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SURFACE ACTIVITY AND PHASE BEHAVIOUR OF POTASSIUM HEPTYLENE DECYL SUCCINATE / WATER BINARY SYSTEM

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ABSTRACT

The surface activity of potassium heptylene decyl succinate (PHDS) at water-air interface was studied. The obtained results showed a very good correlation between the surface activity of PHDS and concentration of surfactant solutions and temperature of the system. The phase behaviour and structure of aggregates in PHDS)/water binary system were investigated. The phase diagram of the PHDS/water binary system was obtained depending on the concentration of components and temperature of the system. It was established that due to the double hydrocarbon chain of the PHDS molecule, the lamellar liquid crystalline phase exists across a wide range of the phase diagram. It was shown that upon the addition of water, the cross-sectional area of the PHDS molecules in lamellar liquid crystals is changed insignificantly. This result was associated with the invariability of the distance of the lipophilic layers of formed lamellar liquid crystals by PHDS molecules. On the basis of video-enhanced microscopic studies, it was established that in two-phase region of the phase diagram, lamellar liquid crystals coexist with water in the form of vesicles.

*Keywords**:** potassium heptylene decyl succinate, surface activity, phase behaviour, surfactant/water binary system, lamellar liquid crystals, vesicle formation.*

INTRODUCTION

Surface-active derivatives of alkylene succinic acid occupy a special place among new types of surfactants. Interest in surfactants based on alkylene succinic acid is due to their valuable colloidal-chemical properties and the possibility of obtaining model compounds with the required functional groups. They combine high surface-active properties, good biodegradability, low toxicity to warm-blooded animals and relatively low cost. Alkylene succinate surfactants have a high adsorption ability in relation to interfaces of various natures and are able to associate in the liquid phase with the formation of micellar particles [1 - 6]. Due to above mentioned properties, alkylene succinic acid derivative surfactants have found wide application in different fields of industry [7 - 9]. In this regard, heptylene decyl succinates draw attention due to their practicality in both aqueous and nonaqueous solutions. The molecules of these surfactants have two hydrocarbon chains. The lengths of these chains are different (-C_7H_{13} and -$C_{10}H_{21}$), and one of them has an unsaturated bond. It is well-known that the chemical structure and length of hydrocarbon chains can affect the surface activity, micelle formation and structure of aggregates in surfactant solutions [1 - 4, 10 - 14]. Many ionic surfactants with a double hydrocarbon chain have well-balanced hydrophilic-lipophilic properties and can form a micellar structure in both aqueous and oily media, depending on the concentration and temperature of the system. However, despite the many results of studies of dispersed systems containing ionic surfactants with one hydrocarbon chain, very few studies have been carried out on ionic surfactants with two lipophilic chains [1 - 5, 14, 15]. Thus, it is of great interest to study the surface activity and micelle-forming ability of surfactants with two hydrocarbon chains in water, such as the surfactant potassium heptylene decyl succinate. It is also important and useful to study the phase behaviour of the PHDS/water binary system and the structure of aggregates in this system.

EXPERIMENTAL

Phase diagram of PHDS/water binary system

Samples of the surfactant combined with water were placed in glass ampoules and sealed on a gas burner. Then, the contents of the ampoule were thoroughly mixed using a vortex mixer. The resulting solutions in the ampoules were placed in a thermostatic water bath at a temperature of 25°C for 24 hours. The phase state of the binary system was determined directly by visual observations using polarizers [16]. A polarizing microscope with a video enhancing device (Nikon Optiphoto 2 type) and a small-angle X-ray scattering were used to determine the phase boundary.

Determination of the type of liquid crystals

The type of liquid crystals was determined based on the video-enhanced microscopic texture and the ratio of the peaks in a small-angle X-ray scattering spectrum of PHDS/water binary system [17, 18]. For such investigations, a video-enhanced polarizing microscope and a small-angle X-ray scattering were used.

Analysis of lamellar liquid crystals

The interlayer distance of lamellar liquid crystals was measured on a RINT 2500 device (Rigaku Corporation) at a temperature of 25°C. The maximum power of the device was 18 kW, and the interlayer distance was measured at 50 kV and 300 mA. The liquid crystal samples were placed in a metal slit and covered with the polyethyleneterephthalate films for the measurement (Mylar seal method), and X-ray scattering was conducted. It was assumed that the lamellar phase consists of infinitely spread surfactant bilayers. Thus, the effective cross-sectional area per surfactant at the interface (a_s) was calculated by the following equations using the value of interlayer spacing, d.

$$d = \frac{d_s}{\varphi_s} \tag{1}$$

$$a_s = \frac{2V_s}{d\,\varphi_s}\ , \tag{2}$$

where φ_s, d_s and V_s are the volume fraction surfactant, the length of surfactant layer and the volume of a surfactant molecule, respectively.

Surface tension of surfactant solutions

Surface tension and critical micelle concentration of aqueous surfactant solution was measured at 25°C, using the Wilhelmy plate technique with an automatic surface tensiometer DCAT 9T (Data-Physics Instruments GmbH). Sets of measurements were taken at 30-min intervals until no significant change occurred. Double distilled water was used to prepare the surfactant solutions.

Molar volume of surfactant

The molar volume of PHDS was calculated by the following equation where, M_s and ρ_s are the molecular weight and the density of the surfactant:

$$V_s = \frac{M_s}{\rho_s}\ . \tag{3}$$

Surfactant PHDS

The surfactant potassium heptylene decyl succinate (PHDS) was received from the surfactant research lab of the Institute of General and Inorganic Chemistry, Uzbek Academy of Sciences. The chemical formula of surfactant PHDS is $RCH(COOK)CH_2COOR^1$, where $R = -H_2C\text{-}CH{=}CH(CH_2)_3CH_3$ and $R^1 = -CH_2(CH_2)_8CH_3$.

RESULTS AND DISCUSSION

Surface activity and phase behaviour of the PHDS/water binary system

The surface-active properties of PHDS were studied based on the surface tension measurements of surfactant aqueous solutions. The results of the surface tension measurements of PHDS aqueous solutions are shown in Table 1. As shown in Table 1, with the increase of the surfactant concentration in solutions, the surface tension of water decreased till 25 - 28 mN m^{-1}. An increase in temperature (from 293 to 333 K) also causes a depression in the surface tension of the surfactant solutions. The obtained results are associated with an increase in the adsorption capacity of amphiphilic molecules at the liquid-gas interface with the increase of surfactant concentrations and temperature of the

Table 1. Surface tension of PHDS aqueous solutions at various concentrations and temperatures of the binary system.

Surfactant	T, K	Surface tension (mN m^{-1}) at various concentrations of PHDS solutions (C 10^3 mol m^{-3})										
		0.012	0.022	0.051	0.115	0.224	0.451	0.902	1.83	3.64	7.23	14.42
PHDS	293	68.7	65.9	61.7	55.8	51.9	39.6	34.6	32.8	30.5	29.5	28.1
	303	67.5	63.5	60.2	55.1	46.9	38.6	31.9	31.6	29.6	28.5	27.2
	313	66.9	62.7	57.9	52.4	43.7	37.8	30.5	30.7	28.4	26.9	26.7
	323	65.2	60.9	56.4	50.9	42.3	36.5	29.8	28.9	27.9	25.4	25.0
	333	63.9	58.9	55.1	48.9	41.7	36.1	29.3	28.6	27.4	25.2	24.9

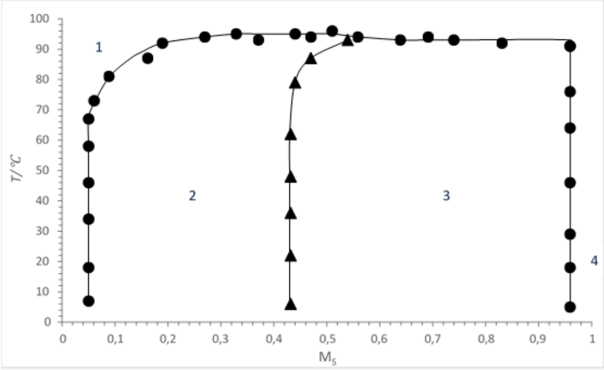

Fig. 1. Phase diagram of the PHDS/water binary system depending on the temperature (T) and surfactant mass fraction (M_s); 1 - micellar phase, 2 - two-phase region (dispersion of liquid crystals in water), 3 - liquid crystalline phase, 4 - micellar phase.

system. At low concentrations, the surfactant molecules adsorb at the water-air interface and decrease the surface tension and free energy of the system. However, with a further increase in surfactant concentration, the surface layer becomes saturated, and then the system removes hydrophobic chains of surfactant molecules from water into a micelle, separating it by the hydrophilic shells of the polar surfactant groups. The formation of micelles leads to a maximum decrease in the total free surface energy and creates a stable system. The critical micelle concentration (CMC) of PHDS obtained from surface tension results is 8.7x10^{-4} mol L^{-1}. The process of micelle formation in PHDS solutions is determined both by the forces of cohesion between lipophilic groups and by that between the hydrophilic surfactant groups and water molecules.

The phase behaviour of the binary PHDS/water system and the structure of aggregates in this system were investigated. The obtained phase diagram of the PHDS/water binary system depending on the temperature and surfactant concentration shown in Fig. 1. In the phase diagram, the PHDS concentration is shown along the horizontal line, and the system temperature is indicated along the vertical line. As shown in Fig. 1, an isotropic aqueous micellar phase formed in the low surfactant concentration region of the phase diagram. It can be assumed that in aqueous solutions of PHDS at low concentrations, the most energetically favourable spherical micelles are present. As the concentration of the surfactant increases, the shape and size of micelles change in the binary system. From the data obtained, it appears that the configuration and conformational transformations of the two hydrocarbon chains of PHDS play an essential role in the association processes of PHDS molecules.

With the increase in the surfactant concentration, the micellar phase passes to an anisotropic liquid crystalline phase. As shown in Fig. 1, a two-phase region that contains dispersions of liquid crystals in water (LC + Water) is formed between the water-micellar and liquid-crystalline phases. The types of liquid crystals were determined from the texture of the system and the ratio of the first and second peaks of the small-angle X-ray scattering spectrum. A video-enhanced microscopic image of the texture of the PHDS/water binary system at a surfactant concentration of 54.3 % is shown in Fig. 2. As shown in Fig. 2, the PHDS/water binary system formed a lamellar liquid crystalline texture. The spectrum of a small-angle X-ray scattering of the PHDS/water binary system at a surfactant concentration of 54.3 % showed that the ratio of the first and second peaks is equal to 1:1/2 and the system has the texture of lamellar liquid

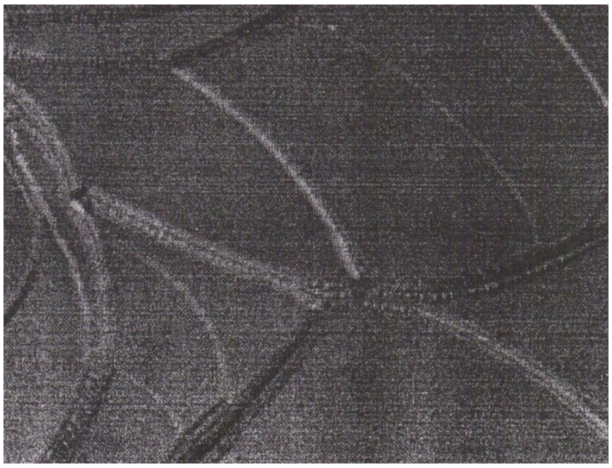

Fig. 2. Video-enhanced microscopic picture of the texture of lamellar liquid crystals in the PHDS/water binary system at 20°C.

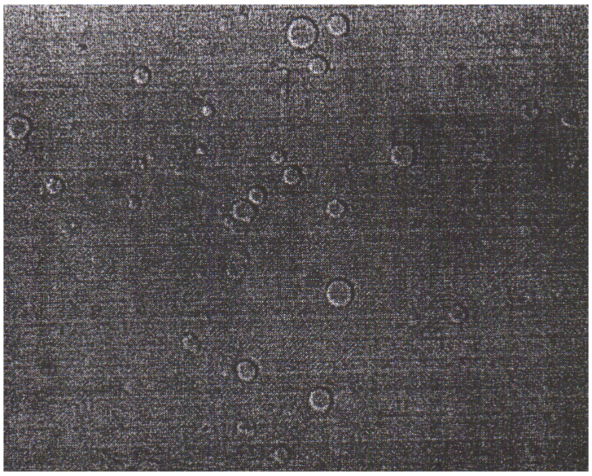

Fig. 3. Video-enhanced microscopic picture of dispersed vesicles in two-phase region of PHDS/water binary system phase diagram at 20°C.

Table 2. The interlayer distance of lamellar liquid crystals (d) and cross-sectional area of surfactant molecule (a_s) depending on PHDS concentration in the system.

d / a_s	Surfactant concentration, $1/M_s$						
	1.09	1.28	1.46	1.66	1.85	1.90	2.11
d	2.78	3.15	3.58	4.36	5.12	5.08	5.21
a_s	0.422	0.425	0.423	0.419	0.416	0.415	0.416

crystals. Thus, the study confirmed that in the surfactant concentration range from 43.5 % to 96.6 %, lamellar liquid crystals formed in the PHDS/water binary system.

At a surfactant concentration between 4.9 and 43.5 % of the phase diagram (Fig. 1), lamellar liquid crystals coexist with water in the form of vesicles, which are useful in many technological processes. The obtained video-enhanced microscopic image of normal vesicles formed by the dispersion of lamellar liquid crystals in area 2 of the phase diagram is shown in Fig. 3. As seen from the obtained phase diagram (Fig. 1), the lamellar liquid crystalline phase dominates over a wide concentration range of the phase diagram. This result is apparently due to the chemical structure of the PHDS, which has two different hydrocarbon chains.

In the obtained phase diagram (Fig. 1), no significant changes in the hydrophilic-lipophilic properties of surfactant PHDS observed with the increase of the temperature of binary system, and therefore, at low temperatures, there is no phase transition. The lamellar liquid-crystalline phase melts and forms a micellar phase at a higher temperature in the system (≈ 96.5°C); this phase merges with the main micellar part of the diagram.

The interlayer distance of lamellar liquid crystals was investigated from the results of the small-angle X-ray scattering spectrum. The cross-sectional area of the surfactant molecule in lamellar liquid crystals was found from the interlayer distance of the lamellar phase in the PHDS/water system. The results are shown in Table 2. As seen in the presented data, the interlayer distance of lamellar liquid crystals gradually increases when the value of the cross-sectional area of the surfactant molecule is almost constant with the dilution of the binary system with water. Since the hydrocarbon chains of the surfactant PHDS form a rigid and inflexible lipophilic layer, solvent (water) molecules cannot penetrate into it. Therefore, the distance between the lipophilic layers of the lamellar liquid crystals remains unchanged. In contrast, water molecules can easily penetrate into the hydrophilic surfactant bilayers. Consequently, with greater intrusion of water molecules into the interior of hydrophilic bilayers, the interlayer distance of lamellar liquid crystals increases with decreasing surfactant concentration. Accordingly, the cross-sectional area of surfactant molecules in lamellar liquid crystals remains almost constant.

CONCLUSIONS

The surface activity of PHDS at liquid-gas interface was studied. The obtained results showed a good correlation between the surface activity of PHDS, its concentration and temperature of the system. The phase diagram of PHDS/water binary system was constructed as a function of the temperature and concentration of the components. At above the critical micelle concentration, PHDS forms a normal micellar solution. At higher concentrations of PHDS, a lamellar liquid crystallin phase dominates in the binary system. Due to the two hydrocarbon chains in surfactant molecule, a lamellar liquid crystalline phase prevails widely in the phase diagram. A lamellar liquid crystalline phase coexists with water in the form of vesicles in the two-phase region. The effective cross-sectional area of the surfactant molecule remains almost constant, although the interlayer spacing of the lamellar liquid crystal increases with the decreasing of surfactant concentration. Thus, the length of the lipophilic layer remains unchanged in the lamellar liquid crystalline phase of binary system upon the addition of water.

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