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SYNTHESIS AND PROPERTIES OF NON-IONIC SURFACE-ACTIVE SUBSTANCES BASED ON HEPTADECANOIC ACID AND PROPYLENE OXIDE

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By interaction of heptadecanoic acid (HDA) with propylene oxide (PO) under the catalytic action of potassium hydroxide, esters with varied content of epoxide units in the heterochain were synthesized. The identification of the final products was carried out using IR and electroconductometry methods. Tensiometric measurements made it possible to specify high surface activity of the obtained esters on the water-air interface and identify the values of critical micelle concentration (CMC). Laboratory tests revealed a good oil-carrying and oil-dispersing ability of the synthesized propoxylates with respect to environmentally harmful thin oil films on the surface of waters with a wide range of mineralization degree. The kinetics of the reaction was retraced by manometric method, the general equation of the reaction rate was received and the values of the main kinetic parameters obtained (rate orders for individual components, initial rates, rate constants, activation energy and pre-exponential factor).

Keywords: heptadecanoic acid, propylene oxide, esters, non-ionic surface-active substances, propoxylate, tensiometric measurements.

INTRODUCTION

Surface-active substances (surfactants) are widely used in all the branches of the national economy as well as in science, medicine and everyday life [1]. Surfactants are of particular importance for oil industry where they are used as reagents for oil recovery, demulsifiers and emulsifiers, components of drilling and washing solutions, bactericides, etc. [2,3].

Surfactants of non-ionic nature have very valuable properties [4]. For example, unlike ionic surfactants, they are not affected by the mineral salts contained in marine and reservoir waters. Most non-ionic surfactants described in the scientific and technical literature are pertaining to oligomeric derivatives of ethylene oxide [5]. However, there are also publications on non-ionic surfactants obtained by oligomerization of propylene oxide (PO) which is a result of large-scale production [4]. PO has several advantages over ethylene oxide (EO). Unlike the latter, the PO being a liquid under ordinary conditions is more convenient in operation and much safer, especially from probability of explosion standpoint. Of interest are studies on the production of propoxy derivatives from higher monobasic carboxylic acids which exhibit enhanced surface activity and are able to remove thin, environmentally dangerous oil films from the water surface [4-12].

Throughout these studies, the present work, first ever in the literature, describes the synthesis and properties (including applied ones) of HDA and PO-based surfactants. Results of the analysis of kinetic regularities of the HDA with PO propoxylation reaction are shown.

EXPERIMENTAL PART

PO was used as a product of "Organic Synthesis" enterprise (Sumgait, Azerbaijan) with a purity of 99.8%. HDA was used in the form of reagent of the grade "clean" of chemical reagents facility (Novocherkassk, Russia). Potassium hydroxide was used in the

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form of reagent of “Chemapol” company (Czech Republic)

The reaction of propoxylation of HDA using PO proceeded in a stainless steel autoclave equipped with a stirring device and a controlled heating system. The unreacted amount of PO was removed from the final system through gently heating a constant mass. The epoxide conversion and the average degree of propoxylation (n) were calculated to comply with results of gravimetric measurements.

The $^1$H and $^{13}$C NMR spectra of HDAdpropoxylate were recorded on a pulse Fourier spectrometer from Bruker (Germany) at an operating frequency of 300 MHz. Used as a solvent was CDCl$_3$ (deuterated chloroform).

The IR spectrum was recorded on an Alpha spectrometer (Bruker, Germany) in the wave numbers ranging from 600 to 4000 cm$^{-1}$. In the IR spectrum of HAD propoxylate with an average degree of propoxylation 3.9 (Fig. 1), the following absorption bands were recorded (cm$^{-1}$): 3375.8 $\nu$ (OH), 2954.0, 2923.1 2853.6 $\nu$ (CH), 1738.6 $\nu$ (C = O), 1466.1, 1418.3 and 1366.8 $\delta$ (CH), 1247.2 $\nu$ (C-O-C of ester fragment) 1172.3-1081.1 (C-O of ether fragment), 1050.1 $\nu$ (CO in the C-OH group), 721.2 $\delta$(CH$_2$).

Fig. 1. Infrared propoxylate spectrum HDA(n=4.45)

In the 1H NMR spectrum of propoxylate (n = 4.45) (Fig. 2a), the following signals ($\delta$, ppm) were revealed: 0.86 (CH$_3$), 1.15, 1.25 (CH$_2$ of the main chain). 1.63, 2.25-2.40, 3.15-3.50, 3.8-4.1; 4.97 (OH). In the NMR $^{13}$C spectrum (Fig. 2b), there are peaks ($\delta$, ppm): 14.1 (CH$_3$), 19.16, 22.66, 24.96, 29.12-29.67 [(CH$_2$)$_n$], 31.90, 34.17-34.52, 65.66-77.05, 174.07 (C-O-O).

Fig. 2 a. $^1$H NMR spectrum of HAD propoxylate (n=4.45)
Surface activity was estimated from the surface tension-σ values in the water-air interface measured by the tensiometer KSV Sigma 702 (Israel) using the Du Nui ring. For distilled water, the surface tension on the boundary with air was 72.1 mN / m (20 °C). The deviation in the measurements is 0.2 mN / m.

The specific electrical conductivity reagent of aqueous solutions was measured by means of Anion 4120 electroconductometer (Russia).

Kinetic studies of the propoxylation reaction of HDA were carried out by a manometric method together with recording the pressure in the autoclave with a special manometer. As PO comes into reaction, the pressure drops. After identifying the conversion of the PO and knowing an appropriate pressure drop, the intermediate pressures were recalculated due to concentrations of the PO obtained, so the kinetic curves of the reaction were built as well.

The oil-collecting and oil-dispersing properties of the obtained HDA propoxylates were examined in line with generally accepted method. In separate Petri dishes, a thin oil film (thickness 0.16-0.17 mm) was formed on the surface of three types of water-distilled, fresh and marine (40 ml each) with 1 ml of oil added (Ramana oil field, near Baku). Using a special stencil, the surface area of the initial oil film was measured (measurement accuracy ~ 10%). The reagent for this film was provided in the volume of 0.02 g (as of 100% product and separately as 5% wt. aqueous dispersion solution). The oil-collecting capacity was characterized by the oil-collecting coefficient-K which shows how much the surface area of the oil film decreases under the effect of the reagent used. For this to happen, the surface area of the resulting thickened oil spot was measured through certain time intervals (τ).

The oil-dispersing activity, i.e. the ability to break the oil film into a fine emulsion in water followed by biochemical degradation of oil droplets, was estimated according to the calculated degree of water surface cleaning from oil-KD (in%).

The water used in these tests had the following characteristics: fresh water-density (20 °C) -996 kg / m³; pH-7-8; total hardness is 4.5 mg-eq / l; content of ions (in g-eq / 100 g):Ca²⁺-0.0052, Mg²⁺-0.0023, Cl⁻-0.0007, SO₄²⁻-0.0044, HCO₃⁻-0.0273, CO₃²⁻-0.0009; density of water of the Caspian Sea- (20°C)-1009.8 kg/m³; pH-7.7; total hardness -69.0mg-eq / l, chemical composition (mg / 1000 g): Na⁺-2650, K⁺-20, Ca²⁺-250, Mg²⁺-900, NH₄⁺-0.15, Cl⁻-500, SO₄²⁻-2800, NO₃⁻-0.1, PO₄³⁻-0.35, SiO₂-0.5.
The Ramana oil had a density (20°C) of 862 kg/m³ and a kinematic viscosity (20 °C) of 16.80 cSt.

**DISCUSSION OF THE RESULTS**

The HDA propoxylation reaction carried out at 120-150°C for 20-24 hours can be described by the following scheme:

\[
\text{C}_{16}\text{H}_{33}\text{O} + n \text{CH}_2\text{CHCH}_3 \rightarrow \text{C}_{16}\text{H}_{33}\text{OH} + n \text{OCH}_2\text{CHO}_n\text{H}
\]

The catalyst of the reaction is potassium hydroxide at the rate of 3% mole of the acid.

The obtained propoxylates at low degrees of propoxylation (up to ~ 3.0) are non-flowing and have a light brown color. At higher values of "n" (above 3.0), the reaction products are fluid and have a dark brown color.

The synthesized propoxy-esters of HDA are easily soluble in kerosene, ethyl- and isopropyl alcohols. Note that these esters are dissolved up to 1 g. in 1 liter of water.

The results of analysis of the surface-active properties of these esters in the water-air interface by the tensometric method are given in Table 1. For comparison, the table also contains data for HDA itself. The table also includes values of the hydrophilic-lipophilic balance (HLB), calculated by the Davies method [1]. Results obtained make it possible to infer that HDA with its weak surface activity following the reaction with PO becomes an ester with obvious surface activity. The HLB values decrease as «n» increases, i.e. rise in hydrophobicity.

**Table 1.** Results of tensiometric measurements of surface tensions in the water-air interface (16 °C) in the presence of various amounts of propoxylates of HDA and HDA itself

<table>
<thead>
<tr>
<th>Reagent</th>
<th>HLB</th>
<th>Concentration of reagent, % wt.</th>
<th>Surface tension at the water-air interface, mN/m</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.01</td>
<td>0.025</td>
</tr>
<tr>
<td>HDA</td>
<td>1.50</td>
<td>51.98</td>
<td>60.97</td>
</tr>
<tr>
<td>HDAdoproxylate(n=2.40)</td>
<td>0.28</td>
<td>59.75</td>
<td>58.93</td>
</tr>
<tr>
<td>«————» (n=3.02)</td>
<td>-0.60</td>
<td>69.90</td>
<td>64.99</td>
</tr>
<tr>
<td>«————» (n=3.49)</td>
<td>-1.28</td>
<td>56.88</td>
<td>55.97</td>
</tr>
<tr>
<td>«————» (n=4.45)</td>
<td>-2.65</td>
<td>47.71</td>
<td>39.49</td>
</tr>
</tbody>
</table>

*Note. In the absence of surfactants, the surface tension of water at the boundary with air at 16 °C is 72.0 mN/m.*

Thus, propoxylate with n = 4.45 in the concentration of 0.7% reduces the surface tension at the above boundary from 72.0 down to 29.6 mN/m. Within the framework of the analyzed concentration interval, micelle formation takes place in case of propoxylates with n = 2.40, 3.02 and 3.49. Stabilization of σ values is found in the concentration of ~ 0.5% (CMC).

Table 2 provides the results of measurements of the specific electric conductivity of aqueous solutions of HDA and
its propoxy-esters in the concentration interval in line with in Table 1. Results of electroconductometric measurements are indicative that the values of \( \kappa \) for solutions of propoxy-esters of HDA are approximately of the same order as for distilled water. This is consistent with the composition and structure of the synthesized esters that have no charged groups. It should be added that HDA itself as a very weak electrolyte is dissociated very insignificantly in water.

Table 2. The results of measurements of the specific electric conductivity of aqueous solutions of HDA and its propoxy-esters (16 °C)

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Concentration of reagent, % wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>HDA</td>
<td>5.9</td>
</tr>
<tr>
<td>HDA propoxylate (n=2.40)</td>
<td>9.3</td>
</tr>
<tr>
<td>«—» (n=3.02)</td>
<td>19.2</td>
</tr>
<tr>
<td>«—» (n=3.49)</td>
<td>13.9</td>
</tr>
<tr>
<td>«—» (n=4.45)</td>
<td>15.4</td>
</tr>
</tbody>
</table>

Note. The specific electrical conductivity of distilled water is 3.2 \( \mu \) S/cm.

Table 3 shows the results of laboratory tests with the HDA propoxylates on their oil-collecting and oil-dispersing ability. Although the HDA itself does not possess oil-collecting or oil-dispersing properties, it has been found that the propoxy-esters of HDA are active fairly good activity in removing thin oil films from the surface of waters with different degrees of mineralization. In the sea water, the highest oil collection ability is shown by ester with \( n = 2.56 \) in the form of an aqueous solution (\( K = 18.34, \tau > 4.5 \) days). In fresh water medium, a reagent with \( n = 4.45 \) in un-thinned form exhibits a value of \( K_{\text{max}} = 19.37 \) within more than 4.5 days. The ester with \( n = 2.56 \) in the form of aqueous solution shows an oil-collecting effect of \( K_{\text{max}} = 17.37 \) (\( \tau > 4.5 \) days). In distilled water, HDA propoxylate with \( n = 4.45 \) in un-thinned state demonstrates initially an oil-collecting ability with value of \( K_{\text{max}} = 30.06 \) which then passes to oil-dispersing activity (\( K_D = 98\% \)). Note that 5% aqueous solution of this ester in distilled water turns out to be an oil collector (\( K_{\text{max}} = 27.18, \tau > 4.5 \) days), and in the sea water it shows mixed activity, first exhibiting dispersive properties (\( K_D = 98\% \), then oil collecting ability (\( K_{\text{max}} = 7.60, \tau > 4.5 \) days).

Taking into consideration good effectiveness of propoxy-esters of HDA as oil-collecting and oil-dispersing reagents which is very important for the liquidation of ecologically dangerous thin oil films that violate the ecological balance at the hydrosphere-atmosphere boundary (the violation of energy exchange with respect to sunlight and the exchange of such gases as oxygen and carbon dioxide influencing the life activity of marine inhabitants), the kinetic regularities of the reaction of HAD propoxylation use PO were investigated.

The rate (\( w \)) equation of the reaction of HAD propoxylation with PO has the following form:

\[
W = k [\text{HDA}]^a [\text{PO}]^b [\text{KOH}]^c
\]

where \( k \) is the rate constant, [HDA] - the concentration of HDA, [PO] - the concentration of PO, [KOH] - the concentration of potassium hydroxide (the catalyst of the reaction),
α, b and c are the orders of the reaction rate with regard of the HDA, PO and KOH concentration.

As is known, in order to determine the order of the reaction rate with respect to the concentration of a component, this concentration varies with constant concentrations of the remaining components. Isooctane was used as a solvent. During the kinetic treatment, the initial reaction site and accordingly initial rate as well as initial concentrations of the reaction components, i.e. [PO]₀, [HDA]₀, and [KOH]₀ were used. From the dependence log $W_o$-lg [PO]₀, it was found that the slope of this straight line, was about 1.0. Therefore, the order of the rate with respect to the concentration of OP (b) was 1.0. Similarly, from the dependence of lg$W_o$-lg [MK]₀ the order of the reaction rate with regard to the concentration of HAD was determined: $\alpha = 2.5$

<table>
<thead>
<tr>
<th>n</th>
<th>Form of reagent application</th>
<th>Distilled water</th>
<th>Freshwater</th>
<th>Seawater</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>τ, часы</td>
<td>K(K_D)</td>
<td>τ, часы</td>
<td>K(K_D)</td>
</tr>
<tr>
<td>2.56</td>
<td>100% product</td>
<td>0</td>
<td>12.53</td>
<td>0</td>
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<tr>
<td></td>
<td>1.50-51.00</td>
<td>15.16</td>
<td>1.50-51.00</td>
<td>10.13</td>
</tr>
<tr>
<td></td>
<td>78.50-108.50</td>
<td>17.37</td>
<td>78.50-108.50</td>
<td>15.31</td>
</tr>
<tr>
<td></td>
<td>5% aqueous solution (disperse)</td>
<td>0</td>
<td>13.08</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1.50-51.00</td>
<td>14.20</td>
<td>1.50-51.00</td>
<td>15.20</td>
</tr>
<tr>
<td></td>
<td>78.50-108.50</td>
<td>13.52</td>
<td>78.50-108.50</td>
<td>17.37</td>
</tr>
<tr>
<td>3.02</td>
<td>100% product</td>
<td>0</td>
<td>16.75</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1.50-51.00</td>
<td>15.20</td>
<td>1.50-51.00</td>
<td>15.20</td>
</tr>
<tr>
<td></td>
<td>78.50-108.50</td>
<td>7.60</td>
<td>78.50-108.50</td>
<td>78.50-108.50</td>
</tr>
<tr>
<td></td>
<td>5% aqueous solution (disperse)</td>
<td>0</td>
<td>17.34</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1.50-51.00</td>
<td>10.13</td>
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<td>15.20</td>
<td>76.50-108.50</td>
<td>97%</td>
</tr>
<tr>
<td>3.49</td>
<td>100% product</td>
<td>0</td>
<td>17.50</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1.50-51.00</td>
<td>15.20</td>
<td>1.50-51.00</td>
<td>10.13</td>
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<tr>
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<td>78.50-108.50</td>
<td>5.07</td>
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<td></td>
<td>5% aqueous solution (disperse)</td>
<td>0</td>
<td>9.57</td>
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<tr>
<td></td>
<td>1.50-51.00</td>
<td>36%</td>
<td>1.50-51.00</td>
<td>14.30</td>
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<tr>
<td></td>
<td>78.50-108.50</td>
<td>12.16</td>
<td>78.50-108.50</td>
<td>98%</td>
</tr>
</tbody>
</table>

Table 3. Results of studies into oil-collecting and oil-dispersing abilities of propoxyl-esters of HDA.
From the $\lg W_o$-$\log [\text{HDA}]_o$ dependence of the order of the reaction rate with respect to the KOH concentration is established: $c = 0.33$. Using the experimentally specified order values, the overall rate equation takes the following concrete form:

$$W = k [\text{HDA}]^{3.33}[\text{PO}]^{[\text{KOH}]}^{0.33}$$

To establish the activation energy ($E$) of the HAD reaction, the reaction at constant concentrations of the component proceeded at three temperatures (120, 130 and 140 °C) (Fig. 3).

**Fig. 3.** Kinetic curves of propoxylation of HDA at various temperatures. Concentration of HDA-0.568 mol / l, PO-2.840 mol / l, potassium hydroxide-0.055 mol / l.

Temperature, °C: 1- Δ - 120; 2- ■ - 130; 3- ● - 140

**Fig. 4.** Kinetic curves of HAD propoxylation in various solvents. Concentration of HDA-0.568 mol / l, PO-2.840 mol / l, potassium hydroxide-0.055 mol/l.

Solvent: 1- ▲ - tetrahydrofuran; 2- ■ - benzene; 3- x-cyclohexane; 4- ● - isoctane
From the corresponding kinetic curves (Fig. 3), the values of the initial rates were found:

- at 120°C $W_0 = 1.666 \cdot 10^{-4} \text{ mol l}^{-1} \text{s}^{-1}$;
- at 130°C $W_0 = 2.222 \cdot 10^{-4} \text{ mol l}^{-1} \text{s}^{-1}$;
- at 140°C $W_0 = 2.916 \cdot 10^{-4} \text{ mol l}^{-1} \text{s}^{-1}$.

Substituting these values of the initial rates and concentrations of the components in the above specific overall equation, the rate constants at three temperatures are established as follows:

- $k_{120} = 0.001010 \text{ mol}^{-3.66} \text{l}^{3.66} \text{s}^{-1}$;
- $k_{130} = 0.001349 \text{ mol}^{-3.66} \text{l}^{3.66} \text{s}^{-1}$;
- $k_{140} = 0.001768 \text{ mol}^{-3.66} \text{l}^{3.66} \text{s}^{-1}$

To find the value of $E$, the logarithmic form of the Arrhenius equation was used:

$$\ln k = \ln A - \frac{E}{RT}$$

where $R$ is the universal gas constant, $T$ is the absolute temperature, and $A$ is the pre-exponential factor. Taking into account the values of "$k$" for three temperatures, the value of the activation energy is calculated:

$E = 37.87 \text{ kJ/mol}$

Knowing the value of $E$, it is easy to calculate the pre-exponential factor as follows: $A = 1.1 \cdot 10^2$.

Taking into account the values of $E$, $A$ and $R$, the Arrhenius equation ($k = A \cdot e^{\frac{E}{RT}}$) takes the following expression:

$$k = 1.1 \cdot 10^2 \cdot e^{\frac{4555.34}{T}}$$

Investigation of the influence of the nature of the solvent (Figure 4) showed that of the solvents used (isooctane, cyclohexane, benzene and tetrahydrofuran), the highest rate is observed in isooctane. In the case of relatively polar tetrahydrofuran, the reaction rate is the lowest.

**CONCLUSIONS**

Catalytic propoxylation of HDA with the help of OP propoxy-esters was obtained in the hetero-chain of which there are up to 4-5 epoxy units. The composition and structure of these esters are confirmed by IR and electro-conductometry methods. Tensiometry method showed high surface activity of the obtained propoxylates at the water-air interface and the value of the critical micelle concentration was determined.

Laboratory studies revealed a good oil-collecting and oil-dispersing abilities of synthesized reagents with respect to thin oil films on the surface of waters with a wide range of mineralization ($K_{max} = 30.06$, duration of action is more than 4.5 days) which allows them to be recommended for removal of these ecologically dangerous films from the surface of natural reservoirs. Using the manometric method, the main kinetic parameters (order of rate with respect to component concentrations, initial reaction rates, rate constants, activation energy and pre-exponential factor) were determined, and the overall equation of the reaction rate was derived.

**REFERENCES**


**СИНТЕЗ И СВОЙСТВА НЕИНОГЕННЫХ ПОВЕРХНОСТНО-АКТИВНЫХ ВЕЩЕСТВ НА ОСНОВЕ МАРГАРИНОВОЙ КИСЛОТЫ И ОКСИДА ПРОПИЛЕНА**

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Взаимодействием маргариновой кислоты с оксидом пропилена под каталитическим воздействи гидроксида калия синтезированы эфиры с различным содержанием звеньев эпоксида в гетероцепи. Идентификация конечных продуктов проведена с помощью методов ИК и электрокондуктометрии. Тензиометрическими измерениями установлена высокая поверхностная активность полученных эфиров на границе вода-воздух и оценено значение критической концентрации мицеллообразования (ККМ). Испытаниями в лабораторных условиях обнаружена хорошая нефтесобирающая и
нефтедиспергирующая способность синтезированных оксипропилатов в отношении экологически вредных тонких нефтяных пленок на поверхности вод с широким интервалом степени минерализации. Манометрическим методом изучена кинетика, выведено общее уравнение скорости реакции и определены значения основных кинетических параметров (порядки скорости по отдельным компонентам, начальные скорости, постоянные скорости, энергия активации и предэкспонента).

Ключевые слова: маргариновая кислота, оксид пропилена, неиногенные поверхностно-активные вещества, оксипропилаты, тензиометрические измерения

PROPİLEN OKSİDİ VƏ HEPTADEKAN TURŞUSU ƏSASINDA QEYRİ-İNONOGEN SƏTHİ-AKTİV MADDƏLƏRİN SİNTEZİ VƏ XASSƏLƏRLƏRİ

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AMEA Y.H. Məmmədəliyev adına Neft-Kimya Prosesləri İnstitutu
Az 1025 Baki, Xocalı prospekti, 30; e-mail: ilhamachem447@mail.ru


Açar sözlər: heptadekan turşusu, propilen oksidi, qeyri-ionogen səthi-aktiv maddələr, oksipropilatlar, tensiometrik ölçülər