SYNTHESİS AND INVESTİGATİON OF THE PROPERTİES OF COMPLEX ESTERS OF PETROLEUM ACİDS İN THE PRESENCE OF A PHASE-TRANSFER CATALYST

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Abstract

For the first time, the interaction of the sodium salt of petroleum acid with bromo derivatives in the presence of tetrabutylammonium bromide (TBAB) has been investigated. The purpose of using a phase-transfer catalyst is that it allows for catalyst recovery after the reaction and ensures high yield due to the biphasic nature of the process. The physicochemical properties of the initial raw materials required for the reaction were determined. The chemical structures of the synthesized compounds were confirmed using modern analytical techniques such as infrared (IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. Additionally, the surface tension properties of the resulting ester were studied, and it was found that the compound reduced the surface tension of water at the air–water interface from 72.2 to 29.5 dyn/cm. Based on these results, the synthesized complex ester has been proposed as a potential surface-active agent.

Keywords: Petroleum acids, complex ester, plasticizer, TBAB (tetrabutylammonium bromide)

Currently, petroleum and petroleum-based products have found wide application both nationally and globally. One of the most common uses of acids derived from natural and synthetic oils—particularly naphthenic acids—is in the synthesis of complex esters [1, 2]. Natural and synthetic petroleum acids are utilized in various sectors as plasticizers, dyes, bioactive agents, and as components in formulations against harmful insects and weeds [3].

The structural diversity and specific properties of these esters continue to attract significant attention from researchers. However, existing literature is primarily focused on the esters of fatty acids and, to a lesser extent, on aromatic acids. The main method for synthesizing esters of naphthenic acids involves their interaction with alcohols in the presence of various catalysts.

Several studies [5] have been dedicated to the esterification of naphthenic acids with ethylene glycol, and the optimal conditions for this process have been determined. The resulting diesters of naphthenic acids exhibit low freezing points and have been proposed as plasticizers. Complex esters obtained from catalytic cracking oils and synthetic fatty acids have also been suggested for use as plasticizers [6]. Furthermore, esters of naphthenic acids synthesized with butanol and triethanolamine have been recommended as substitutes for dibutyl phthalate in the production of polyvinyl chloride plasticizers and Textovinit, due to their greater availability and accessibility.

Synthetic lubricating oils derived from complex esters of naphthenic acids and monohydric alcohols are characterized by high flash points and low viscosity; however, their antioxidant properties are relatively poor. Nevertheless, these properties can be improved, as all esters of naphthenic acids exhibit high sensitivity to antioxidant additives.

It is worth noting that the development of novel functionally substituted compounds based on readily available and inexpensive raw materials—such as petroleum refining by-products—with targeted structural characteristics is considered a relevant research direction. These compounds are capable of undergoing various chemical transformations, thereby enabling the synthesis of new products with desired and complex properties. From an environmental perspective, research in this area is also considered to be of great importance [8, 9].

Experimental Part

Literature sources indicate that halogenated derivatives of petroleum acids have been synthesized in the presence of acidic catalysts such as sulfuric acid, KU–2 resin, and others [6]. Recent studies have shown that the use of ionic liquid catalysts enables esterification reactions to proceed not only with high yields but also in an environmentally benign manner. In addition to halogenated alcohols, the interaction of sodium salts of petroleum acids with halogen-containing compounds has also been investigated. This interaction is primarily based on the mechanism of dehydrohalogenation, as reported in several publications [9–11].

In the present study, the interaction reaction between the sodium salts of petroleum acids and bromo derivatives was investigated, and the process was carried out according to the following scheme and mechanism:

$$RCOONa + BrCH_2CHBrCH_3 \xrightarrow[-NaBr]{TBAB} RCOOCH_2CHBrCH_3 \quad (1)$$

$$RCOO^-Na^+ + [(C_4H_9)_4N]^+Br^- \rightleftharpoons [(C_4H_9)_4N]^+RCOO^- + NaBr \quad (2)$$

(aqueous phase)

$$[(C_4H_9)_4N]^+RCOO^- \rightleftharpoons [(C_4H_9)_4N]^+RCOO^- \quad (3)$$

(aqueous phase) (organic phase)

The physicochemical properties of some of the raw materials used in the present study are provided below:

Table 1.

Physicochemical Properties of the Raw Materials

Physicochemical Properties of the Raw Materials	Petroleum acid	1,2 – dibromopropane	Catalyst Tetrabutylammonium Bromide (TBAB)
Density, at 20°C, g/cm³	0.9544	1.98	1.039
Boiling point, °C	120 – 190/6.65 MPa	141	102
Melting point, °C	–	~ -70	102 – 106
Molecular weight, g/mol	206	201.98	322.37
Acid value	272.53	–	–
Refractive index, n_{20}^{D}	1.4592	1.527 – 1.530	1.422

The synthesis of complex esters of naphthenic acids was carried out in the laboratory in two main stages. In the first stage, naphthenic acid reacted with sodium hydroxide to form the corresponding sodium salt. In the second stage, the obtained sodium naphthenate reacted with dibromopropane, resulting in the synthesis of the ester compound.

Initially, 50 mL of distilled water was added to a 100 mL three-necked flask. Then, 1.7 g of naphthenic acid was added, and under stirring, a 0.4 g solution of sodium hydroxide was gradually added dropwise. The mixture was stirred until completely dissolved and allowed to react for 10–15 minutes to ensure completion of the reaction. The progress of the reaction was monitored by pH measurements and adjusted until a neutral pH was achieved. The resulting sodium naphthenate was then separated from the aqueous phase and dried.

In the next stage, 2.81 g of sodium naphthenate was added to a 100 mL three-necked flask. Then, 2.02 g of dibromopropane and 0.16 g of the phase-transfer catalyst, tetrabutylammonium bromide (TBAB), were added. The reaction mixture was then supplemented with 30 mL of diethyl ether or 0.05 g of toluene as a solvent and stirred at 70-80°C for 4-6 hours.

After the reaction was complete, the mixture was cooled and separated into aqueous and organic phases using a separatory funnel. The organic phase was dried with Na_2SO_4 and filtered. The solvent was then removed using a rotary evaporator, and the resulting product was analyzed. The purity and structure of the product were confirmed using FT-IR spectroscopy and nuclear magnetic resonance (^{1}H and ^{13}C NMR) methods.

The obtained results showed that the synthesized product was a high-purity naphthenic ester, and the reaction yield ranged from 70-85%. The infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy results of the complex esters obtained in the process are as follows:

IR:
1750 cm^{-1} – C=O (carbonyl)
1150 cm^{-1} – C-O-C (ether)
540 cm^{-1} – C-Br
NMR:
^{1}H-NMR (δ, ppm)
4.1-4.3 – Ether CH_2
0.9 – CH_3
11.5 – Carboxyl proton (residual)
^{13}C-NMR (δ, ppm)
173 – Carbonyl C
64-66 – OCH_2

This method is highly efficient and optimal for the synthesis of complex esters. After the completion of the process, the yield of the complex ester was 87%.

Table 2.

Physicochemical Properties of the Obtained Complex Ester

Sample	Density (g/cm³)	$T_{qay.}$, °C	$T_{freez..}$, °C	$T_{flash,}$ °C	Mr
$RCOOCH_2CHBrCH_3$	0.960	185 – 195/ 0.4 – 0.5 kPa	-23	250	458

TBAB is an appropriate catalyst for increasing interphase contact. It accelerates the reaction rate by 2-3 times and ensures a high yield under milder conditions.

The surface-active properties of the obtained ester were investigated, and it was found that it significantly reduces the surface tension. Specifically, at a concentration of 1.0% by mass in water, the surface tension decreases from 72.2 to 29.5 dyn/cm.

The surface tension values of the obtained ester at the air-water interface are presented in the following table.

Table 3.

Surface-active Properties of the Obtained Ester at the Water-Air Interface, at 20°C

Ester concentration in water, mass %	Surface tension value, dyn/cm
0.1	56.3
0.25	46.7
0.5	38.5
1.0	29.5

Conclusion

An effective method has been developed for the synthesis of halogen atom-containing saturated esters of naphthenic acids derived from petroleum. This method is based on the interaction of sodium salts of the aforementioned naphthenic acids with halogen-containing saturated and unsaturated C_3 hydrocarbons in the presence of a phase-transfer catalyst, tetrabutylammonium bromide.

Optimal conditions for the synthesis of mono-esters with high yields through the interaction of sodium naphthenate with 1,2-dibromopropane in two-phase systems have been determined. The obtained mono-ester has been proposed as a surfactant.

References:

1. Sədiyeva N.F. TiO2-nin katalitik iştirakı ilə 1,3-butandiol əsasında təbii və sintetik neft turşularının mürəkkəb monoefirlərinin alınması və onların tədqiqi. // Azərb. MEA Aspirantlarının elmi konfransının materialları. 2006, I hissə, Bakı: Elm, s. 143-148.

2. İsgəndərova S.A., Əzizov A.H., Nuriyev L.H. və s. Sirkonium duzlarının iştirakı ilə etilenqlikolun, dietilenqlikolun və təbii neft turşularının mürəkkəb efirlərinin alınması və onların tətbiq sahələrinin öyrənilməsi. // Azərbaycan Dövlət Neft Akademiyasının 85 illik yubileyinə həsr olunmuş "Zərif üzvi sintez və kataliz" III Beynəlxalq elmi konfrans.14-16 dekabr. Bakı. 2005-ci il, səh. 305-307.

3. Зейналов Э.Б., Нуриев Л.Г., Агаев Б.К. и др. Области применения нефтяных кислот, их солей и эфиров. // Нефтепереработка, нефтехимия, катализ (Сборник трудов ИНХП НАНА), Баку: Элм, 2010, с. 92-106..

4. Зейналов С.Б., Кязимова Т.Н., Шарифова С.К. Эпихлоргидрин. Баку: Элм, 2000. 186 с

5. Алиева А.Г., Мамедова Н.А., Велиев М.Г. // Азерб. хим. журн. 2009. № 2. С. 194–197.

6. Велиев М.Г., Мамедова Н.Г., Мустафаев С.А., Садыгов О.А // Нефтехимия. 2009. Т. 49. № 3. С. 247–252.

7. Мустафаев С.А., Велиев М.Г., Мамедова Н.А. // Экоэнергетика. Баку. 2005. № 2. С. 31-33; Mustafaev S.A., Veliev M.G., Mamedova N.A. // Ekoenergetika. Baki. 2005. N 2. P. 31-33 (in Russian).

8. Велиев М.Г., Шатирова М.И., Аскеров О.В., Гахраманов Р.Ф. // Изв. вузов. Химия и хим. технология. 2001. Т. 44. Вып. 1. С. 59-62; Veliev M.G., Shatirova M.I., Askerov O.V., Gakhramanov R.F. // Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol. 2001. V. 44. N 1. P. 59-62 (in Russian).

9. Н.А.Мамедова, С.А.Мустафаев, М.Г.Велиев Выделение и очистка нефтяных кислот из масляных фракций // Neft kimyası və neft emalı prosesləri. 2007. Bakı . №3. s. 16 – 19.

10. М.Г.Велиев, С.А.Мустафаев, А.Г.Шахмамедова, Н.А.Мамедова, Н.К.Ниязова Синтез И Изучение Антимикробной Активности Предельных И Непредельных Эфиров Нефтяных Нафтеновых И Циклогексанкарбоновых Кислот. Azərbaycan kimya jurnalı № 2 2014.

11. Н.А. Мамедова, С.А. Мамедханова, А.Г. Талыбов, С.З. Ахмедова, Х.Ф. Фарзанех, П.М. Керимов Синтез Сложного Непредельного Гликолиевого Эфира На Основе Моноэфира Природной Нефтяной Кислоты С Использованием Ионно-Жидкостного Катализатора. Нефтепереработка И Нефтехимия №11. 2016 s. 28 – 31.