

Research Article

Study of the Oil-Collecting Properties of Cationic Salts

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Abstract

Octylamine, nonylamine, dodecylamine, and hexadecylamine were reacted with ethylenechlorohydrin in equimolar proportions, and the cationic salts octylethylammonium chloride (OEAC), nonylethylammonium chloride (NEAC), dodecylethylammonium chloride (DDEAC), and hexadecylethylammonium chloride (HDEAC) were obtained, respectively. The composition and structure of the salts obtained were identified by IR and UV spectroscopy methods. The specific electrical conductivity of aqueous solutions of the salts obtained by the electron conductometric method was measured, and their electrolyte nature was determined. The surface tension values of the cationic salts were calculated at the air boundary in a tensiometer. It was shown that all four of the salts are surfactants. It was determined that as the length of the alkyl radical in the cationic increases, its surface activity increases. The oil-collecting abilities of OEAC, NEAC, DDEAC, and HDEAC cationic salts were studied in laboratory conditions. In the conducted studies, oil (Pirallahi field oil) was poured onto 3 types of water with different mineral content - distilled, fresh water, and seawater, and formed a thin layer. It was determined that cationic salts demonstrate high oil-collecting abilities both in the form of 100% product and 5% solution. It was shown that in all cases the oil-collecting ability of 100% products is superior to that of aqueous solutions. The oil-accumulating abilities of OEAC and DDEAC salts and their aqueous solutions are the same. The oil-accumulating abilities of the first and third cationic salts among NEAC, DDEAC, and HDEAC are higher. The oil-collecting abilities of OEAC and DDEAC salts and their aqueous solutions lag behind those of the HDEAC salt. It was concluded that an increase in the length of the alkyl radical in the salt composition has a positive effect on the oil-accumulating ability.

Keywords: cationic salts, specific electrical conductivity, surface activity, oil accumulation coefficient, oil collecting

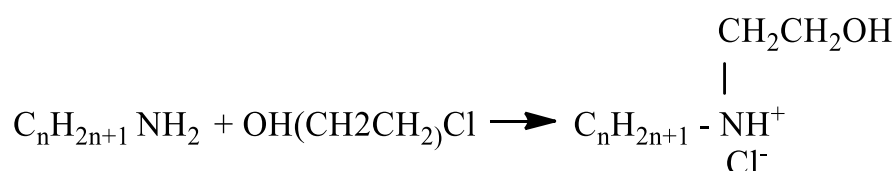
1. Introduction

When oil and petroleum-derived pollutants enter aquatic environments, volatile components evaporate first. Their evaporation is particularly intense at first. Then the evaporation process weakens, which is characteristic of crude oils. It has been shown that crude oils release up to 90% of their components into the atmosphere, diesel fuel up to 75%, and heavy oils and oil residues up to 10%. Thus, oil products that fall into water bodies, which are considered environmentally hazardous, pollute both the hydrosphere and the atmosphere. Unfortunately, it should be noted that the world's waters are very seriously polluted with oil and oil products, and pollution continues. Preventing pollution of water bodies and cleaning polluted waters is one of the main global problems in the world [1], [2]. Oil spills and oil products on the surface of a water body are cleaned by mechanical, physical, and chemical methods. It is possible to clean oil stains with a thickness of more than 0.1 mm by mechanical methods. When the thickness of the spilled oil layer is less than 0.1 mm, it is usually convenient to use surfactants to remove it from the water surface, and various surfactants are used for this purpose [3], [4]. The emulsifying ability of surfactants is considered valuable when removing oil-based pollutants from the water surface. A number of surfactants have the ability to convert the oil layer into a thin dispersion. In this case, the surfactant must have sufficient stabilizing ability in relation to the oil particles. It is convenient to use organic and polymeric surfactants to cover and collect oil on the water surface [5], [6].

According to the ability to remove a thin oil layer, surfactants are divided into oil collectors and oil dispersants [7]. The use of reagents with a collecting effect is of particular interest. These reagents prevent oil from being spilled on the water surface and collect it in a single spot. The principle of action of collecting reagents with a surface-active nature is based on their spontaneous flow and the formation of surface pressure when applied to the surface of the water-air phase separation. When collecting, reagents are applied along the perimeter of the oil layer; its area decreases, and its thickness increases significantly. Their effect is based on the pressure created by the monomolecular layer of surfactant when it flows along the water surface. The main indicators that determine the effectiveness of the reagent and the possibility of their practical application are the flow rate, the formation of a monolayer, long-term stability, low consumption, and low toxicity. From this point of view, it is practically very convenient to use the property of cationic compounds, such as surfactants, to remove a thin oil layer on the water surface.

2. Materials and Methods

Octylamine, nonylamine, dodecylamine, and hexadecylamine were reacted with ethylenechlorohydrin in equimolar ratios to obtain octylethylammonium chloride (OEAC), nonylethylammonium chloride (NEAC), dodecylethylammonium chloride (DDEAC), and hexadecylethylammonium chloride (HDEAC) salts, respectively. The general scheme of the reactions performed is as follows:



here $n = 8, 9, 12, 16$

The structure and composition of the obtained cationic salts were identified by IR spectroscopy. IR spectra were recorded on an ALPHA Fourier spectrometer (Bruker, Germany) at a wavelength of $600\text{--}4000\text{ cm}^{-1}$. The results of the analysis of the spectroscopy of cationic salts. As can be seen from the values of the absorption bands in the IR spectra of the mentioned salts are similar.

NEAC and HDEAC cationic salts were also characterized by UV–Vis spectroscopy. The UV–Vis spectra were recorded in ethanol using a Specord UV–Vis spectrometer. The analysis results showed that in both cases, ammonium groups are observed at a wavelength of 211 nm.

The electrical conductivity of OEAC, NEAC, DDEAC, and HDEAC cationic salts was determined on a conductometer of the “Anion-4120” brand (made in the Russian Federation). For this, aqueous solutions of salts with different concentrations were prepared. The results of the conducted research are given in Table 1.

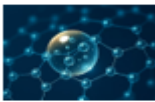
Table 1. Measurement results of the specific electrical conductivity of cationic salts (in $\mu\text{C}/\text{cm}$).

Concentration of cationic salt, % by mass	OEAC	NEAC	DDEAC	HDEAC
0.0001	30.0	–	5.1	–
0.0005	64.1	–	6.7	–
0.001	87.8	–	8.9	–
0.025	–	59.0	–	60.2
0.05	98.6	–	11.3	–
0.1	117.7	–	12.4	–
0.7	–	214.8	–	226.0

3. Results and Discussion

As can be seen from Table 1, the value of electrical conductivity increases as the concentration of the solution increases. The increase in specific electrical conductivity proves that the cationic salts OEAC, NEAC, DDEAC, and HDEAC have polar properties.

The surface activity of the obtained cationic salts was determined in a “Sigma-702” tensiometer. Therefore, aqueous solutions of cationic salts OEAC, NEAC, DDEAC, and HDEAC with different concentrations were



prepared, and the surface tension values at the interface with air were calculated. The results of the research work carried out are given in Table 2.

Table 2. The surface tension values of cationic salts OEAC, NEAC, DDEAC, and HDEAC at the water-air interface (in mN/m).

Concentration of cationic salt, % by mass	OEAC	NEAC	DDEAC	HDEAC
0.0001	49.3	–	–	–
0.00025	45.1	–	–	–
0.0005	39.7	–	–	–
0.00075	37.1	–	–	–
0.01	32.4	–	29.4	–
0.05	28.4	–	28.2	–
0.75	25.2	–	27.6	–
0.1	23.3	–	25.3	–
0.2	21.6	40.8	24.1	33.3
0.5	–	31.9	–	25.5
0.7	–	26.4	–	29.5

From the results given in Table 2, it is clear that with an increase in the concentration of aqueous solutions of cationic salts, the surface tension values decrease. In other words, their surface-activity properties increase. From the point of view of surface activity, the OEAC cationic salt demonstrates higher efficiency. Thus, the tension value at a concentration of 0.2 decreases to 21.6 mN/m. In the case of the DDEAC cationic salt, the surface tension value at the same concentration is equal to 24.1 mN/m. In general, it can be concluded from the values shown in the table that the longer the length of the alkyl radical in the cationic, the greater its surface tension value.

Studies of the oil-collecting ability of OEAC, NEAC, DDEAC, and HDEAC cationic salts were carried out in laboratory conditions according to the methodology [2]. In the studies, oil taken from the Pirallahi field (density 0.9244 g/cm³ at 20 °C, kinematic viscosity 105 sSt at 30 °C), distilled, potable (density 0.996 g/cm³ at 20 °C, hardness 4.5 mg-eq/g) and seawater (Caspian Sea water, density 1.0098 g/cm³ at 20 °C, total hardness 69 mg-eq/g) are applied and a thin layer of ~ 0.165 mm is formed. The oil collection efficiency of the obtained cationic salts is evaluated by the change in the area of the oil slick on the water surface due to the action of the reagent. Cationic salts are used in these studies as a 100% product and a 5% solution. The oil-collecting activity is estimated by the accumulation rate, in other words, the ratio of the area of the oil layer to the area of the oil spot formed by the action of the reagent (K) and the retention time of the collected oil (t). The results of the studies conducted to determine the oil-accumulating ability of the obtained cationic salts are given in Table 3.

Table 3. Oil-collecting ability of cationic salts OEAC, NEAC, DDEAC, and HDEAC.

Reagent status	Distilled water		Fresh water		Sea water	
	τ, time	K	τ, time	K	τ, time	K
OEAC salt						
100% product	0–0.5	30.4	0–0.5	20.5	0–0.5	19.4
	1.0–2.0	42.3	1.0–2.0	51.7	1.0–2.0	40.2
	3.0–15.0	53.2	3.0–168.0	40.5	3.0–15.0	57.6
	24.0–168.0	60.8			24.0–168.0	60.8
5% product	0–0.5	8.6	0–0.5	9.6	0–0.5	19.4
	1.0–2.0	26.8	1.0–2.0	23.9	1.0–2.0	22.5
	3.0–168.0	30.4	3.0–168.0	30.4	3.0–168.0	30.4
NEAC salt						
100% product	0–0.5	30.5	0–0.5	38.1	0–0.5	30.5
	1.0–2.0	42.3	1.0–2.0	46.6	1.0–2.0	58.7
	3.0–15.0	53.2	3.0–15.0	58.9	3.0–15.0	60.8
	24.0–190.0	72.5	24.0–190.0	71.5	24.0–190.0	80.6
5% product	0–0.5	40.5	0–0.5	40.5	0–0.5	38.7
	1.0–2.0	53.7	1.0–2.0	59.8	1.0–2.0	60.8
	24.0–190.0	60.5	3.0–190.0	60.5	3.0–190.0	80.6
DDEAC salt						

100% product	0–0.5	30.4	0–0.5	20.5	0–0.5	19.4
	1.0–2.0	42.3	1.0–2.0	51.7	1.0–2.0	40.2
	3.0–15.0	53.2	3.0–168.0	40.5	3.0–15.0	57.6
	24.0–168.0	60.8			24.0–168.0	60.8
5% product	0–0.5	8.6	0–0.5	6.6	0–0.5	19.4
	1.0–2.0	26.8	1.0–2.0	23.9	1.0–2.0	22.5
	3.0–168.0	30.4	3.0–168.0	30.4	3.0–168.0	30.4
HDEAC salt						
100% product	0–0.5	30.9	0–0.5	35.1	0–0.5	38.4
	1.0–2.0	55.2	1.0–2.0	43.2	1.0–2.0	55.3
	3.0–15.0	60.8	3.0–15.0	55.7	3.0–15.0	60.8
	24.0–168.0	80.6	24.0–168.0	60.8	24.0–168.0	80.6
5% product	0–0.5	30.4	0–0.5	45.1	0–0.5	43.6
	1.0–2.0	42.5	1.0–2.0	53.9	1.0–2.0	65.5
	3.0–168.0	79.2	3.0–168.0	60.7	3.0–168.0	80.6

The experimental results given in Table 3 show that the OEAC cationic salt exhibits a strong oil recovery ability from waters with different mineralization levels, both as an aqueous 5% solution and as an undiluted product. The maximum oil recovery coefficient is 60.8 in the case of a 100% product, and the duration of reagent action is $t \sim 7$ days. When this salt is applied in the form of a 5% reagent, the maximum K value is recorded at 30.4, $t \sim 7$ days. The NEAC cationic salt also has higher oil recovery properties than all three waters. The maximum K value is 80.6, and in fresh and distilled water, respectively, it is 60.5 and 72.5. The effective action time of the reagent is more than 190 hours. In the case of the DDEAC cationic salt, when using a 100% product, $K = 60.8$, $t \sim 7$ days. When applied as a 5% reagent, the accumulation coefficient of this salt is 30.4, recorded at $t \sim 7$ days. When using the HDEAC cationic salt as an oil-collecting reagent, it accumulates the oil layer on the surface of seawater and distilled water into a single spot with a maximum oil collection coefficient of 80.6, and in fresh water, 60.8.

4. Conclusion

From the oil recovery efficiency of the cationic salts of OEAC, NEAC, DDEAC, and HDEAC themselves and their 5% aqueous solutions, it can be concluded that the oil recovery activity of OEAC, DDEAC salts, and their aqueous solutions is the same. In all cases, the oil-collecting ability of 100% products of the salts is superior to the same property of their 5% aqueous solutions. Among the investigated salts, NEAC and HDEAC salts demonstrated higher oil-collecting efficiency. The oil recovery efficiency of the HDEAC salt and its 5% aqueous solution is higher than the oil-collecting ability of OEAC and DDEAC salts and their aqueous solutions. Therefore, an increase in the length of the alkyl radical in the salt increases the oil-collecting ability. The duration of the reagent action is more than 7 days.

Author Contributions

All authors contributed to the conception, investigation, analysis, writing, and revision of the manuscript. All authors have read and approved the final version of the manuscript.

Conflict of Interest

The authors declare no conflicts of interest.

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Abbreviations

Octylethylammonium Chloride (OEAC), Nonylethylammonium Chloride (NEAC), Dodecylethylammonium Chloride (DDEAC), Hexadecylethylammonium Chloride (HDEAC), Ultraviolet–Visible Spectrometer (UV–Vis spectrometer).

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