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SYNTHESIS OF OCTYL ESTER OF METHACRYLIC ACID USING AN IONIC LIQUID CATALYST: REACTION CONDITIONS AND PRODUCT YIELD

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ABSTRACT

The current study focuses on the synthesis of the octyl ester of methacrylic acid utilizing an ionic liquid catalyst. The aim was to investigate the reaction conditions and determine the resulting product yield. The research methodology involved conducting a series of experiments where various reaction parameters such as temperature, time, catalyst concentration, and reactant ratio were systematically varied. The reaction progress was monitored using analytical techniques such as Infrared spectroscopy and nuclear magnetic resonance spectroscopy. The findings revealed that the reaction temperature and catalyst concentration significantly influenced the esterification process, while the reactant ratio had a minor impact. Moreover, it was observed that higher temperatures and increased catalyst concentrations led to higher product yields. The obtained results provide valuable insights into the synthesis of octyl ester of methacrylic acid using ionic liquid catalysts and lay the foundation for further optimization of reaction conditions in future studies.

Keywords: ionic liquids, catalyst, octyl ester of methacrylic acid, high yield.

Introduction

The development of effective methods for synthesizing esters based on methacrylic acid is of wide interest, as these esters show promise as monomers for producing polymer materials for various purposes [1-3].

Classical methods for the synthesis of esters of (meth)acrylic acids are well-known and involve the reaction of (meth)acrylic acid with the corresponding alcohols in the presence of acid catalysts additionally, the cation exchange catalyst KU-2 has been employed. However, under these conditions, the yield of the target product did not exceed 67-80%.

In this context, the development of effective catalytic systems for the synthesis reactions of (meth)acrylic acid esters is an urgent task [4-6].

Taking into account the aforementioned objective, studies were carried out on the synthesis of octyl ester of (meth)acrylic acid in the presence of an ionic-liquid (IL) catalyst, morpholine hydrosulfate, which was synthesized by reacting morpholine with sulfuric acid.

Experimental part

The synthesis of the specified ionic liquid was carried out in a round-bottomed flask equipped with a thermometer, a reflux condenser, a dropping funnel, and a mechanical stirrer placed in an ice bath.

A solution of morpholine in acetonitrile was loaded into the flask. At a temperature of 0-5^{o}C, 98% sulfuric acid was added dropwise to the solution with stirring for 2 hours to maintain the specified temperature in the reaction zone. After the addition of acid, stirring of the reaction mixture continued at room temperature for 3 hours. Crystalline product formation was observed during the reaction. At the end of the reaction, the product was filtered and dried at a temperature of 500C, under a vacuum at a pressure of 2 mm/Hg for several hours. The structure of morpholine hydrosulfate was confirmed IR and ^{1}H ^{13}C NMR spectroscopy.

Esterification was carried out in a three-neck flask equipped with a magnetic stirrer, a reflux condenser, a thermometer, and a water separator (Dean-Stark nozzle) designed to trap a mixture of benzene and water.

The calculated amount of (meth)acrylic acid and octyl alcohol were loaded into the reaction flask at a molar ratio of components equal to 1.2:1. The solvent was benzene, with hydroquinone comprising 2% of the amount of methacrylic acid to prevent possible polymerization of both the starting acid and the final product - ester. For the reaction, an ionic liquid catalyst based on morpholine and sulfuric acid was employed at a concentration of 2 mol %. The process was conducted at a temperature of 90^{o}C with a reaction duration of 5 hours until an equilibrium state was reached, as indicated by the cessation of the release of reaction water. In this case, the acid number of the reaction mixture remained constant. After completing the reaction, the mixture was cooled to room temperature, and the resulting ester was purified from unreacted acid by washing with a 2% potassium hydroxide solution and water until a neutral reaction (indicated by phenolphthalein). Following atmospheric distillation of the solvent, the raw ether underwent analysis and subsequent vacuum distillation. The yield of the obtained esters was 95%.

A comparative analysis of the experimental results showed that when KU-2 was used as a catalyst, the yield of the target product did not exceed 70%. The studies have established that the use of ionic liquid morpholine hydrosulfate as a catalyst can significantly reduce the reaction time and increase the yield of the target product compared to other known catalysts. Traditionally, the synthesis of esters is conducted in the presence of mineral acids as catalysts, used only once, leading to high water consumption during washing. Although the use of cation exchangers eliminates this disadvantage, these catalysts can give rise to side reactions, particularly in this case, polymerization. Also, the disadvantages of cationic catalysts include their swelling, low thermal stability, and insufficient selectivity [8].

Results and discussions

In the ongoing research, the synthesis of decyl- and octyl esters of methacrylic acid was carried out using morpholine hydrosulfate as a catalyst, as well as in the presence of the well-known cation exchange catalyst KU-2. In the case of using an ionic-liquid catalyst - morpholine hydrosulfate, the process concluded with almost complete conversion of the starting components, achieving a yield of methacrylic acid esters up to 95%. The resulting ether was easily extracted from the ionic liquid through simple separation, and then the ionic liquid, after processing, demonstrated the ability to be reused multiple times without a noticeable decrease in activity.

After the fifth processing, the conversion of methacrylic acid esters remained no less than 90% (Table 1).

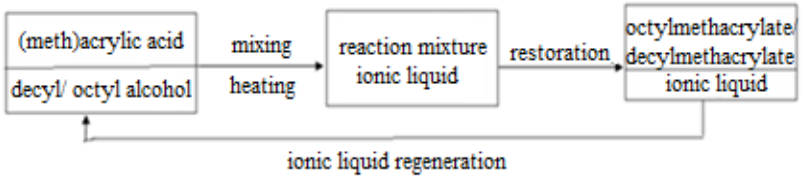
Table 1. Conversion of methacrylic acid using ionic liquid based on morpholine and sulfuric acid

Ionic liquid	Degree of manifestation, (%)					
	Cycle	1	2	3	4	5
Morpholinehydrosulfate		95%	94%	92%	90%	87%

Reaction duration – 5 hours; temperature – 80-90^{0}C, ionic-liquid catalyst –2%

The ionic liquid is recovered from the system without undergoing purification or dehydration.

The scheme and the expected mechanism of the reaction can be presented in the following form:



In order to determine the optimal conditions for synthesizing the octyl ester of methacrylic acid with the synthesized morpholine hydrosulfate as a catalyst, we studied the influence of various factors. These factors included the ratio of the reacting components, catalyst concentration, temperature, and reaction duration on the yield of the target product. The ratio of methacrylic acid (MAA) to octyl alcohol (OA) was varied within a molar range of 1:5, and the catalyst amount ranged from 1% to 3% wt. based on the acid. The reactions were carried out at a temperature of 80°C.

Table 2. Influence of reaction conditions on the yield of methacrylic acid octyl ester.

MAA: OA	**IL catalyst, % wt.**	**Reaction temperature, ^{0}C**	**Yield of ester, % wt**
1:1,2	1,0	85	80,0
1:1,2	2,0	85	93,0
1:1,2	3,0	85	95,0
1:2,0	2,0	85	86,7
1:3,0	2,0	85	88,3
1:5,0	2,0	85	89,6

Based on the research, optimal conditions for synthesizing methacrylic acid octyl ester using an ionic-liquid catalyst, specifically morpholine hydrosulfate, were determined. A yield of 95.0% by weight was achieved under the following conditions: a molar ratio of methacrylic acid to octyl alcohol at 1:1.2, 3% wt of the ionic-liquid catalyst, a reaction temperature of 80-85°C, and a reaction duration of 5 hours. Employing this method and the established conditions, the synthesis of acrylic acid octyl ester was successfully conducted with a yield of 96.2% by weight based on the acid.

The chemical structure of (meth)acrylic acid esters was identified using IR spectroscopy on a BRUKER ALPHA IR-Fourier spectrometer in the wave frequency range of 600-4000 cm^{-1}, employing a SeZn crystal. Additionally, 1H and 13C NMR spectroscopy were performed on a Bruker WP-300 device (300 MHz) using CD_3COCD_3 as the solvent.

The IR spectrum of methacrylic acid octyl ester exhibits the following absorption bands: (1377 cm^{-1}) deformation and (2856 cm^{-1}) stretching vibrations of the CH bond of the CH_3 group; (723 cm^{-1}) pendulum motion; (1454 cm^{-1}) deformation and (2926 cm^{-1}, 2956 cm^{-1}) stretching vibrations of the CH bond of the CH_2 group; (1719 cm^{-1}) stretching vibrations of the C=O group; and (1160 cm^{-1}) stretching vibrations of the C-O bond in the carboxyl fragment of the acid. Additionally, there are (888 cm-1, 937 cm^{-1}) bending vibrations and (1638 cm-1) stretching vibrations of the C=C bond (Figure 1(b)).

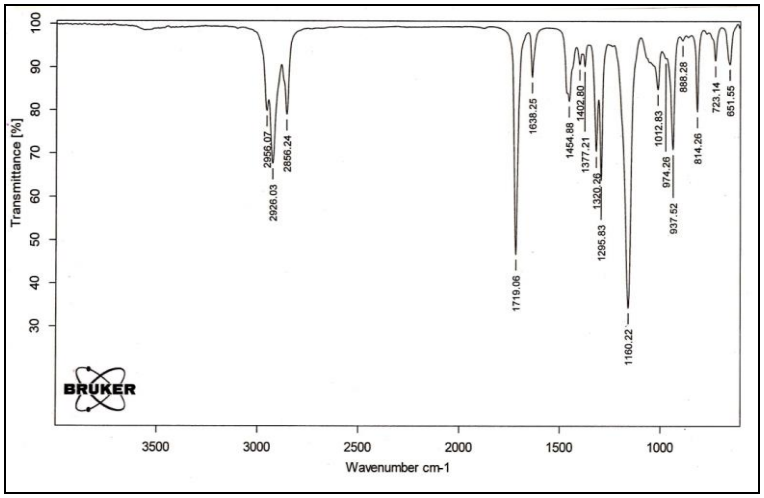


Fig. 1. IR spectrum of methacrylic acid octyl ester.

The $_1H$ NMR spectra of octyl ester of methacrylic acid, synthesized using an ionic-liquid composition as a catalyst, exhibit the following signals: 0.89 ppm. (m, $3H_1$ CH_3), 1.2 ppm (m, 10 CH, 5 CH_2), 1.6 ppm (m $2H_1$ CH_2), 3.5 ppm (m, $2H_1$ CH_2O), 5.8 and 6.6 ppm ($2H_1$ = CH2), and 6.1 ppm (m, 1H, =CH).

The ^{13}C NMR spectrum of the resulting acrylic acid ester reveals a distinctive peak in the 13.5 ppm region, corresponding to the vibrations of the carbon atom in the CH_3 group. Additional observed peaks at 22.4, 25.8, 29.2, 29.3, 31.74, and 32.87 ppm are associated with the vibrations of carbon in the CH_2 group of the octyl moiety of the ether. Furthermore, a signal at 64.1 ppm can be attributed to the vibrations of carbon in the OCH2 fragment of the acrylate group (fig.2).

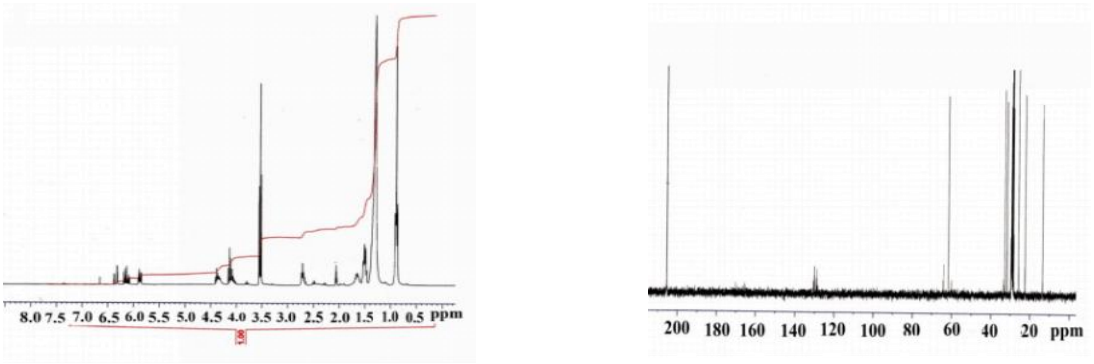


Fig. 2. NMR spectrum of octyl ester of acrylic acid.

Conclusion

The conducted studies demonstrate the feasibility of utilizing the ionic-liquid catalyst morpholine hydrosulfate in the synthesis reactions of octyl ester of (meth)acrylic acids. The results indicate high yields, ensuring the successful production of the target products.

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İON MAYE KATALİZATORUNDAN İSTİFADƏ EDƏRƏK METAKRİL TURŞUSUNUN OKTİL EFİRİNİN SİNTEZİ: REAKSİYA ŞƏRAİTİ VƏ MƏHSUL SƏMƏRƏSİ

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XÜLASƏ

Cari tədqiqatda ion maye katalizatorundan istifadə edərək metakril turşusunun oktil efirinin sintezinə yönəlmişdir. Məqsəd reaksiya şəraitini araşdırmaq və nəticədə məhsulun məhsuldarlığını müəyyən etmək idi. Tədqiqat metodologiyası temperatur, vaxt, katalizatorun qatılığı və reaktivlərin nisbəti kimi müxtəlif reaksiya parametrlərinin sistematik olaraq dəyişdirildiyi bir sıra təcrübələrin aparılmasını əhatə edirdi. Reaksiya gedişatı İQ spektroskopiya və NMR spektroskopiyası kimi analitik üsullardan istifadə etməklə izlənilmişdi. Tədqiqatlar müəyyən etdi ki, reaksiya temperaturu və katalizator qatılığı efirləşmə prosesinə əhəmiyyətli dərəcədə təsir göstərdiyi halda, reaksiyaya girən maddələrin nisbəti az təsir göstərir. Bundan əlavə, daha yüksək temperaturun və artan katalizator qatılığı məhsulun daha yüksək məhsuldarlığına səbəb olduğu müşahidə edilmişdir. Alınmış nəticələr ion maye katalizatorlarından istifadə etməklə metakril turşusunun oktil efirinin sintezi haqqında dəyərli fikirlər verir və gələcək tədqiqatlarda reaksiya şəraitinin daha da optimallaşdırılması üçün zəmin yaradır.

Açar sözlər: ion mayeləri, katalizator, metakril turşusunun oktil efiri, yüksək məhsuldarlıq.

СИНТЕЗ ОКТИЛОВОГО ЭФИРА МЕТАКРИЛОВОЙ КИСЛОТЫ С ИСПОЛЬЗОВАНИЕМ ИОННОГО ЖИДКОГО КАТАЛИЗАТОРА: УСЛОВИЯ РЕАКЦИИ И ВЫХОД ПРОДУКТА

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РЕЗЮМЕ

Настоящее исследование посвящено синтезу октилового эфира метакриловой кислоты с использованием ионного жидкого катализатора. Целью было исследование условий реакции и определение выхода полученного продукта. Методика исследования заключалась в проведении серии экспериментов, в которых систематически варьировались различные параметры реакции, такие как температура, время, концентрация катализатора и соотношение реагентов. За ходом реакции следили с помощью аналитических методов, таких как инфракрасная спектроскопия и спектроскопия ядерного магнитного резонанса. Результаты показали, что температура реакции и концентрация катализатора существенно влияют на процесс этерификации, тогда как соотношение реагентов оказывает незначительное влияние. Более того, было замечено, что более высокие температуры и повышенные концентрации катализатора привели к более высоким выходам продукта. Полученные результаты дают ценную информацию о синтезе октилового эфира метакриловой кислоты с использованием ионных жидких катализаторов и закладывают основу для дальнейшей оптимизации условий реакции в будущих исследованиях.

Ключевые слова: ионные жидкости, катализатор, октиловый эфир метакриловой кислоты, высокий выход.