR and NMR spectroscopy. According to our best knowledge, synthesis of compounds 5 and 6 has not been undertaken before this study. It is known [42,43] that FTIR spectroscopy is traditionally used for characterization of chemical structure of polymeric ionic liquids.

2. Materials and methods

2.1. Materials

MEA, TRIS, N,N-dimethylformamide dimethyl acetal (DFDA), isopropanol were used as received from Sigma-Aldrich without further purification.

Concentration of MEA was 100% according to its specific documentation. Tris was pure at 99.9% value. Concentration of used DFDA was up to 100% with small traces of N,N-dimethylformamide not higher than 1%. Purity of isopropanol was 99.9%, suitable for HPLC.

2.2. Instrumentation

The NMR spectra of compounds (4) and (6) were recorded on a FT NMR spectrometer JNM-ECA 500 (Jeol, Japan) at 500.16 (¹H) and 125.77 MHz (¹³C) from solutions in Chloroform-d (CDCl₃) (δ 7.25 ppm). Scan number 16 and 512 for ¹H and ¹³C, respectively; the chemical shifts were determined with an accuracy of ± 0.5%.

FTIR measurements for compounds (1–6) were performed using a Nicolet Magna-750 FTIR spectrometer (resolution 4 cm⁻¹; 64 scans, detector: MCT) equipped with attenuated total reflectance (ATR) cell for the acquisition of spectra at room temperature. All spectra were baseline corrected to monitor evolution of absorption bands as a function of time of contact with CO₂. This allowed for a comparison of the intensity of IR absorptions and to correlate the relative amount of functional groups.

Gel-Permeation chromatography measurements were performed using OMNISEC system equipped with two Viscotek T6000M columns with using Malvern dual detector 270: Light scattering instruments - Right-angle light scattering (RALS), Low-angle light scattering (LALS).

For measurements of the relative viscosity $\eta_{rel} = t / t_0$ of diluted solutions of polymer IL we have used capillary viscometer Ostwald-Fenski VPZh-4 ECROS. We have compared flow time *t* of the solution of polymer IL diluted in isopropyl alcohol through the capillary with the flow time *t*₀ of the solvent. We have measured the viscosity at constant temperature and the change of temperature was less than ± 0,02 °C. The flow time was more than 100 s in order to minimize an error.

2.3. Synthetic procedures

2.3.1. Synthesis of hydroxy-containing amidines

Hydroxy-containing amidine (3) has been prepared by dissolving 0.01 mol of MEA (1) into 0.01 mol of N,N-dimethyl formamide dimethyl acetal (DFDA) and stirring for 3 hrs in the flask equipped with magnetic bar and jacketed Dean-Stark trap at temperature of 40 °C following by increasing the temperature to 60 °C and stirring for additional 30 min. The yield of compound 3 was evaluated as 98% by measuring amount of collected methanol. FTIR: $\nu(\text{cm}^{-1})$ 3293 (ν_{OH} weak), 2911 (ν_{CH_3} medium), 2826 (ν_{CH_2} medium), 1644 ($\nu_{\text{C=N}}$ weak), 1380 (ν_{CC} medium), 1029 (ν_{CO} weak), 1092 (δ_{COH} medium), 923 (δ_{HCH} medium), 870 (δ_{HCH} medium), 800 (δ_{CNC} medium).

2.3.2. Synthesis of tris-hydroxyl-containing amidine (4)

Synthesis of tris-hydroxyl-containing amidine (4). Compound 4 has been prepared by slow addition of solid tris-hydroxymethylaminomethane (2) 11.8 g (0.099 mol) partially using several portions (not more than 0.3–0.4 g each) to a round bottom flask containing 13.3 ml (12 g, 0.099 mol) of DFDA and equipped with magnetic bar,

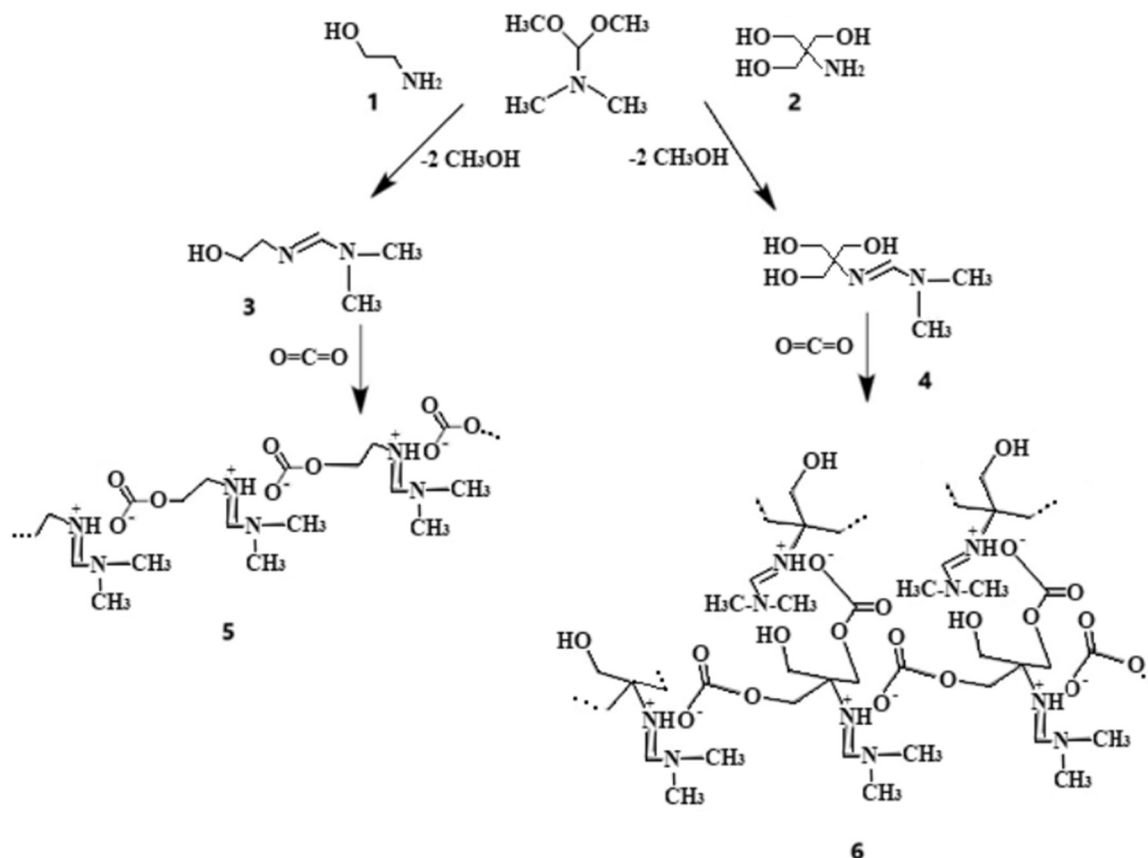


Fig. 1. Reaction of N,N-dimethylformamide dimethyl acetal with MEA (1) and TRIS (2) formation of hydroxyl-containing amidines (3 and 4) following by its interaction with CO₂ leading to formation of polymeric ionic liquids (5 and 6).

jacketed Dean-Stark trap and water bath preheated at temperature of 50 °C. Next portion was added only when the previous one was totally dissolved. After total dissolving, stirring was continued for 3 h at 50 °C following by increasing the temperature to 60 °C and stirring for additional 30 min. The yield of compound 4 was evaluated as 97% by measuring amount of collected methanol. ¹H NMR (500 MHz, CHLOROFORM-D) δ 3.24 (s, 6H, CH₃), 3.44 (d, 4H, CH₂), 4.21 (s, 3H, OH), 6.81 (s, NCHN). ¹³C NMR (125.77 MHz, CHLOROFORM-D) δ 37.58 (CH₃), 37.93(CH₃), 64.21(CH₂), 70.54 (C), 156.60 (NCHN). FTIR: ν(cm⁻¹) 3309 (ν_{OH} medium), 2936 (ν_{CH} medium), 2828 (ν_{CH} medium), 1629(ν_{C=N} strong), 1384 (ν_{CC} medium), 1025(ν_{CO} strong), 1096(δ_{COH} medium), 936(δ_{HCH} medium), 869(δ_{HCH} medium), 800(δ_{CNC} medium).

2.3.3. Conversion of amidines to the ionic liquids

Conversion of amidines to the ionic liquids (5 and 6) has been performed at 25 °C by bubbling CO₂ into corresponding amidine. Upon bubbling CO₂, within 80 min of reaction the solutions did not show any formation of precipitates, remaining colorless and clear, but became noticeably more viscous. The flow rate of gaseous CO₂ was chosen such that about 3–4 bubbles per second were fed through the amidine. The amount of absorbed CO₂ has been evaluated by weighing the flasks containing compounds 3 and 4 before and after bubbling CO₂ in the content of these flasks for 80 min. Considering that the single molecules of hydroxy-containing amidines 3 and 4 are capable to retain one molecule of CO₂ each, the yields of compounds 5 and 6 can be estimated as 91% and 86%, respectively. For quantitative evaluation of the increased viscosity 4 aliquots (0.50 g each) have been taken from the reaction mixtures after every 20 min of bubbling CO₂ and after dilution with 15 ml of isopropanol the prepared solutions were placed into Cannon-Fenske viscometer and the efflux times were measured at temperature of 25 °C.

2.3.4. Synthesis of polymeric IL

Synthesis of polymeric IL (5) after 40 min FTIR: ν(cm⁻¹) 3225 (ν_{OH} weak), 2930 (ν_{CH3} medium), 2821 (ν_{CH2} medium), 1705(ν_{C=O} strong), 1643(ν_{C=N} strong), 1292 (ν_{CC} medium), 1092(δ_{COH} medium), 1031(ν_{CO} strong), 902(δ_{HCH} medium), 823(δ_{HCH} medium), 800(δ_{CNC} medium).

Synthesis of polymeric IL (6) after 40 min ¹H NMR (500 MHz, CHLOROFORM-D) δ 3.26 (s, CH₃), 3.47 (s, CH₂), 4.05 (s, 2 H, OH), 5.20 (s, NH), 6.84 (s, NCHN). ¹³C NMR (126.77 MHz, CHLOROFORM-D) δ 49.67 (CH₃), 64.25 (CH₂), 70.68 (C), 155.2 (C=O), 156.57 (C=N), 164.02 (C=O).

Synthesis of polymeric IL (6) after 70 min ¹H NMR (500 MHz, CHLOROFORM-D) δ 3.28 (s, CH₃), 3.48 (s, CH₂), 4.06 (s, 2 H, OH), 5.30 (s, NH), 6.86 (s, NCHN). ¹³C NMR (126 MHz, CHLOROFORM-D) δ 49.63 (CH₃), 64.19 (CH₂), 70.64 (C), 155.30 (C=O), 156.52 (C=N), 163.93 (C=O).

FTIR: ν(cm⁻¹) 3238 (ν_{OH} medium), 2927 (ν_{CH} weak), 2828 (ν_{CH} weak), 1697(ν_{C=O} medium), 1650(ν_{C=O} weak), 1627(ν_{C=N} medium), 1505(δ_{HNH} weak), 1444(δ_{HNH} weak), 1370 (ν_{CC} medium), 1306(δ_{HCH} weak), 1258(δ_{COH} medium), 1096(δ_{COH} medium), 1027(ν_{CO} strong), 936(δ_{HCH} medium), 869(δ_{HCH} medium), 800(δ_{HNH} medium), 664(δ_{CCC} medium).

In addition to measuring the relative viscosity the control of reaction between amidines (3 and 4) with CO₂ has been performed by measuring the FTIR spectra of aliquots taken from the reaction mixtures after every 20 min of bubbling CO₂. It was shown that in case of interacting MEA-based amidine (3) with CO₂ the intensities ratio of absorbance bands at 1705 and 1644 cm⁻¹ can be used for evaluation of converting amidines to amidinium species [38,39]. In the similar manner the changes in the intensities' ratio of absorbance bands at 1696 and 1629 cm⁻¹ can be used for monitoring the reaction between TRIS-based amidine (4) and CO₂.

3. Results and discussions

3.1. FTIR measurements

In the IR spectra of amidines treated with CO₂ a new relatively strong band in the spectral region between 1700 and 1500 cm⁻¹ can be observed. According to the literature data [38,39], this band is related to the formation of amidinium group C=N + .

FTIR spectra that are shown in Fig. 2A display the characteristic bands of amidine (3) before and after its reaction with CO₂.

From comparison of FTIR spectra of hydroxyl-containing amidine (3) before bubbling CO₂ and after bubbling CO₂ for 80 min (Fig. 2A), as well as spectra measured after 10, 20, 40, 60 and 80 min of reaction it was obvious that the intensity of the band at 1644 cm⁻¹ decreases within 80 min of bubbling and the intensity of the band at 1705 cm⁻¹ increases. The choice of mentioned bands in the FTIR spectra for monitoring the reaction of amidines with CO₂ is in agreement with the previously published results [38,39]. This change of the intensities of peaks at 1644 and 1705 cm⁻¹ indicates the formation of the IL (5) presented in Fig. 1.

Moreover, it was found that the ratio of these two intensities is proportional to the time of interaction between CO₂ and amidine (Fig. 3A). Fig. 3B illustrates the increase of viscosity of amidine (3) solution during process of bubbling CO₂. The evaluation of the relative increase of viscosity has been performed through calculation of the ratio of efflux times (R_{et}) from the following equation: $R_{et} = \tau_s/\tau_o$, where τ_s is the efflux times measured for solutions of prepared from the samples taken from reaction vessel after 20, 40, 60 and 80 min of reaction and τ_o is the efflux time measured for solution of amidine (3). It can be seen that the parameter R_{et} increases quite rapidly in the first 40 min of the reaction, then the rate slows down and it reaches a plateau after 60 min. In our opinion, this may mean that after 60 min of reaction, almost all of the amidine (3) was spent on interacting with CO₂.

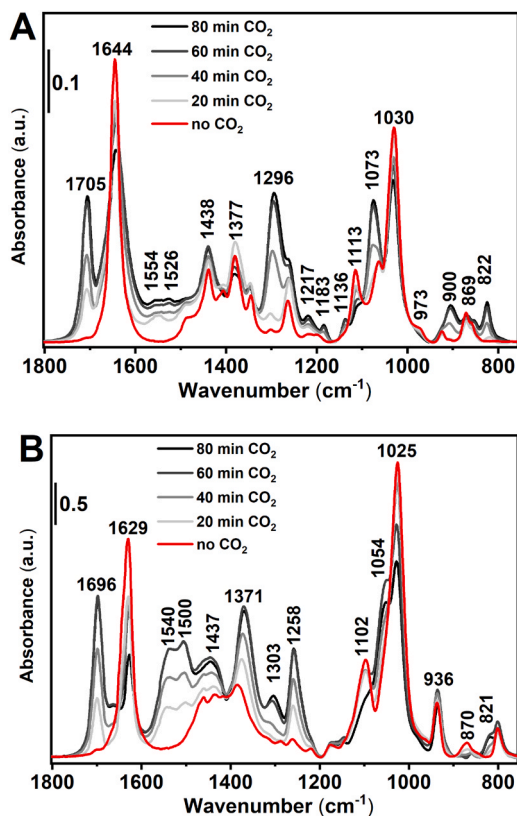


Fig. 2. FTIR spectra of amidine (3) before bubbling CO₂ and after bubbling CO₂ for 80 min (A). FTIR spectra of amidine (4) before bubbling CO₂ and after bubbling CO₂ for 80 min (B).

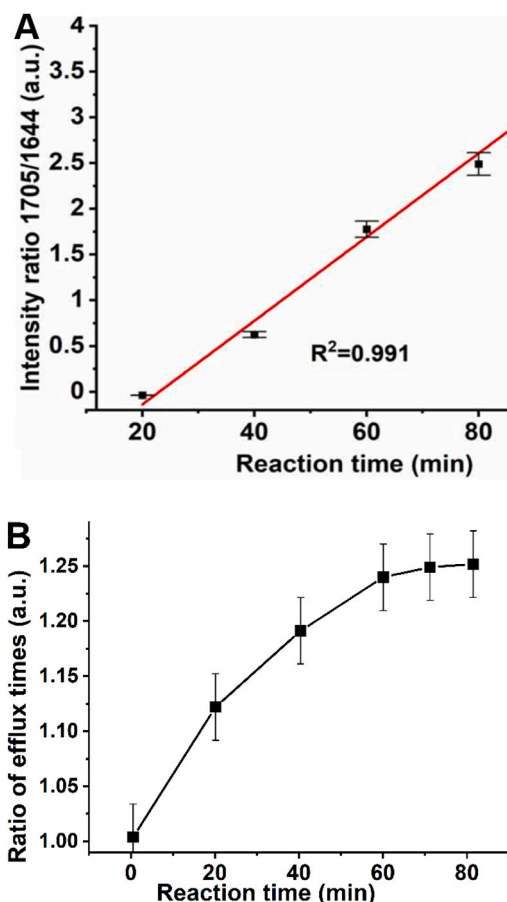


Fig. 3. Monitoring of CO₂ consumption during bubbling CO₂ into amidine (3): A – changes in the ratio of bands' intensities at 1644 and 1705 cm⁻¹ in FTIR spectra; B – changes in the viscosity of reaction solution (through measuring the efflux times).

On the basis of the measured FTIR spectra of hydroxyl contained amidine (4) before bubbling with CO₂ and after bubbling during 80 min (Fig. 2B) as well as on the basis of spectra measured 10, 20, 40, 60 and 80 min after the reaction start one may see that the intensity of 1629 cm⁻¹ decreases and intensity of a peak at 1696 cm⁻¹ increases also a new peak at 1650 cm⁻¹ emerges. We believe that formation of this new peak relates to the fact that two hydroxyl groups of amidine (4) participate in formation of IL (6).

Fig. 4B illustrates the increase of viscosity of amidine (4) solution during process of bubbling CO₂. Similar to observation presented in Fig. 3B, the parameter R_{et} increases quite rapidly in the first 40 min of the reaction. Despite some differences in the changes of the parameter R_{et} presented in Figs. 3B and 4B in the time between 40 and 60 min of reaction, it is important to point out that in both cases the values of parameter R_{et} reach a plateau after 60 min. This similarity indicates that the mechanisms of reactions between CO₂ and amidines (3) and (4) have no significant differences.

In our opinion, the noticeable increase viscosity of reaction mixture illustrated in Fig. 4B provides additional evidence that in the formation of polymeric ionic liquid (6) participate two hydroxyl groups of amidine (4), as it is presented in Fig. 1.

The results gel-permeation chromatography measurements (Fig. 5) performed in solution of polymeric ionic liquid prepared by reaction of TRIS-based amidine with CO₂ in i-propanol show rather low molecular weight of investigated compound: ($M_w = 637$, $M_n = 349$; $M_w/M_n = 1.828$).

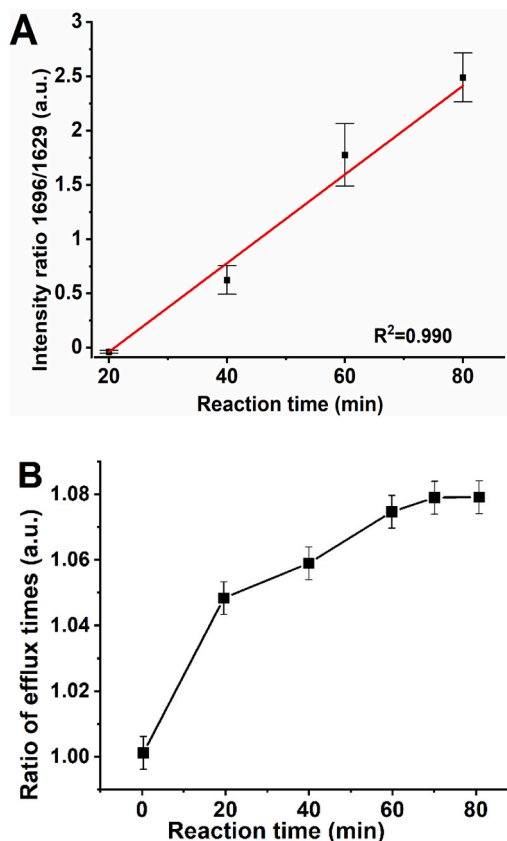


Fig. 4. Monitoring of CO₂ consumption during bubbling CO₂ into amidine (4) A – changes in the ratio of bands' intensities at 1696 and 1629 cm⁻¹ in FTIR spectra; B- changes in the viscosity of reaction solution (through measuring the efflux times).

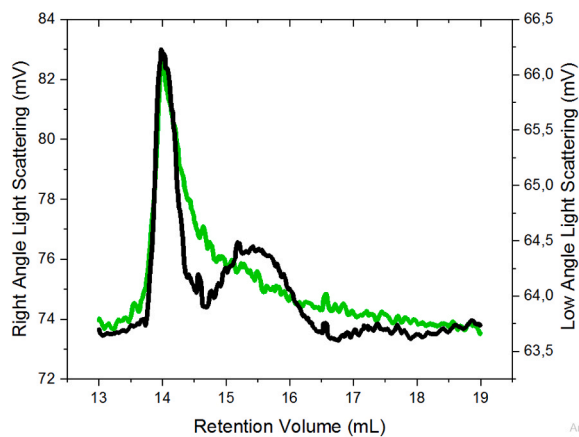


Fig. 5. Chromatogram of in solution of polymeric ionic liquid prepared by reaction of TRIS-based amidine with CO₂ in isopropanol: green – RALS, black – LALS.

3.2. NMR Measurements

As we have mentioned above the results of measuring of changes in the viscosity of reaction solution and FTIR spectra correlate with NMR ¹H and ¹³C spectra for amidine (4) before and during bubbling with CO₂.

The Supporting Information contains NMR spectra for amidine and ionic liquid (Fig. 6S, 7S). The spectra were processed using the MNova program.

Analysis of ¹H NMR spectra of amidine (4) and IL (6) indicates the

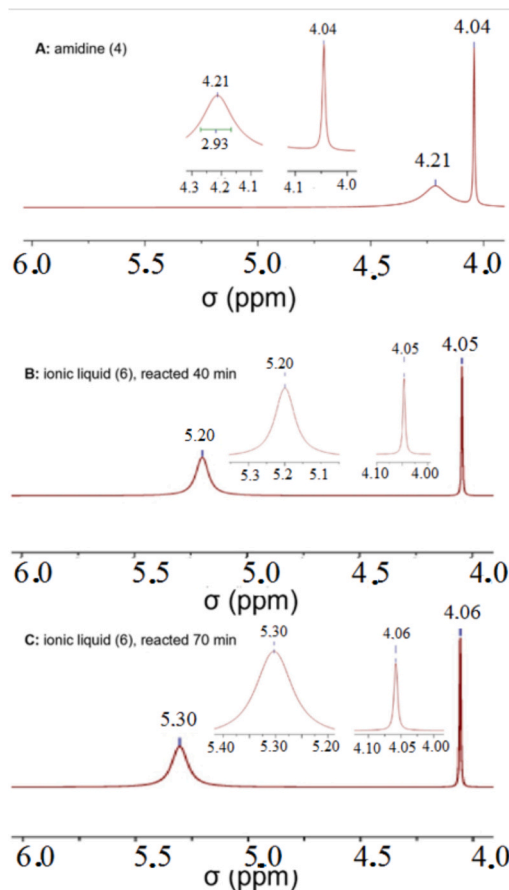


Fig. 6. ¹H NMR spectra of amidine (4) –A, ionic liquid (6) prepared after reaction of amidine with CO₂ for 40 min – B and for 70 min - C.

presence of the following peaks: (δ , ppm) 6.81 (s, NCHN), 4.21 (s, 3H, OH) for amidine (4) and peaks (δ , ppm) 6.84 (s, NCHN), 5.20 (s, NH), 4.05 (s, 2H, OH) for IL (6) after 40 min and peaks (δ , ppm) 6.86 (s, NCHN), 5.30 (s, NH), 4.06 (s, 2H, OH) for IL (6) after 70 min. As a result of reaction of CO₂ with amidine (4) the protonation of imide group by hydroxyl group proton of another amidine molecule takes place (Fig. 1). This leads to formation of the polymeric IL (6).

Previously the authors of study [27] observed that due to reaction of amidine with CO₂ the ¹H NMR spectrum of amidine showed downfield shifting of the R-CH₂-O protons from 3.9 to 4.2 ppm indicating that CO₂ was chemically bound through the alcohol. The data for downfield of proton NMR signal of amines upon proton transfer from oxygen to nitrogen under CO₂ bubbling were also presented in the papers [38,44]. We suggest that downfield shifting of protons from 4.21 (s, 2H, OH) (Fig. 6A) to 5.20 ppm (s, H, NH) (Fig. 6B) and to 5.30 ppm (s, H, NH) (Fig. 6C) in cases of reaction for 40 and 70 min, respectively, can be explained in the similar manner.

Analysis of ¹³C NMR spectra of amidine (4) and IL (6) indicates the presence of the following peaks: δ 37.58 (CH₃), 49.62 (CH₃), 64.21 (CH₂), 70.54 (C), 75.34 (CH₂), 156.60 (CH) – for amidine (4) and for IL (6) we have ¹³C NMR (126.77 MHz, CHLOROFORM-D) δ 36.60 (CH₃), 49.67 (CH₃), 64.25 (CH₂), 70.68 (C), 75.29 (CH₂), 155.2 (C=O), 156.57 (C=N), 162.91 (C=O), 164.05 (C=N).

In our opinion, these spectral data additionally confirm suggestion that the reaction of formation of IL (6) involves participation of two hydroxyl groups (Fig. 1). As one can see from Fig. 7A near the peak at 156.60 ppm (C=N) – for amidine (4) new three peaks appear which belong to IL (6) formed as result of an absorption of CO₂ by amidine. After reaction for 40 min and 70 min the following peaks are present: 155.2 (C=O), 156.57 (C=N), 162.91 (C=O), 164.05 ppm (C=N)

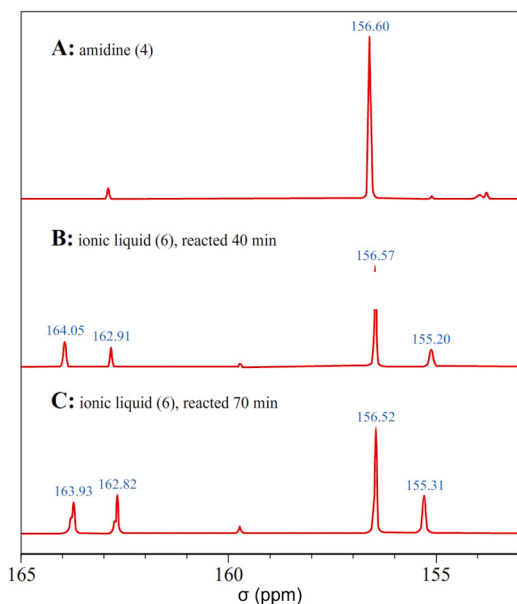


Fig. 7. ¹³C NMR spectra of amidine (4) –A, ionic liquid (6) prepared after reaction of amidine with CO₂ for 40 min – B and for 70 min – C.

(Figs. 7B) and 155.31(C=O), 156.52 (C=N), 162.82 (C=O) 163.93 ppm (C=N) (Fig. 7C), respectively.

4. Conclusions

In 2021, NOAA's Global Monitoring Laboratory observed that carbon dioxide alone accounted for about two-thirds of the total thermal impact of all human-produced greenhouse gases [45]. Our study offers an alternative method for using concentrated atmospheric CO₂ sustainably, which could help with the problem of global warming. Briefly, we illustrated how two aliphatic amines with hydroxyl groups and N,N-dimethylformamide dimethyl acetal reacted forming hydroxy-containing amidines (HCAs), and how the resulting products reacted with carbon dioxide to form polymeric ionic liquids (PILs). Particularly this investigation includes the synthesis of two HCAs prepared by condensation of amino-alcohols such as monoethanolamine and *tris*(hydroxymethyl)aminomethane (TRIS) with N,N-dimethylformamide dimethyl acetal, as well as the confirmation of the HCAs' structure by NMR and FTIR spectroscopy. The study also considers the use of FTIR method for investigation of interaction between HCAs and carbon dioxide leading to formation of PILs. The formation of PILs is confirmed by measurements of their viscosity in solutions in isopropanol and, in case of reaction TRIS-based HCA with CO₂, by measurement of molecular weight of prepared PIL. Additionally, the possibility of participating two hydroxyl groups of this HCA molecule in investigated reaction is discussed.

Author statement

All authors conceived and planned the experiments. Irina Irgibaeva, Alibek Eralinov carried out the experiments. Anuar Aldongarov, Asel Zhapakova contributed to sample preparation. Nikolay Barashkov, Tamara Sakhno and Yuriy Sakhno contributed to the interpretation of the results. Nikolay Barashkov took the lead in writing the manuscript. All authors provided critical feedback and helped shape the research, analysis and manuscript.

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.

Data availability

Data will be made available on request.

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Authors of the manuscript

Declaration of interest.

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