

Colloidal-Chemical Parameters of Petroleum-collecting and Dispersing Surfactants Based on Vegetable Oil Acid Fractions and 2-(Chloromethyl) Oxirane

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ABSTRACT. Novel surfactants have been synthesized by catalytic chloropropoxylation reaction of carboxylic acid fractions of sunflower, olive, cottonseed, soya-bean, castor and corn oils with 2-(chloromethyl)oxirane. Colloidal-chemical parameters as well as petroleum-collecting and petroleum-dispersing capacities of the synthesized chloropropoxylate esters having heterochain of various lengths have been determined. Influence of carboxylic acid fractions composition and length of chloroxypropylene chain on petroleum-collecting and dispersing capacities has been revealed.

Key words: Nonionic surfactants, Chloropropoxylates, Fatty acids, Petroleum-collecting

INTRODUCTION

As is well known, crude oil when transported by tankers is rather often spilled in water basins due to accidents or some other reasons. Thick oil slicks can be removed off the water surface by common mechanical methods using special devices but after such recovering thin oil films inevitably remain on the water surface causing serious problems to ecology.^{1,2} Such films deteriorate energy- and gas exchange at the water-air interface that negatively impacts life activity of marine fauna and flora. For removal of thin oil films from the surface of water basins special surfactants are used that may be petroleum collectors or dispersants.³⁻⁵ Dispersants transform continuous oil films into tiny suspended particles (fine emulsion) which further undergo biochemical destruction under the action of sunlight, wind, microorganisms and so on.^{6,7} Petroleum-collecting surfactants enable to transform thin petroleum films into thickened spots of much smaller surface areas which are easily removal by mechanical devices.⁵

Such surfactants entering the ocean, sea, river and lake water must not be ecologically hazardous. One of the most important challenges with this regard is a use of ecologically safe and economically reasonable raw materials for obtaining highly-efficient petroleum-collecting and petroleum-dispersing chemicals.

A mixture of sorbitan monooleate, sorbitan monopalmitate, diethyleneglycol monoethyl ether and n-paraffins having from C₁₀ to C₁₃ (20:5:35:40% w/w) have been used for collecting processes,⁴ but most of these mixtures have

one or more of the following disadvantages: low effectively, complicated procedure and high cost, and ecologically unsuitable.

On the other hand, chloropropoxylate-type surfactants are very effective petroleum-collectors and dispersants.^{8,9}

Thus, in this work we focused on the following aims: *i*) to synthesise a new type chloropropoxylates; *ii*) to study the influence of the substituents nature (from C₁₄ to C₁₈) and ratio of starting materials on the colloidal-chemical parameters as well as petroleum-collecting and petroleum-dispersing capacities; *iii*) to apply the chloropropoxylates as surfactants for the petroleum-collecting from oil slicks on sea water.

MATERIALS AND METHODS

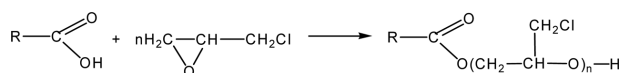
Materials

2-(chloromethyl)oxirane (CMO) is a product of "Organic Synthesis" factory (Sumgayit, Azerbaijan) with 99.97-99.98% purity. Kerosene is purified from aromatic compounds by treatment with sulphuric acid up to reaching the value of surface tension (γ) equaling 26 mN m⁻¹. Cottonseed oil (purity 99.5%) was supplied by "Masloprombaza" Ltd. (Russia), soya-bean oil (purity 97-98%) - by "Kurant" Ltd. (Russia), corn oil (purity 99.9%) and sunflower oils (purity 99.9%) - by "Baku Oil Factory" Ltd. (Azerbaijan), castor oil (purity 99.8%) - by "Azerfarm" Ltd. (Azerbaijan), olive oil (purity 99.9%) - by "Ana gida ve ihtiyac maddeleri" A.S. (Turkey).

NaOH - "pure" is the product of Merck (Germany).

Synthesis of chloropropoxylates

The studied surfactants are synthesised by catalytic interaction of 2-(chloromethyl)oxirane with carboxylic acid fractions isolated from triglycerides of vegetable oils. As a catalyst, sodium hydroxide is used. Structure and composition of the obtained chloropropoxylates have been investigated by various physical-chemical methods.¹⁰ The general scheme of the conducted reaction is as follows:



where R is hydrocarbon radical of individual carboxylic acids of acid fraction and "n" is the average chloropropoxylation (or CMO oligomerisation) degree showing an average number of chloropropoxy units in heterochain (n = 1-10).

Procedure for Studying Petroleum-collecting and Petroleum-dispersing Capacities

Investigations of petroleum-collecting and dispersing ability of chloropropoxylates of different natural fractions have been carried out on the example of Ramany (density and kinematic viscosity at 20 °C are respectively 0.86 g cm⁻³ and 0.16 cm² s⁻¹ Absheron peninsula, Azerbaijan) crude oil (thickness of the film 0.165 mm) and two types of water: distilled and of Caspian sea. In these experiments a film was formed by one mL of crude oil on the surface of 40 mL water and then 0.02 g of the tested reagents were introduced. The chloropropoxylates of the natural carboxylic acids fractions were used as both undiluted products and 5% wt. solutions.

Petroleum-collecting and dispersing ability was estimated by the coefficient of collection-K (the ratio of the initial area of petroleum film surface and the surface area of the petroleum spot formed under the action of the reagent) within the time of observation in the experiment ~τ (hour).

Surface-Tension Measurements

All the surface tension measurements were carried out using purified kerosene to make the solutions. The solutions kept at the desired temperature were measured 45 s after transfer to the thermostated measuring dishes. The actual temperature within the dishes was controlled prior to and after the measurement by means of a thermocouple. Deviations from the desired temperature were ±0.2 °C at temperatures. The surface tension as a function of concentration was measured at 20 °C using by stalagmometer.

Kerosene solutions of the studied surfactants are prepared directly before experiments. Surface tension of these kerosene solutions at the interface with water has been measured by stalagmometric method.¹¹

RESULTS AND DISCUSSION

Surface Activity and Petroleum-collecting, Petroleum-dispersing Capability

Earlier it has been established that chloropropoxylates of individual carboxylic acids have a sufficient petroleum-collecting and petroleum-dispersing capability. Chloropropoxylates of the carboxylic acids having 8 and more carbon atoms in the carbon chain exhibit more efficient petroleum-collecting properties.¹²

Comparison of petroleum-collecting and dispersing efficiencies of chloropropoxylates of saturated and unsaturated carboxylic acids containing the same number of carbon atoms showed that chloropropoxylates of the saturated carboxylic acids are more effective.¹³

It is known from literary sources¹⁴ that two or more surfactants create synergism or antagonism effects. Namely for this reason it was of great interest to study petroleum-collecting and petroleum-dispersing properties of chloropropoxylates of the acid fractions of natural oils containing fragments of unsaturated acids to various extents.

In *Table 1* there have been shown colloidal-chemical parameters of acids fractions obtained from certain vegetable oils and chloropropoxylates thereof.

Plots of the surface tension (γ) at 20 °C of kerosene solution of chloropropoxylates of carboxylic acids fractions of vegetable oils vs. the ln of their bulk phase concentration in mol dm⁻³ (lnC) in water are shown in *Fig. 1* (See, Electronic Supplementary Information, *Fig. S1-S5*). The values of critical micellization concentration (CMC) were taken as the concentrations at the point of intersection of the two linear portions of the γ-lnC plots.

Maximum interfacial excess concentrations (Γ_{max}, in mol cm⁻²) were determined on the basis of the values of Γ calculated by the equation

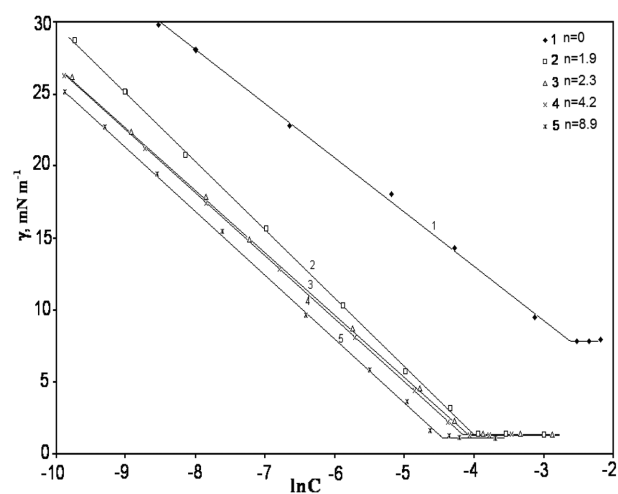
$$\Gamma = (1/RT)(-\delta\gamma/\delta\ln C)$$

where $(-\delta\gamma/\delta\ln C)_T$ is the slope of γ-lnC plot at constant absolute temperature T and R is universal gas constant (8.314 J mol⁻¹ K⁻¹).

Minimum area per molecule (A_{min}, in nm²) at the kerosene-water interface was determined using the relationship

Table 1. Colloidal-chemical parameters of carboxylic acids fractions isolated from vegetable oils and their chloropropoxylates (20 °C)

Vegetable oils	Chloropro-poxylates and values of "n"	CMC×10 ² , mol dm ⁻³	Γ _{max} ×10 ¹⁰ , mol cm ⁻²	A _{min} , Å ²	π _{CMC} , mN m ⁻¹	γ _{CMC} , mN m ⁻¹	C ₃₀ ×10 ³ , mol dm ⁻³	ΔG _{mic} , kJ mol ⁻¹	ΔG _{ad} , kJ mol ⁻¹
Sunflower oil	0	7.43	1.54	108	38.2	7.8	8.35	-21.4	-16.1
	1.9	1.83	1.95	85	44.7	1.3	0.98	-26.7	-19.5
	2.3	1.69	1.77	94	44.7	1.3	0.55	-28.1	-19.7
	4.2	1.56	1.80	92	44.7	1.3	0.47	-28.4	-19.9
	8.9	1.16	1.82	91	44.8	1.2	0.39	-28.9	-20.6
Olive oil	0	6.59	1.64	101	34.7	11.3	17.02	-19.7	-16.4
	0.9	2.28	1.86	89	42.9	3.1	1.41	-25.8	-19.0
	1.9	1.05	1.89	88	42.8	3.2	0.74	-27.3	-20.9
	2.6	0.98	1.91	87	43.1	2.9	0.72	-27.4	-21.0
	3.9	0.91	2.00	83	43.1	2.9	0.70	-27.5	-21.2
	7.8	0.88	2.18	76	43.5	2.5	0.68	-27.5	-21.3
Cottonseed oil	0	14.81	2.51	66	38.8	7.2	35.3	-17.9	-14.4
	1.5	1.94	3.10	54	39.6	6.4	5.46	-22.5	-19.4
	1.6	1.87	3.58	46	41.3	4.7	5.16	-22.6	-19.5
	4.0	1.24	4.22	39	43.9	2.1	3.21	-23.8	-20.5
	9.0	0.45	4.39	38	43.9	2.1	1.23	-26.1	-22.9
Soya-bean oil	0	5.39	1.83	91	44.8	1.2	1.69	-25.3	-16.9
	0.8	2.47	2.01	83	42.6	3.4	1.65	-25.4	-18.8
	2.7	1.83	2.03	82	43.0	3.0	1.62	-25.4	-19.5
	4.5	1.66	2.05	81	42.6	3.4	1.59	-25.5	-19.8
	9.1	1.50	2.13	78	41.9	4.1	1.56	-25.5	-20.0
Castor oil	0	7.43	1.64	101	37.5	8.5	0.59	-27.9	-16.1
	0.9	5.50	1.65	100	41.0	5.0	0.52	-28.2	-16.8
	1.8	4.78	1.31	127	43.5	2.5	0.50	-28.3	-17.2
	2.4	4.42	1.32	126	42.9	3.1	0.45	-28.6	-17.4
	4.2	2.90	1.49	111	42.9	3.1	0.30	-29.5	-18.4
	8.4	3.08	1.51	110	42.9	3.1	0.29	-29.6	-18.3
Corn oil	0	5.84	2.63	63	42.9	3.1	7.58	-21.7	-16.7
	0.8	3.47	1.71	97	43.5	2.5	1.36	-25.9	-18.0
	1.0	2.15	1.58	105	43.1	2.9	1.20	-26.2	-19.1
	2.2	2.06	1.91	87	43.8	2.2	1.13	-26.3	-19.2
	5.0	1.38	2.06	81	44.0	2.0	1.05	-26.5	-20.2
	7.1	1.36	2.11	79	44.0	2.0	0.95	-26.7	-20.3

**Fig. 1.** Surface tension vs. ln of the concentration of chloropropoxylates of carboxylic acids fraction of sunflower oil in kerosene solution.

$$A_{\min} = 10^{14}/N\Gamma_{\max}$$

where N is Avogadro's number.

One of the most important parameters of surfactants is surface pressure (π_{CMC}) calculated as

$$\pi_{\text{CMC}} = \gamma_0 - \gamma_{\text{CMC}}$$

where γ_0 is the surface tension of water at the interface with kerosene and γ_{CMC} is the interfacial surface tension of the surfactants solution at the CMC.

As is seen from *Table 1*, for all acid fractions with an increase of the chloropropoxylation degree (n) the CMC values decrease. The CMC values for vegetable oil-origin acid fractions themselves (except cottonseed oil-based acid fraction) are rather close [(5.39-7.43)×10⁻² mol dm⁻³]. A comparably higher value of CMC for cottonseed oil

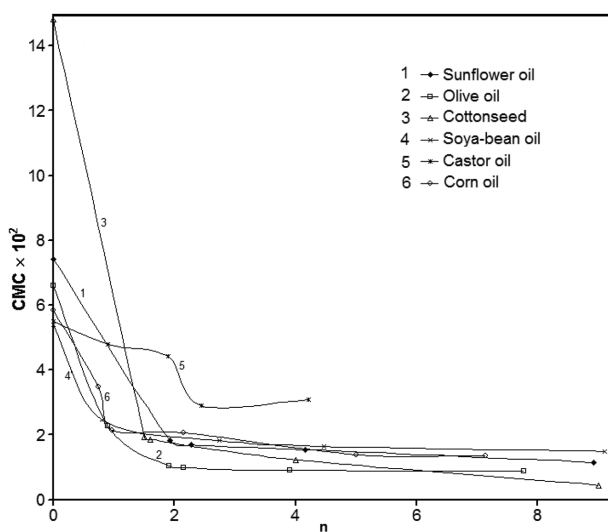


Fig. 2. CMC vs. "n" of chloropropoxylates of carboxylic acids fractions of vegetable oils.

acid fraction may be explained by a larger amount of saturated carboxylic acids therein.

In Fig. 2 a dependence of CMC values from chloropropoxylation degree is depicted. It may be noticed from this figure that the character of the CMC values change depending on chloropropoxylation degree is similar for the chloropropoxylates of sunflower, corn and soya-bean oils. The CMC values at $n \approx 2$ for these three series of chloropropoxylates are very close. Further rise of chloropropoxylation degree slightly impacts the CMC values.

It is interesting that for the chloropropoxylates of olive oil-origin acid fraction the values of CMC after $n=1$ are lower than for the above-indicated three series chloropropoxylates. This fact may be related to the very high contents of oleic acid in olive oil-based acid fraction (up to 83%). At the meantime, in the case of chloropropoxylates of castor oil-origin acid fraction the character of the CMC values change in dependence from "n" is different, the CMC variation being smaller. This circumstance may be interrelated with the dominance (up to 85%) of such an unsaturated acid as ricinoleic acid (C_{18} , 1 double bond) which has a hydroxyl group at the 12th carbon atom.

As is seen from Table 1, with an increase of chloropropoxylation degree Γ_{max} in most cases rises whereas A_{min} mainly decreases. The values of γ_{CMC} are relatively lower for chloropropoxylates of corn oil acid fraction and still lower in the case of chloropropoxylates of sunflower oil-origin carboxylic acids fraction.

From Table 1 it may also be noticed that the value of π is higher for those chloropropoxylates which are obtained

on the basis of the acid fractions richer in unsaturated carboxylic acids (for example, 44.7 mN m^{-1} for sunflower oil-origin and 41.3 mN m^{-1} in the case of cottonseed oil-based acids chloropropoxylates).

As is known,¹⁵ spreading pressure for crude oils is in the interval $30\text{--}35 \text{ mN m}^{-1}$. Therefore, the values of p should exceed 35 mN m^{-1} for exhibition of high petroleum-collecting and dispersing capability by surfactants.

There have been carried out researches on petroleum-collecting and dispersing properties of the synthesized chloropropoxylates as well as respective carboxylic acids fractions themselves. These products have been applied in undiluted form and as 5% wt. solutions. The media for these tests were distilled and sea (the Caspian) water. From the table it is seen that as an undiluted reagent the sunflower oil-origin acid fraction and its chloropropoxylates have a high petroleum-collecting capability in distilled water (K_{max} equals 25.1 for acid fraction and 21.5 for the chloropropoxylate $n=1.9$) whereas in the sea water dispersing of the petroleum film takes place. 5% wt. heptane solution of the chloropropoxylate collects petroleum film in the distilled water with $K_{max}=20.3$ ($\tau=30$ days), in the sea water mostly petroleum dispersing taking place.

In the case of the corn oil acid fraction chloropropoxylates the ester of $n=0.8$ is the most preferable. As undiluted reagent in the distilled water K_{max} is 15.2 and t is 28 days. In the sea water K_{max} is equal to 15.2. When applying 5% heptane solution of the mentioned chloropropoxylate in the medium of saltless water K_{max} equals 15.1, the duration of the collecting action being 6.25 days. In the sea water the same solution also demonstrates collecting ability ($K_{max}=11.5$ and $\tau=5$ days).

Among chloropropoxylate derivatives of soya-bean oil acid fraction the ester of $n=0.8$ is the most noteworthy, having in undiluted form very long duration of action in the sea water (~ 54 days) and $K_{max}=16.0$.

Chloropropoxylates having $n=2.6$ and 3.9 are distinctive among olive oil acid fraction derivatives with CMO. The first ester collects petroleum in all cases, K_{max} reaching 20.3 in the sea water (for unthinned reagent) whereas the second one is an efficient dispersant as a diluted chemical (τ exceeds 11 days).

The most efficient chloropropoxylate of the cottonseed acid fraction is the ester of $n=1.6$ which is mainly a collector. K_{max} of its heptane solution is 14.6 in the sea water and 12.2 in the distilled water, τ equaling respectively 1 and 16 days.

Among castor oil acid fraction chloropropoxylates the esters of $n=4.2$ and 1.8 are more salient which are col-

lectors in all cases, the first of them as 5% heptane solution showing in the sea water medium $K_{\max}=15.2$.

From the comparative analysis of the obtained data on petroleum-collecting and dispersing capacities of chloropropoxylates of the considered vegetable oils acid fractions it ensues that the esters having 1-4 CMO-based units in the heterochain are more efficient, cottonseed and olive oils-based ones being more preferable. It is interesting that in these acid fractions carboxylic acids with several double bounds are at lesser amounts. Besides, from *Table 1* it may be noticed that CMC of these two acid fractions chloropropoxylates (n up to 4) are smaller than for other vegetable oil-based chloropropoxylates. Therefore, CMC may be referred as one of the most important factors impacting petroleum-collecting capacity. Taking this moment into account, determination of thermodynamic parameters of these esters would be very useful.

It may also be concluded that castor oil acid fraction chloropropoxylates are less effective than the similar derivatives of the other vegetable oil acid fractions. That is presumably due to additional hydroxyl group in the alkyl fragment of ricinoleic acid constituting a dominant part of this acid fraction.

Standard Free Energies of Micellization and Adsorption at the Kerosene Solution/Water Interface

Standard free energies of micellization ΔG_{mic} for the synthesized chloropropoxylates have been calculated by equation¹⁶

$$\Delta G_{\text{mic}} = RT \ln(\text{CMC}/\omega),$$

where $\omega = (\text{mol of H}_2\text{O})/(\text{dm}^3 \text{ of H}_2\text{O})$.

Standard free energies of adsorption ΔG_{ad} for these chloropropoxylates have been determined using the relationship¹⁶

$$\Delta G_{\text{ad}} = RT \ln(C_{30}/\omega) - (30 \text{ mN m}^{-1})(A_{\text{min}})$$

where C_{30} is the concentration of surfactant when the reduction of surface tension equals 30 mN/m.

The found values of ΔG_{mic} and ΔG_{ad} are listed in the table. From these data it may be concluded that micellization process has a spontaneous character ($\Delta G_{\text{mic}} < 0$). As chloropropoxylation degree rises, the values of ΔG_{mic} decrease. This means that with a rise of "n" formation of micelles becomes easier. This is explicable because, as is known, with an increase of chloropropoxylation degree hydrophylic-lipophylic balance of the surfactant decreases and the solubility in hydrocarbons improves. As a result, CMC diminishes.

All values found for ΔG_{ad} are negative. Moreover, they

are more negative than those of ΔG_{mic} , *i.e.* adsorption of the mentioned chloropropoxylates at the kerosene-water interface is associated with a larger decrease in free energy of the system.

CONCLUSIONS

Chloropropoxylates synthesized on the basis of carboxylic acids fractions of vegetable oils have a high surface activity. With elongation of the heterochain of the chloropropoxylates their CMC and A_{min} values generally decrease, whereas Γ_{max} mainly increases and π changes slightly.

Chloropropoxylates of olive and cottonseed oils acid fractions of "n" up to 4 possess a high petroleum-collecting capacity in both distilled and sea waters.

With an increase of the amount of unsaturated acids in the acid fraction surface activity rises. Presence of hydroxyl-group in the alkyl fragment of the carboxylic acid in the fraction negatively impacts petroleum-collecting properties.

Micellization of the chloropropoxylates is spontaneous and becomes easier with a rise of the oligomeric heterochain length but adsorption of these surfactants at the kerosene/water interface has a larger spontaneity.

A comparison between all the characteristics of the proposed surfactants and those of the previously known petroleum-collecting reagents⁴ indicates that the current surfactants show better characteristics than several reported compounds, being superior in terms of the response time and high effectiveness.

A procedure for the petroleum-collecting in the sea water was also developed, and the developed method is reproducible, rapid, cheap and simple. For these reasons, it can be used in a diversity of objects - environmental and industrial samples.

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