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SYNTHESIS AND STUDY OF SURFACTANTS BASED ON TETRADECANOIC ACID, 1,2-DIAMINOETHANE AND N –(2-AMINOETHYL)-1,2-ETHANEDIAMINE

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ABSTRACT

In this study, we synthesized and characterized the surface-active properties of products obtained from tetradeconoic acid, 1,2-diaminoethane and N –(2-aminoethyl)-1,2-ethanediamine. The composition and structure of the synthesized compounds were confirmed by IR spectroscopy, and their physicochemical properties were determined. Aqueous solutions of the synthesized products were prepared over a wide range of concentrations, and their surface tension was measured using a tensiometer at the water-air interface. Based on the obtained data, isotherms were constructed for calculating key colloidal chemical parameters: critical micelle concentration, surface tension at CMC, maximum adsorption, (G_{max}), minimum surface area of the molecule at the air-water interface (A_{min}), surface pressure (π_{CMC}). Electrical conductivity properties were investigated using the conductometric method. Plots of specific electrical conductivity as a function of concentration were constructed, and the corresponding thermodynamic parameters, including the Gibbs free energy of micellization (ΔG_{mic}) and adsorption (ΔG_{ads}), were calculated. The oil-collecting capacity of the synthesized surfactant was studied under laboratory conditions against thin (<1 cm) films of Balakhany oil on the surface of waters with varying mineralization (seawater, freshwater, and distilled water). The effectiveness of the reagents was assessed both in their original form and in 5% aqueous solutions.

1. Introduction

Surfactants are amphiphilic molecules widely used in chemistry, biology, and pharmaceuticals [1]. They consist of a polar head group, which can be anionic, cationic, nonionic, or zwitterionic, and a hydrophobic tail, which can have varying lengths and structures. It is well known that surfactants form micelles at concentrations above the critical micelle concentration (CMC). Research into micellization processes has been conducted for many years, and thousands of papers on this topic are published annually [2-6]. The micellar behavior of anionic and cationic surfactants is influenced by the presence of nonelectrolytes in solution [7-9]. Much attention has also been paid to the effect of non-aqueous polar solvents on the micellization of cationic surfactants [10-12]. Previously, Evans et al. [13] suggested that solvent hydrogen bonds are necessary for micelle formation. However, later studies showed that the structure of water and its hydrogen bonds are not always necessary for surfactant self-association [14-17].

2. Experimental part

Spectral analysis methods were employed to characterize the synthesized products. Infrared spectra were recorded using an ALPHA IR Fourier spectrometer (BRUKER, Germany) within the wavenumber range of 600–4000 cm^{-1}. UV–Vis spectra were obtained on a JENWAY UV/Vis 6850 dual-beam spectrophotometer operating in the 100–400 nm range with an optical resolution of 0.1 nm.

Surface tension measurements of aqueous surfactant solutions were conducted at 25 °C using a KSV Sigma 702 tensiometer (Attension Biolin Scientific, Finland) equipped with a Du Noy platinum ring. Specific electrical conductivity was measured with an ANION-402 conductometer (Russia).

Tetradecanoic acid (Aldrich, 98%), 1,2-diaminoethane (97%), N-(2-aminoethyl)-1,2-ethanediamine (97%), were used as starting materials. Thissalts were synthesized from tetradecanoic acid and each of the amine components. The obtained products exhibited a yellowish appearance. The salt synthesized from tetradecanoic acid and N-(2-aminoethyl)-1,2-ethanediamine in a 1:1 molar ratio formed at 70–85 °C over 10–11 h, producing a brownish solid, the salt synthesized from tetradecanoic acid and 1,2-diaminoethane in a 1:1 molar ratio formed at 70–80 °C over 10–11 h, producing a brownish solid. Surface tension values for distilled water (71.5 mN/m at 25 °C) aligned with standard reference values and were used to verify the measurement accuracy. Critical micelle concentration (CMC) values for the surfactants were determined from surface tension isotherms.

Electrical conductivity measurements were calibrated to 25 °C and showed a deviation of less than 1% from true values. Distilled water exhibited a conductivity of 2–2.8 μS/cm. After dissolving 0.025 g of each synthesized salt in 25 mL of distilled water, the conductivity of the solutions was measured, and CMC values were derived from conductivity–concentration plots.

Petrocollecting and petrodispersing properties of the synthesized surfactants were evaluated using established procedures. 40 mL of water with varying mineralization was placed in a Petri dish, followed by the addition of 1 mL of Balakhani crude oil forming a film of approximately 0.17 mm in thickness. A surfactant or its 5 wt.% solution was applied to the periphery of the oil film. The initial oil-film area and subsequent areas of dispersed oil patches were periodically measured. The surface-cleaning coefficient (K_d, %) was calculated as the ratio of the initial to the final oil-film area.

3. Results and discussion

The reaction schemes are presented below:

$C_{13}H_{27}COOH + H_2N\text{-}(CH_2)_2\text{-}NH_2 \rightarrow C_{13}H_{27}COOH\cdots NH_2\text{-}(CH_2)_2\text{-}NH_2$

Salt of tetradecanoic acid with 1,2 diaminoethane (1)

$C_{13}H_{27}COOH + H_2N\text{-}(CH_2)_2\text{-}NH_2\text{-}(CH_2)_2\text{-}NH_2 \rightarrow C_{13}H_{27}COOH\cdots NH_2\text{-}(CH_2)_2\text{-}NH_2\text{-}(CH_2)_2\text{-}NH_2$

Salt of tetradecanoic acid with N –(2-aminoethyl)-1,2-ethanediamine (2)

The structures of the synthesized salts were confirmed using Fourier-transform infrared spectroscopy (FTIR, BRUKER, Germany) in the wavenumber range of 600–4000 cm^{-1}, as well as UV–Vis spectroscopy. The corresponding spectra are presented below.

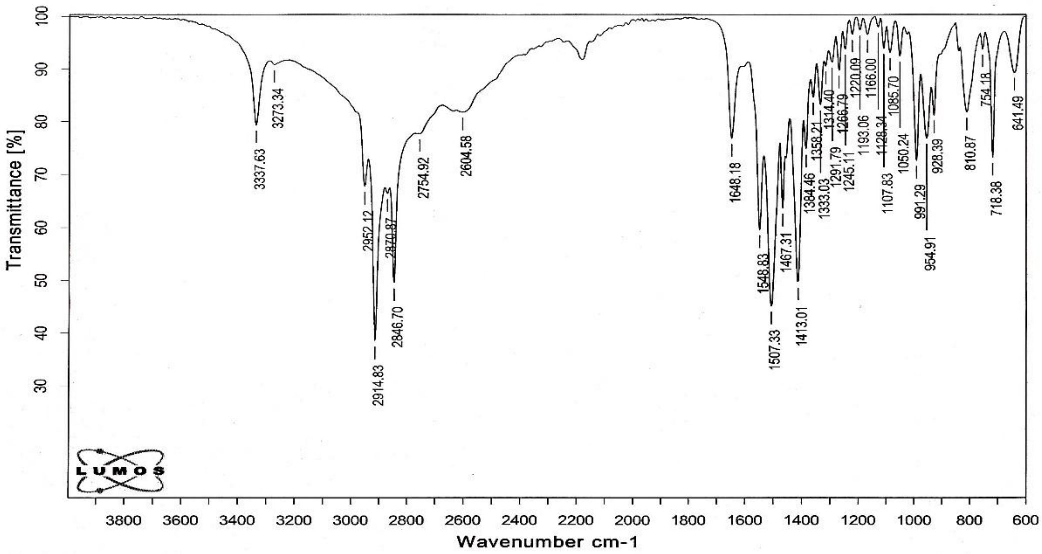

Fig. 1 IR spectrum of tetradecanoic acid salt with 1,2 diaminoethane

The IR spectrum of the sample (Fig. 1) contains the following absorption bands:

deformation (1467 cm^{-1}) and stretching (2846, 2870, 2914, 2957 cm^{-1}) vibrations of the C–H bond of the CH_3 and CH_2 groups; stretching (1050, 1085, 1107 cm^{-1}) vibrations of the C–O bond; stretching (1413, 1507 cm^{-1}) vibrations of the COO^- group; deformation (1548 cm^{-1}) and stretching (3273, 3337 cm^{-1}) vibrations of the H–N bond; ammonium band (2604, 2754 cm^{-1}).

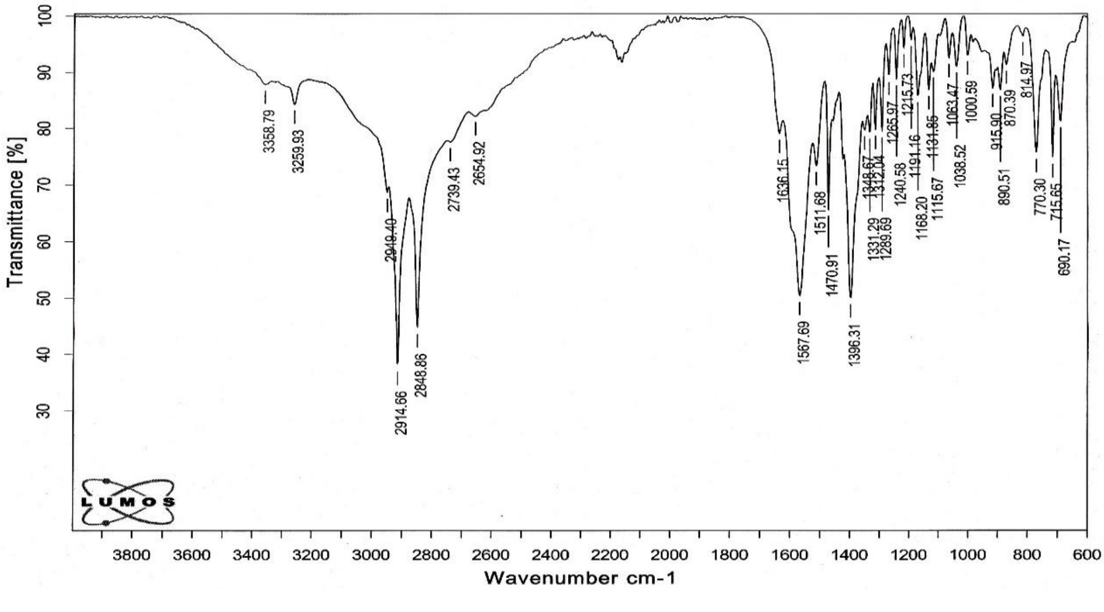

Fig.2 IR spectrum of tetradecanoic acid salt with N-(2-aminoethyl)-1,2-ethanediamine

The IR spectrum (Fig. 2) of a sample of the salt of tetradecanoic acid with N-(2 aminoethyl)-1,2-ethanediamine has the following absorption bands: deformation (1470 cm^{-1}) and stretching (2848, 2914, 2949 cm^{-1}) vibrations of the C–H bond of the CH_3 and CH_2 groups; stretching (1000, 1038, 1068 cm^{-1}) vibrations of the C–O bond; stretching (1396, 1567 cm^{-1}) vibrations of the COO^{-} group; deformation (1511 cm^{-1}) and stretching (3259, 3358 cm^{-1}) vibrations of the H–N bond; ammonium band (2654, 2739 cm^{-1}).

In Fig. 3, the absorption band n→σ*, belonging to the nitrogen atom, appears at 220 nm of the spectrum, in Fig. 4 - 230 nm.

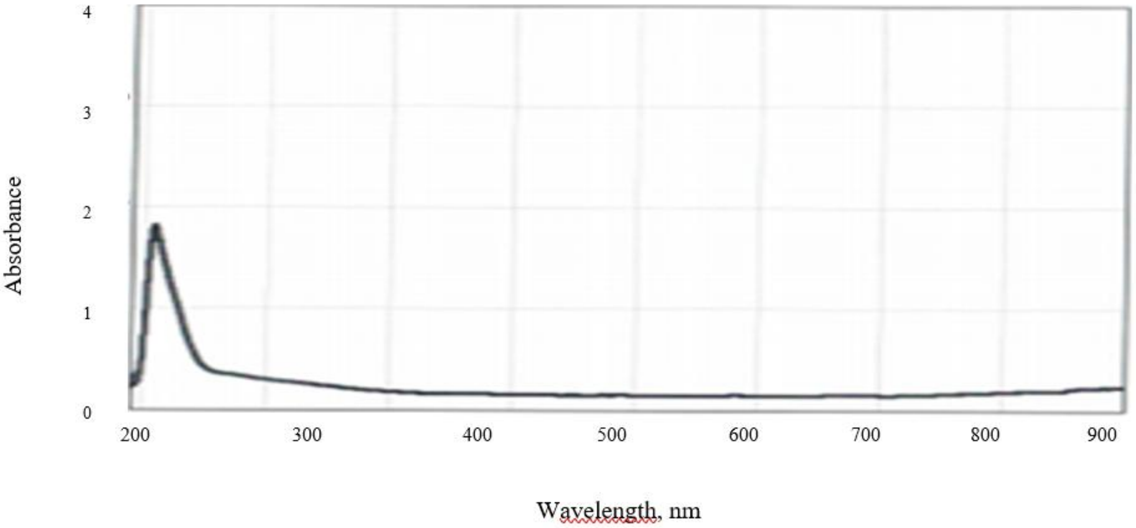

Fig 3 UV absorption spectrum of tetradecanoic acid salt with 1,2 diaminoethane

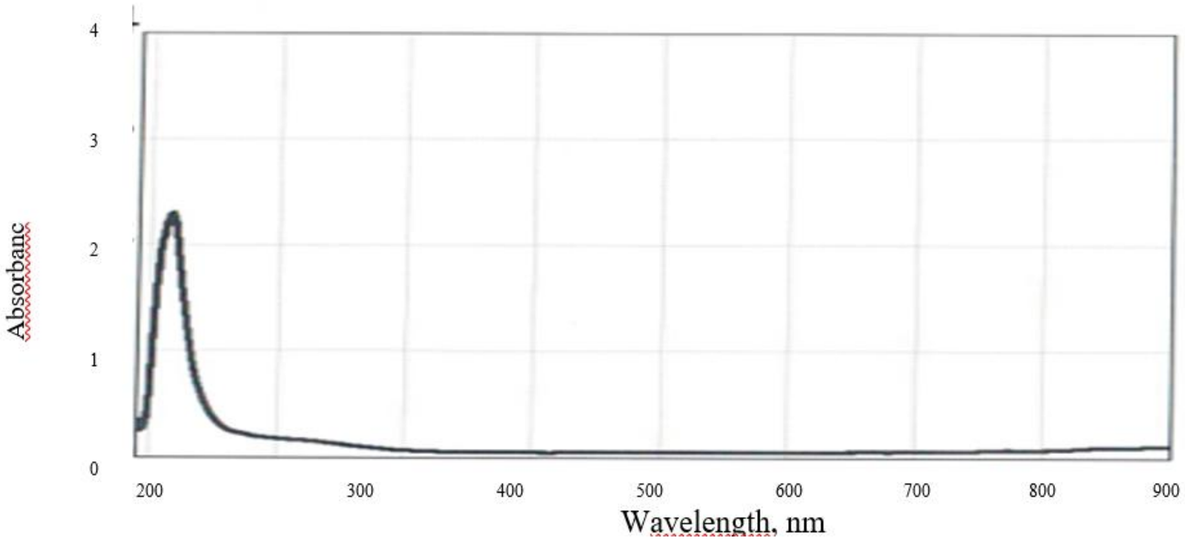

Fig. 4 UV absorption spectrum of tetradecanoic acid salt with N –(2-aminoethyl)-1,2- ethanediamine

Surface tension measurements of aqueous solutions of the synthesized surfactants were performed using a KSV Sigma 702 tensiometer (Attension Biolin Scientific, Finland) equipped with a Du Noy platinum ring at the air–water interface. This instrument was employed to evaluate the surface-active properties of this surfactants. The surface tension of the formed salts depending on various concentrations was determined from the graph in Fig. 5, the CMC (critical concentration of micelle formation) was determined.

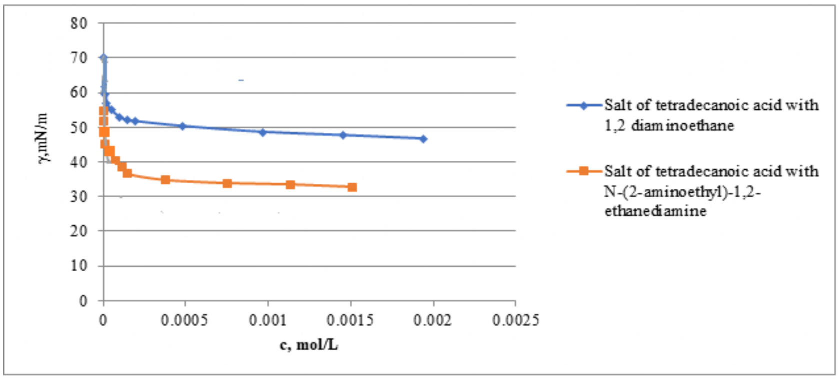

Fig.5 Surface tension diagram of surfactants at the water-air interface depending on the concentration

Table 1 summarizes the surface activity parameters of the synthesized surfactants, calculated from the data presented in Fig. 5. The critical micelle concentration (CMC) of the obtained salts was determined, along with the surface pressure at the CMC (π_{CMC}), $C_{(20)}$ (the concentration required to reduce the surface tension by 20 mN/m), adsorption efficiency

($pC_{20} = -\log C_{20}$), and the CMC/C_{20} ratio, which reflects the interfacial activity of the surface-active substances [18,19]. The maximum surface adsorption (Γ_{max}) and the minimum area per surfactant molecule at the water–air interface (A_{min}) were calculated using the equation given below.

$$\Gamma_{max} = \frac{1}{n * R * T} * \lim_{c \to CMC} \frac{d\gamma}{d\ln c} \qquad (3)$$

where n is the number of dissociated ions, equal to 2 and 3, respectively, for the salt of tetradecanoic acid with 1,2 diaminoethane and N -(2-aminoethyl)-1,2-ethanediamine, R is the universal gas constant (8.314 J /mol*K), T—absolute temperature;

$$A_{min} = \frac{1}{N_A * \Gamma_{max}} \qquad (4)$$

Referring to Table 1, it can be said that the product of tetradecanoic acid with N –(2-aminoethyl)-1,2-ethanediamine has a minimum maximum adsorption value (Γ_{max}), it has a large surface area per surfactant molecule

Table 1. Results of surface activity of synthesized surfactants

Surfactants	$CMC*10^4$ (mol/l)	γ_{cmc} (mN/m)	π_{cmc} (mN/m)	$C_{20}*10^4$ mol/l)	pC_{20}	CMC/C_{20}	$\Gamma_{max}*10^{10}$ (mol/sm^2)	$A_{min}*10^2$ (mm^2)
Salt of tetradecanoic acid with 1,2 diaminoethane	1.46	28.12	19	0.0003	3.46	0.42	0.73	227.48
Salt of tetradecanoic acid with N -(2-aminoethyl)-1,2-ethanediamine	1.4	26.58	34.98	0.075	5.12	0.54	0.67	248.23

As shown in Table 1, the salt of tetradecanoic acid with N -(2-aminoethyl)-1,2-ethanediamine exhibits the lower critical micelle concentration (CMC) and the highest surface pressure (26 mN/m). In contrast, the salt formed with 1,2 diaminoethane shows low value maximum adsorption value (Γ_{max}), indicating that each surfactant molecule occupies a larger interfacial surface area.

Figure 6 presents the electrical conductivity measurements of concentrated solutions of the synthesized salts, along with the corresponding plots of conductivity as a function of concentration. Based on these plots, several thermodynamic parameters related to electrical conductivity were determined; the calculated values are summarized in Table 2.

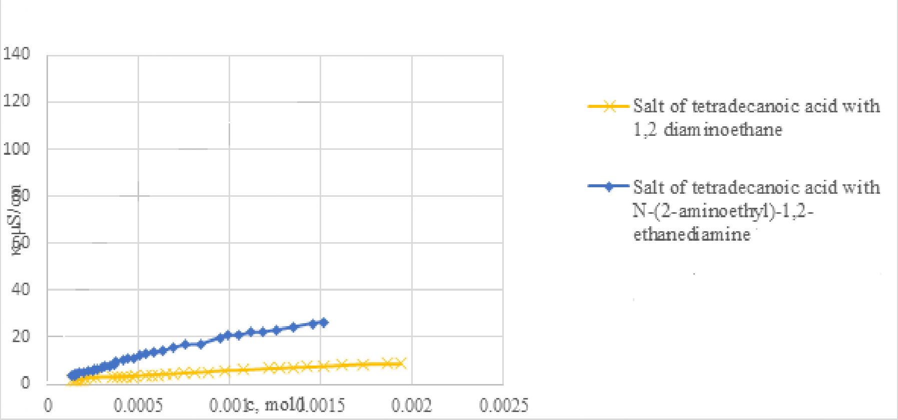

Fig. 6 Specific electrical conductivity of synthesized surfactants

The slopes of the linear regions before (S_1) and after (S_2) the critical micelle concentration (CMC) were determined. In addition, key thermodynamic parameters, including the Gibbs free energy of micelle formation (ΔG_{mic}) and the Gibbs free energy of adsorption (ΔG_{ads}), were calculated using the following equations

$$\begin{gathered}\Delta G_{mic} = (2-\alpha) * R * T * \ln(CMC) \\ \Delta G_{ads} = \Delta G_{mic} - 0.6023 * \pi_{CMC} * A_{min},\end{gathered} \qquad (5)$$

where A_{min} represents the surface area of one surfactant molecule at the water-air interface at CMC [20].

Table 2. Parameters of the specific conductivity of the synthesized surfactants

Surfactans	α	β	Δ G_{mic} kJ/mol	Δ G_{ads}, kJ/mol
Salt of tetradecanoic acid with 1,2 diaminoethane	0.84	0.13	-23.79	-26.6
Salt of tetradecanoic acid with N -(2-aminoethyl)-1,2-ethanediamine	0.45	0.54	-34.17	-39.49

As shown in Table 2, both the Gibbs free energy of micelle formation (ΔG_{mic}) and the Gibbs free energy of adsorption (ΔG_{ads}) are negative, indicating that these processes are thermodynamically spontaneous. Notably, for all three salts, ΔG_{ads} exhibits more negative values than ΔG_{mic}, suggesting a stronger thermodynamic preference for adsorption over micellization. This behavior is characteristic of surface-active substances, which tend to adsorb at interfaces prior to forming micelles [21,22].

In laboratory conditions, the petroleum-collecting ability of the synthesized surfactants was investigated, addressing the environmentally significant challenge of removing thin oil films from water surfaces. The experiments were conducted using a 0.17 mm Balakhan oil film in aqueous media with different degrees of mineralization, including distilled, fresh, and seawater. Salt of tetradecanoic acid with 1,2 diaminoethane, when applied in its undiluted form, exhibited petroleum-collecting activity in seawater for up to 6 days, with a collection coefficient of 13.51. The same surfactant, used as a 5 wt.% aqueous solution, also demonstrated oil-collecting behavior, achieving a collection coefficient of 12.16. Salt of tetradecanoic acid with N-(2-aminoethyl)-1,2-ethanediamine showed superior petroleum-collecting performance, promoting more efficient oil film aggregation. In seawater, the maximum collection coefficient reached 20.26, and the retention time of the collected oil exceeded 6 days. These findings demonstrate the potential of the synthesized surfactants for mitigating oil contamination on water surfaces and highlight their prospective.

4. Conclusion

Tensiometric and conductometric methods investigations were employed to evaluate the properties of the surface-active substances in synthesized surfactants, and their key colloidal–chemical parameters were determined. Comparative analysis revealed the salt of tetradecanoic acid with N -(2-aminoethyl)-1,2-ethanediamine exhibits lower values of the critical micelle concentration, the minimum cross-sectional area of the polar group, surface pressure, and the efficiency parameter, as well as reduced surface tension at the CMC and lower maximum adsorption values. Laboratory experiments confirmed the effectiveness of the synthesized reagents in collecting thin oil films from water surfaces across a wide range of mineralization levels. Among the tested compounds, the salt of tetradecanoic acid with N -(2-aminoethyl)-1,2-ethanediamine demonstrated superior performance, highlighting its promise for the removal of environmentally hazardous oil films from natural water bodies. The obtained results support the feasibility of employing surfactants of this type in environmental protection

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