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## Carbon Dioxide Sorption by an Ionic Liquid Monomer that Is 2-Methacryloxyethyl Diethylammonium Chloride and Copolymers Based on It

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### Abstract

The sorption process of carbon dioxide by an ionic liquid monomer (ILM) that is 2-methacryloxyethyl diethylammonium chloride, homopolymer based on it, as well as copolymers obtained by copolymerization of the indicated monomer with styrene and methacrylic acid at the molar ratios of 1 : 2 and 1 : 1, respectively, was studied. A relatively high level of absorptive capacity of ILM in comparison with the homopolymer and copolymers based on it was found. The observed relatively high absorptive capacity of CO<sub>2</sub> of the studied ILM is explained by the interaction of the contrarily charged fragment of the monomer molecule. Thus, a decrease in the absorptive capacity of samples in the transition from the monomer to the homopolymer on its base and further to copolymers distinguished by the content of ILM links in the macrochain composition, and consequently, fragments with opposite charges. It was demonstrated that the sorption process of CO<sub>2</sub> of the studied samples was reversible and one could reach complete desorption of CO<sub>2</sub> with the recovery of their adsorptive effect. Based on the results obtained, the ILM indicated and its homopolymer and copolymers on its base can be recommended as sorbents for CO<sub>2</sub> adsorption.

**Key words:** sorption, ionic liquid monomer, regeneration, sorbent, capture of carbon dioxide

### INTRODUCTION

One of the global issues of mankind is the existing problem associated with environmental pollution by industrial gases. A modern approach to solving the indicated problem includes the application of ionic liquids (IL) in the emerging chemical technologies.

Ion liquids are molten salts with the melting points below 100–150 °C found in the liquid condition in a broad temperature range right up to 400 °C and possessing by a unique set of properties. The interest to IL has begun to grow at an accelerated rate in the last 20 years, which is testified by the number of publications, reviews, monographies and patents devoted to

their synthesis, the study of properties and applications [1–5].

Due to a complex of unique properties inherent to IL, they find a broad application range not only as a new alternative to traditional solvents, catalysts of the reaction medium, monomers in the synthesis processes of homo- and copolymers characterized by a new set of operational properties, as well as a sorbent in the gas purification processes [3, 6, 7]. The application of IL allows developing technologies meeting the major criteria of green chemistry, *i. e.* minimizing the amount of waste, increasing the eco-friendliness of processes. Aside from that, an opportunity of regenerating IL and insignificant losses in comparison with

volatile solvents, as well as preventing equipment corrosion, in turn, leading to environmental pollution, ensures reducing the cost of the processes on an industrial scale.

The preparation of new sorbents to absorb carbon dioxide that pollutes the atmosphere, creating environmental problems is of great practical importance. To that end, various technologies based on absorption phenomena, the application of membranes *etc.* are used.

Aqueous solutions of amines are widely used in industry for carbon dioxide adsorption; despite high efficiency, they have a number of disadvantages, in particular, due to the volatility of these reagents, the process is less eco-friendly and cost-effective. From the ecological and economical viewpoints, among promising reagents used for the removal of CO<sub>2</sub>, ion liquids, their mixtures with amines and polymers based on ion liquids attract interest.

Due to high solubilities of carbon dioxide in IL, their use for capturing CO<sub>2</sub> (with the minimum sorption of other produced gases) gained a lot of interest for researchers. As is known, the reagents used as a sorbent for CO<sub>2</sub> should have high sorption and desorption rates, stability, therefore, IL in this aspect, may become a promising alternative to solvents used in industrial methods of CO<sub>2</sub> removal.

The solubility of CO<sub>2</sub> in IL and unlimited opportunities to regulate solubility degrees by replacing anions and cations in the composition of IL determines the prospects of their use as a sorbent for capturing CO<sub>2</sub>.

An opportunity to use IL, in particular, (CH<sub>3</sub>)<sub>4</sub> NF · 4H<sub>2</sub>O for separation of CO<sub>2</sub> was reported in the USA patents [8, 9] and work [10]. To efficiently capture CO<sub>2</sub> by conversion into carbonate salt and the involvement of water and the weakly basic bifluoride ion is required.

Ionic liquids based on 1-butylimidazole and 2-bromopropylamine hydrobromide after the replacement of anions by BF<sub>4</sub> show high sorptive qualities: the degree of capture of CO<sub>2</sub> by IL approaches maximum and amounts to mole per mole sorbent [11].

To remove CO<sub>2</sub> IL with the carboxylate fragment are especially attractive [12]. It was demonstrated that 1-butyl-3-methyl-imidazolium acetate showed a higher absorptive capacity of CO<sub>2</sub> than 1-butyl-3-methyl-imidazolium tetrafluoroborate.

Polymers synthesized on the base of ionic liquid monomers (ILM) also have a capacity to absorb CO<sub>2</sub> and often show elevated sorptive capacity in comparison with regular IL [13]. In particular, it was found that sorption indicators of poly(*p*-vinylbenzyl trimethyl ammonium tetrafluoroborate (P[VBTMA][BF<sub>4</sub>]), poly(2-(methacryloxy) ethyl trimethyl ammonium tetrafluoroborate (P[MATMA][BF<sub>4</sub>]), poly[1-(*p*-vinylbenzyl-3-butylimidazolium) tetrafluoroborate [P[VBB<sup>+</sup>][BF<sub>4</sub>]], poly(1-(2-methacryloxy) ethyl-3-butylimidazolium tetrafluoroborate and some other IL were much higher than those of the corresponding monomers and low-temperature IL [bmim][BF<sub>4</sub>].

The present article gives the research results on using 2-(methacryloxy) ethyl diethyl ammonium chloride (ILM), its homopolymer and copolymers with styrene and methacrylic acid as the sorbent quality of a sorbent for CO<sub>2</sub>.

## EXPERIMENTAL

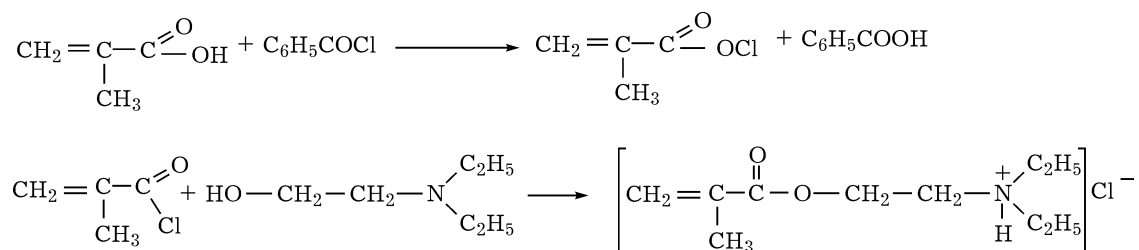
The synthesis of the indicated ILM was carried out in two stages. Methacrylic acid chloride was synthesized at the first stage by the interaction of methacrylic acid with benzyl chloride and target 2-methacryloxyethyl diethylammonium chloride was obtained by the subsequent reaction with diethanolamine (Scheme 1).

The structure of the obtained ILM was confirmed using the methods of IR and NMR spectroscopy (Figs. 1, 2).

The IR spectrum of the sample was registered using a Bruker ALPHA Optik GmbH IR-FT spectrometer (Germany) in a range of 600–4000 cm<sup>-1</sup>. NMR spectra of the sample were removed on a Bruker-300 Fourier spectrometer (AFR) with a frequency of 300 MHz (solvent is EtOD).

The IR spectrum of the indicated ILM is characterized by the availability of adsorption bands attributed to specific fragments of methacrylic acid in the region of 733, 1318, 1457, 2884, 2971 cm<sup>-1</sup> (C–H), 864, 938, 1015 cm<sup>-1</sup> (=CH) 1717 cm<sup>-1</sup> (C=O), 1072, 1163 cm<sup>-1</sup> (–C–O–C–), as well as by the presence of adsorption bands (2475, 2572 and 2659 cm<sup>-1</sup>) related to the ammonium fragment.

Proton NMR signals related to the protons of the methyl group at a multiple bond of the



Scheme 1.

acryl fragment are displayed as a doublet in the region of  $\delta = 6.214$  and  $5.715$  ppm, proton signals of the methyl group at the multiple bond of the acryl fragment appear as a singlet in the region of  $\delta = 1.984$  ppm. The methylene protons of the  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{OCH}_2-$  fragment appear as a triplet at  $\delta = 4.612$  ppm, and the methylene protons of  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{OCH}_2-$  fragment – around  $\delta = 3.609$  ppm. The methylene protons at the  $-\text{N}-(\text{CH}_2)_2$  fragment appear as a quartet in the region of  $\delta = 3.361$  ppm, and the methylene protons of  $\text{C}-(\text{CH}_3)_2$  groups at the indicated monomer fragment – as a triplet at  $\delta = 1.386$  ppm.

The  $^{13}\text{C}$  NVR spectrum of the synthesized monomer is characterized by the presence of the methylene carbon signal in the region of  $\delta_c = 126.19$  ppm, the carbon atom of the  $\text{CH}_2=$  group  $-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$  at  $\delta_c = 166.33$  ppm, the methyl

group carbon in the fragment  $=\overset{\text{CH}_3}{\underset{|}{\text{C}}}-\text{C}$  in the region of  $\delta_c = 135.65$  ppm.

Signals characterizing the methylene carbon atoms of the  $\text{O}-\text{CH}_2-\text{CH}_2-\text{N}$  fragment appear in the region of  $\delta_c = 59.06$  and  $55.83$  ppm. Signals of the carbon atoms of the methylene groups in the  $-\text{N}-\text{CH}_2-$  group appear at  $\delta_c = 47.75$  and  $50.18$ , and signals of the carbon atoms of the methyl groups of the  $-\text{N}-\text{C}-\text{CH}_3$  fragment can be found around  $\delta_c = 17.52$  and  $16.38$  ppm.

The obtained ILM is a gel-like substance with a slight yellow colour, very soluble in water, ethanol and diethylformamide (DEFA). The specific electrical conductivity of a 1 % aqueous solution is  $1.3 \cdot 10^{-5} \text{ S/cm}$ .

Copolymerisation of the synthesized ILM with styrene and methacrylic acid is carried out in an aqueous medium at a temperature of  $80^\circ\text{C}$ .

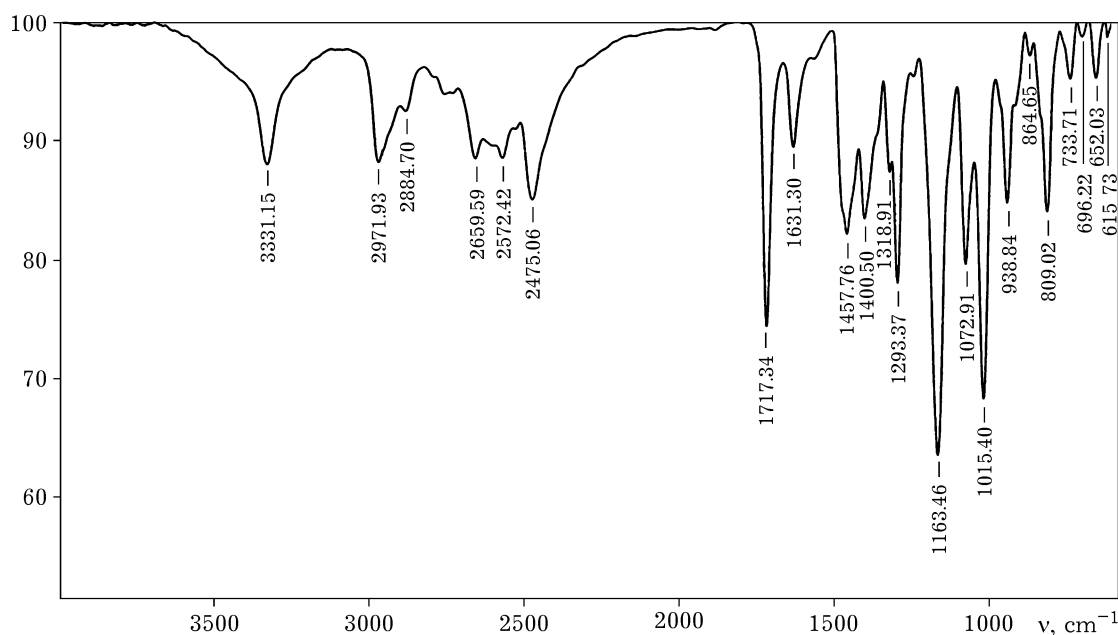


Fig. 1. IR spectrum of 2-methacryloxyethyl diethylammonium chloride (ILM).

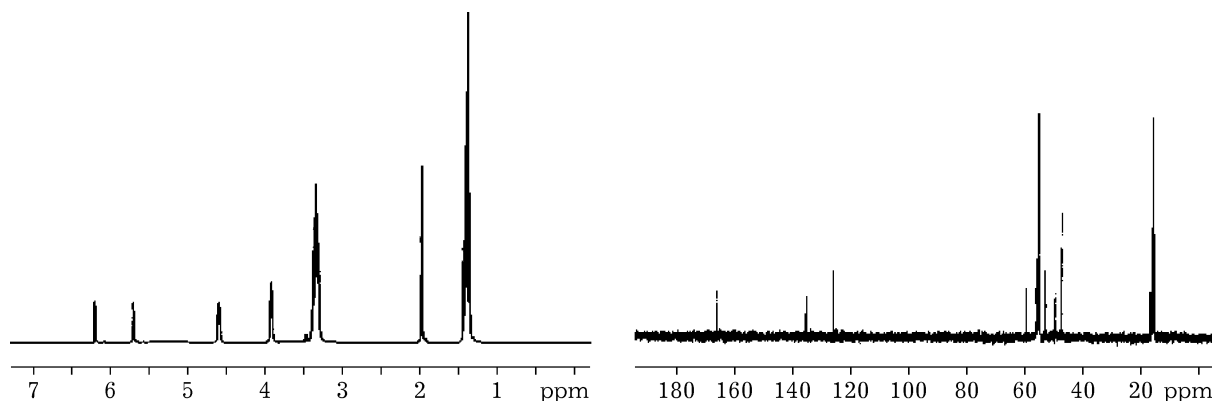


Fig. 2. NMR spectrum of 2-methacryloxyethyl diethylammonium chloride (ILM).

## RESULTS AND DISCUSSION

Based on the research carried out on sorption of pure carbon dioxide in ILM at a temperature of 20 °C it was found that the absorptive capacity of ILM in relation to CO<sub>2</sub> was high enough, and the process proceeded fast enough. Within 5 min, the mass increment of the monomer is 3.5 %, and in the next 10, 20 and 30 min – 5.5, 8.1 and 9.3 mass %, respectively. Further, equilibrium is nearly observed.

Adsorption of CO<sub>2</sub> by the indicated IL is a reversible process and the sorbed gas can be removed by heating of samples at 50 °C for 5–10 min. The removal of CO<sub>2</sub> proceeds at room temperature, however, takes relatively longer time. For 5 min, 85 % of adsorbed CO<sub>2</sub> is desorbed. The ionic liquid monomer reduced in such a way was used again in 5 cycles, and identical results were observed.

Adsorption process dynamics of carbon dioxide by the indicated ILM at a temperature of 20 °C is given in Fig. 3, curve 1.

A similar picture was also observed upon the study of the sorption process of CO<sub>2</sub> by a homopolymer synthesized by radical polymerization of the indicated ILM (see Fig. 3, curve 2). As can be seen, the homopolymer shows lower absorptive capacity in comparison with the studied ILM that is raw materials for the synthesis of this polymer. The homopolymer increment for 35 min is 7.2 mass %, and the maximum adsorption of CO<sub>2</sub> is observed for 35 min; herewith, the sorbent increment is 8.0 mass %. Regeneration of the polymer sorbent at the end of the adsorption process can be carried out by the method

of CO<sub>2</sub> desorption at a temperature of 40 °C. The regenerated polymer can be used again.

The observed decrease in the degree of absorption of CO<sub>2</sub> when moving from ILM to polymers on its base is apparently driven by decreasing a free volume available for CO<sub>2</sub> molecules, resulting from weakening of cation anion interactions between fragments with negative and positive charges located along the macrochain.

A decrease in absorptivity of CO<sub>2</sub> was also observed when moving from the homopolymer to 2-methacryloxyethyl diethylammonium chloride (ILM) copolymers with styrene or methacrylic acid synthesized at a molar ratio of ILM components and comonomer of 2 : 1 and 1 : 1 for styrene and methacrylic acid, respectively. The results obtained are also given in Fig. 3. As can be seen, the absorptive capacity of a copolymer containing styrene or methacrylic acid as a comonomer is significantly lower than that of ILM and the homopolymer based on it. Thus,

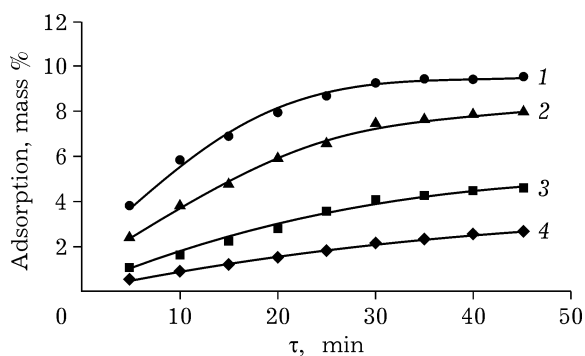


Fig. 3. Dynamics of the process adsorption of ILM (1), its homopolymer (2) and copolymer with styrene (3) and methacrylic acid (4) at a temperature of 20 °C.

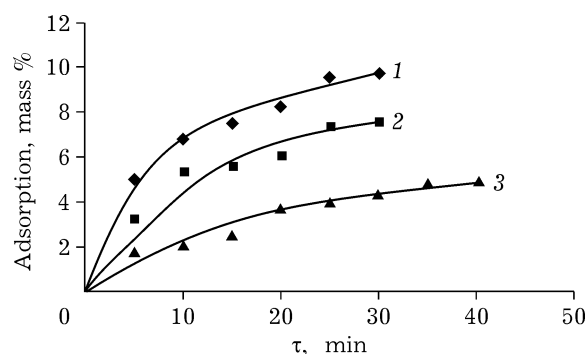


Fig. 4. Dynamics of the process adsorption of ILM (1), its homopolymer (2) and copolymer with styrene (3) at temperature of 30 °C.

the sample increment of ILM copolymer with styrene for 20 and 30 min is 2.6 and 4.0 mass %. Accordingly, unlike the ILM and its homopolymer, CO<sub>2</sub> adsorption by the copolymer proceeds longer and only after 40 min, stabilization that is only 4.5 mass % of the sample mass increment is observed. The maximum increment for a sample of the ILM copolymer with methacrylic acid under similar conditions is only 2.2 mass %.

A copolymer of ILM with styrene shows a relatively low degree of CO<sub>2</sub> adsorption and the increment for 30 min is 2.2 mass %. The results obtained enable to speak of a decrease in the adsorption degree of CO<sub>2</sub> by a polymer sample with a decrease of ILM proportion in it, *i. e.* fragments of the ionic nature.

The monomer samples studied and polymer products on its base are gaseous substances; however, their rigidity in the transition from a monomer to a homopolymer is increased. In particular, with a small load for a monomer, a reverse deformation is observed, and copolymers the plasticity of copolymers is much lower, which is probably due to a decrease in the interaction between cation-anion fragments in the composition of the sample in the transition from a monomer into a polymer and copolymers, a decrease in the retention degree of CO<sub>2</sub> was observed with a decrease in the concentration of ILM in the composition of a copolymer product, since a polymer synthesized with a molar ratio of ILM to styrene of 1 : 10 almost does not absorb carbon oxide under the studied conditions.

It should be noted that all the samples studied based on the indicated ILM after CO<sub>2</sub> adsorption can be regenerated by heating to 50 °C or vacu-

uming of the system with constant temperature. Considering acceleration of the process of CO<sub>2</sub> desorption the effect of temperature mode for the sorption rate of CO<sub>2</sub> was studied by us (Fig. 4).

It was demonstrated that the rate of CO<sub>2</sub> adsorption was somewhat increased with an increase in temperature by 10 °C (from 20 to 30 °C) and the maximum weight increment is observed at a temperature of 30 °C in case of ILM (9.5 mass %) for 25 min, homopolymer (7.3 mass %) – for 20 min, and ILM copolymer with styrene – for 35 min. The rate and the volume of CO<sub>2</sub> adsorption are almost not changed with a decrease in temperature in the system to 15 °C.

## CONCLUSION

Thus, it was found using a series of studies conducted that 2-methacryloxyethyl diethylammonium chloride ILM synthesized by the interaction of methacrylic acid chloride with diethylethanolamine, homopolymer, based on the indicated monomer, and its copolymers with styrene and methacrylic acid had a relatively high absorption capacity of CO<sub>2</sub>. Based on the results obtained, the specified ILM and its homopolymer are of interest as environmentally friendly sorbents for carbon dioxide absorption.

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