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INVESTIGATION OF THE COLLOIDAL PROPERTIES OF 1-METHYLENE-(3-ALLYL-2-HYDROXY-5(OCTYL- 2)PHENYL)PIPERIDINIUMCHLORIDE

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The article presents the results of studies for revealing the basic laws of the surface tension dependence processes of aqueous solutions of 1-methylene-(3-allyl-2-hydroxy-5(octyl-2)phenyl)piperidinium chloride on aqueous solution–air and an aqueous solution–kerosene boundary depending on structure and concentration. Adsorption conditions were determined, critical micelle formation constants were calculated, and conclusions regarding the possibility of their use as a surfactant were drawn.

Keywords: surfactant, surface tension, aqueous solution–air, aqueous solution–kerosene, adsorption.

doi

Introduction

It is known that surfactants are widely used in various fields of techn: as detergents, to protect metals from corrosion, to increase oil recovery, in the textile, varnish and food industries, in the manufacture of cosmetics, in the processes of emulsion polymerization and solubilization etc. [1–3]. The broad application spectrum of surfactants, including ionic ones, is mainly related to the high adsorption ability of surfactant molecules at various phase boundaries, as well as their ability to micelle formation in solutions. The ability to micelle formation is possessed not by all surfactants, but only those that have the optimal hydrophobic-lipophilic balance of the surfactant molecule [4].

A comprehensive expansion of their application fields poses a task for researchers to search for new surfactants with specific properties.

This article presents the results of our research on the adsorption capacity investigation of the new surfactant synthesized by us 1-methylene-(3-allyl-2-hydroxy-5(octyl-2)phenyl)piperidiniumchloride (comp. I) at the interface: aqueous solution–air and an aqueous solution–kerosene as well as revealing its ability to micelle formation in aqueous solutions.

Compound I

Experimental part

The above-mentioned compound (with a yield of 90%) was synthesized by triple condensation of 2-allyl-4-(octyl-2)phenol with piperidine and formaldehyde (under Mannich reaction conditions at an equimolar ratio, temperature 70–75°C and time 4 hours), followed by interaction with hydrogen chloride at room temperature.

The structure of the synthesized compound was confirmed by NMR spectroscopy.

The solutions of the obtained surfactant were prepared on bidistilled water, the volumes of which were previously determined at

$25 \pm 0.020^{\circ}\text{C}$ with an accuracy of ± 0.005 ml. The surface tension of the obtained solutions was determined at 298.15 K by the hanging drop method on a DSA 30 KRÜSS SCIENTIFIC instrument (Germany) with an accuracy of ± 0.01 . The electrical conductivity (κ , $\text{cm}\cdot\text{Ohm}^{-1}$) of the solutions was also determined.

Results and discussion

Figure 1 shows the dependence of the surface tension of solutions on concentration compound I at 298.15 K (curve 1). As is seen, isotherm of the surface tension of the solutions assures that compound I has significant surface activity (g).

Fig. 1. The isotherms of the surface tension of aqueous solutions (curve 1) of compound I and its adsorption at the aqueous solution–air interface (curve 2) at 298.15 K.

As it is known, the dependence of the surface tension of solutions on the surfactant concentration is given by the Shishkovsky equation [5]

$$\sigma = \sigma_0 [1 - B \ln(C/A + 1)], \quad (1)$$

where A and B are equation constants.

In the region of relatively high concentrations of surfactants with high surface activity, assuming that $A \ll C$, equation (1) can be represented as [6]

$$\sigma = a - b \ln C \quad (2)$$

where $a = \sigma_0 + b \ln A$, $b = B \sigma_0$.

Figure 2 shows the dependence $\sigma = f(\ln C)$. From the linear section of this dependence, the constants of the Shishkovsky equation $A = 6.237 \cdot 10^{-5}$, $b = 7.346$ ($B = 0.102$), and, therefore, the Langmuir equation constants – $K_{\text{ads}} = 16033$, $G_{\text{max}} = 2.96 \cdot 10^{-6}$ mol/m² were found.

Fig. 2. Dependence $\sigma = f(\ln C)$ for aqueous solutions of the compound I.

Using the Langmuir equation (K_{ads} , G_{max}), the adsorption isotherm of the studied surfactant at the solution–air interface was calculated (curve 2, Figure 1). Knowing the adsorption equilibrium constant (K_{ads}), using the relation (3)

$$\Delta G_{\text{адс}} = -RT \ln K_{\text{адс}}, \quad (3)$$

it is possible to calculate the free Gibbs energy of the surfactant adsorption process at the aqueous solution–air interface, $\Delta G_0 = -24.0$ kJ/mol.

The value of maximum adsorption (G_{max}) allows us to determine the area occupied by the surfactant molecule in a dense monomolecular adsorption layer (ω_{min}) at the aqueous solution–air interface

$$\omega_{\text{min}} = 1 / G_{\text{max}} \cdot N_A, \quad (4)$$

as well as the thickness of the monomolecular layer (h)

$$h = G_{\text{max}} M / \rho, \quad (5)$$

where N_A – Avogadro number, M and ρ – the molar mass and density of the adsorbed substance (the density of surfactant cations in a dense monomolecular layer is taken to be equal to the density of compound I).

As it can be seen from Figure 2, an almost horizontal section is observed on the $\sigma = f(\ln C)$ dependence curve at a value of $\sigma \approx 30$ mNm, which should be associated with micelle formation [7]. According to the curve $\sigma = f(\ln C)$, the critical concentration of micelle formation (CCMF) is 0.018 mol/l. This CCMF value is also confirmed by the results of measuring of the electrical conductivity of the compound aqueous solutions.

Fig. 3. Dependence $\ln \kappa = f(\ln C)$ for aqueous solutions of compound I at 298.15 K.

Figure 3 shows the dependence of the electrical conductivity logarithm of surfactant solutions (κ) on $\ln C$. The observed decrease in the slope of the curve $\ln \kappa = f(\ln C)$ at a concentration of 0.018 mol/l is associated with the micelle formation, which leads to a decrease in the electrical conductivity [8]. As for the first kink in the curve $\ln \kappa = f(\ln C)$, it must in all probability be connected with the process of pairing of salt ions preceding micelle formation. Schematically, this paired associate formed due to the hydrophobic effect can be represented as

The formation of associates with a double charge should be accompanied by an increase in the conductivity of the solution [9] (Hoffmeister series). Thus, taking the critical micelle concentration equal to 0.018 mol/l (18 mol/m), according to the ratio

$$\Delta G_{\text{mic}}^0 = RT \ln \text{CCMF} \quad (6)$$

it is possible to calculate the free micelle formation enthalpy, $\Delta G^0 = -9.96$ kJ/mol.

It is known that in the case of colloidal surfactants capable to micelle formation, surface activity (g) can be determined through the critical concentration of micelle formation:

$$g = \sigma_0 - \sigma_{\text{CCMF}} / \text{CCMF} \quad (7)$$

Taking $\sigma_{\text{CCMF}} = 30 \cdot 10^{-3}$ N/m and $\sigma_0^{25} = 71.95$ N/m, we obtain that the surface activity of the surfactant synthesized by us is $g = 2.32 \cdot 10^{-3}$ N·m²/mol. It is known that if the surface activity of a surfactant molecule is great, their adsorption capacity will also be higher. According to the [10], the adsorption capacity of a surfactant

is estimated by the negative logarithm of the surfactant concentration, at which the surface tension of the solution decreases by 20 mN/m ($\text{PC}_{20} = -\lg C$ ($-\Delta\sigma = 20$)). The value of this concentration is $C = 0.0031$ mol, and $\text{Pc}_{20} = 5.78$.

The dependence of surface tension at the aqueous solution-kerosene interface on the concentration of surfactants in the aqueous medium was also studied. As mentioned earlier, regularities are observed during the adsorption of water-soluble surfactants at the interface between an aqueous solution and a liquid hydrocarbon that are similar for the solution-air interface [9]. It should be noted that the adsorption process of surfactant molecules at the aqueous solution-kerosene interface should be complicated by the process of distribution of surfactant molecules between the aqueous and kerosene phases, which to one degree or another should take place in the system and as a result, the equilibrium concentrations of surfactants in the aqueous phase should not correspond to their initial concentrations. However, assuming in a first approximation that such an interphase distribution of surfactant molecules does not significantly change the concentration of the aqueous phase, the colloidal-chemical and molecular parameters of the investigated surfactant at the aqueous solution-kerosene interface using the same laws as in the case of the aqueous solution-air were determined.

The surface tension of water and kerosene at the boundary with air at 25°C is respectively equal to $\sigma_{01} = 71.95$, $\sigma_{02} = 29$ mN/m, and at the water-kerosene boundary according to Antonov's rule [11] it should be equal to $\sigma_{12} = \sigma_{01} - \sigma_{02} = 42.95$ mN/m. Some difference in the measured surface tension at the water-kerosene interface ($\sigma_{12}^P = 46.3$ mN/m) from the value calculated according to the Antonov rule can in all probability be explained by a decrease in the surface tension of the non-polar phase caused by the transition of some components with large values of surface tension to the water in comparison with kerosene (sulfur, nitrogen and oxygen compounds), which should significantly have an impact on the decrease in surface tension of the non-polar hydrocarbon phase. The results of measuring of surface tension at the boundary of an aqueous solution of compound I and kerosene are shown in Table.

The results of measuring of surface tension at the boundary of an aqueous solution of compound I and kerosene

Phase boundary	$G_{\max} \cdot 10^6$, mol/M	$\omega_{\min}$, nm ²	h, nm	$g \cdot 10^3$, N·m ²	PC ₂₀	ΔG_{mic}^0 , kJ/mol	ΔG_{alc}^0 , kJ/mol
Water solution–air	2.963	0.56	1.08	62.1	3.34	–9.96	–24.0
Water solution– kerosene	2.695	0.62	0.98	73.7	3.65	–	–25.92

Fig. 4. Dependence $\sigma=f(\ln C)$ for aqueous solutions of compound I at the aqueous solution–kerosene interface.

Figure 4 shows the dependence $\sigma=f(\ln C)$ for the aqueous solution–kerosene interface. Processing of the experimental data of the linear part of the $\sigma=f(\ln C)$ dependence curve allows us to calculate the corresponding constants of the Shishkovsky and Langmuir equations, as well as the molecular parameters ($\omega_{\min}$, h) of compound I at the aqueous solution–kerosene interface:

$$A'=2.815 \cdot 10^{-5}, \quad b'=6.68 (B=0.144);$$

$$K'_{\text{ads}}=34902; \quad G'_{\text{max}}=2.695 \cdot 10^{-4} \text{ mol/cm}^2.$$

From the value of the adsorption equilibrium constant of compound I (K_{ads}), using the relation (3), the Gibbs free energy of the surfactant adsorption process at the aqueous solution–kerosene interface was calculated.

Using relations (4) and (5), the area occupied by the surfactant molecule in a dense monomolecular adsorption layer ($\omega_{\min}$), as well as the thickness of this layer (h) were calculated. The colloidal chemical parameters of compound I for the aqueous solution–kerosene phase boundary are shown in Table.

Due to the fact that micelle formation does not take place in aqueous solutions at the

border with kerosene, the surface activity of surfactants is calculated in both cases using the ratio:

$$g = \lim_{c \rightarrow 0} \left(-\frac{\sigma_0}{\Delta c} \right), \quad (6)$$

As it can be seen from Figure 4, in the region of relatively high surfactant concentrations on the curve $\sigma=f(\ln C)$ for the aqueous solution–kerosene interface, surface tension is not observed, although there is a tendency to such stability. The fact that the molecular parameters of the surfactant molecule ($\omega_{\min}$, h) at both phase boundaries practically coincide, confirms that a monomolecular adsorption layer is also formed at the water–kerosene interface. However, the fact that a further increase in the surfactant concentration does not lead to a constant surface tension at this boundary is most likely due to the fact that the micelle formation process is hindered by the distribution of surfactant molecules between the aqueous and kerosene phases in accordance with the distribution law [10] and, on the other hand, a change in the structure of the adsorption layer at the aqueous solution–kerosene interface.

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**ИССЛЕДОВАНИЕ КОЛЛОИДНЫХ СВОЙСТВ
1-МЕТИЛЕН-(3-АЛЛИЛ-2-ГИДРОКСИ-5(ОКТИЛ-2)ФЕНИЛ)ПИПЕРИДИНИЙХЛОРИДА**

З.М.Джавадова

Приводятся результаты исследований по выявлению основных закономерностей зависимости процессов поверхностного натяжения водных растворов 1-метилена-(3-аллил-2-гидрокси-5(октил-2)фенил) пиперидинийхлорида на границе водный раствор–воздух и водный раствор–керосин в зависимости от его структуры и концентрации. Определены условия адсорбции, вычислены критические константы мицеллообразования и сделаны выводы относительно возможности их использования как ПАВ.

Ключевые слова: *поверхностно-активное вещество, поверхностное натяжение, водный раствор–воздух, водный раствор–керосин, адсорбция.*

**1-METİLEN-(3-ALLİL-2-HİDROKSİ-5(OKTİL-2)FENİL)PİPERİDİNİYXLORİDİN
KOLLOİD XASSƏLƏRİN TƏDQIQI**

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1-Metilen-(3-allil-2-hidroksi-5(oktil-2)fenil)piperidiniyxlordin sulu məhlullarının səthi gərilməsinin əsas qanunauyğunluqlarını müəyyən etmək üçün aparılan tədqiqatların nəticələri verilmişdir. Tədqiqatlar quruluşdan və qatılıqdan asılı olaraq su–hava və su–kerosin sərhəddində aparılmışdır. Adsorbsiya şəraiti müəyyən edilmiş, kritik mitselloəmələgəlmə sabiti hesablanmış və onun səthi-aktiv birləşmə kimi təklif olunması müəyyən edilmişdir.

Açar sözlər: *səthi–aktiv maddə, səthi gərilmə, sulu məhlul–hava, sulu məhlul–kerosin, adsorbsiya.*