

Aqueous Solutions of Hydroxypropyl Cellulose, Tween 80 and Their Binary Mixtures: Colloid-Chemical Aspects

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Abstract—Tensiometry, dynamic light scattering, and rheology have been used to study the colloid-chemical properties of hydroxypropyl cellulose, Tween 80, and binary mixtures thereof in an aqueous medium and at water/decane and water/air interfaces. The efficiency of a reduction in the interfacial energy under dynamic and static conditions, the surface activity of the components, capability of self-organization in bulk and at interfaces, as well as emulsifying efficiency of the systems, have been analyzed. It has been found that, in a narrow concentration range and at a certain ratio of the components, they exhibit a synergetic effect with respect to a reduction in the interfacial energy, with this effect being due to the formation of a Tween 80–polymer bilayer via hydrogen bonding between hydroxyl groups of hydroxypropyl cellulose and ethoxy units of Tween 80.

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INTRODUCTION

The study of self-organization processes in surfactant/polymer/water systems is an important fundamental task of colloid chemistry. These processes may, to a substantial extent, govern the surface and bulk properties of three-component (or more) systems based on surfactants and polymers, these properties being of decisive significance for their efficient application in different fields of industry, medicine, and pharmacology.

The diversity of the types of self-organized structures in such systems is a consequence of the wide spectrum of interactions (electrostatic, van der Waals, dispersion, and hydrogen interaction) between their components. Molecular structures of polymers and surfactants, as well as the component concentrations and ratios in an aqueous medium, are of great significance [1–4]. The properties of surfactant–polymer–water systems are studied using tensiometry [5–8], viscometry [6, 8, 9], dye solubilization [5, 6, 10], small-angle neutron scattering [11], NMR [12, 13], dynamic and static light scattering [10, 14–16], and fluorescence [17–19] methods.

At present, systems based on synthetic linear polymers and low-molecular-mass ionogenic surfactants, such as poly(ethylene oxide) (PEO)/sodium dodecyl sulfate [10, 11, 13, 16, 18, 19], poly(vinylpyrrolidone)/sodium dodecyl sulfate [5, 12, 16, 18, 19], PEO/tetradecylammonium bromide [19], and PEO/cetyltrimethylammonium bromide [20, 21], have been studied most comprehensively. Supramo-

lecular complexes formed by polymers and surfactants are often described in terms of the “pearl necklace” model, in which spherical micelles are threaded onto a polymer chain [4, 11–13].

The problems concerning the self-organization of uncharged polysaccharides and nonionogenic surfactants (NSs) in aqueous media remain to be studied. Moreover, an opinion has arisen that there are no interactions between the components in such systems [22]. However, static light scattering [15] and fluorescence [17] studies have, on the contrary, shown the existence of interactions between NS micelles and linear nonionogenic cellulose derivatives in aqueous media. The rheological investigations of aqueous dispersions of a branched polysaccharide (guar gum) both in the presence of NSs (polyethoxylated alcohols [23], and polyethoxylated ethers [24]) and in their absence have shown that these dispersions are viscoelastic liquids, with the anomaly of their viscosity being enhanced in the presence of NSs. The authors of [23, 24] have related the observed effects to the formation of polymer–NS complexes, which are more hydrophobic than polymer macromolecules, via hydrogen bonding between ethylene-oxide chains of NSs and hydroxyl groups of glutaric gum.

The effect of the addition of Triton X-100 (polyethoxylated (9–10) 4-(1,1,3,3-tetramethylbutyl)phenol) on the relative viscosity (η_{rel}) of an aqueous 0.05 wt % carboxymethyl hydroxypropyl guar solution was studied in [8]. Triton X-100 concentration (C_{Tr}) was varied in a wide range from 2.0×10^{-6} to

4.4×10^{-3} M (which is nearly 14.5 times higher than the critical micelle concentration (CMC) of the NS). It was found that the η_{rel} values remained unchanged at $C_{\text{Tr}} < 0.7$ CMC and dramatically decreased with a further rise in NS concentration. In the opinion of the authors of [8], this effect was caused by the compaction of polymer macromolecules because of their hydrophobization due to the interaction with the polar groups of the NS. For aqueous hydroxypropyl guar-gum solutions, a minimum was revealed in the dependence of the intrinsic viscosity on Triton X-100 concentration ($C_{\text{Tr}} = 4 \times 10^{-5} - 1 \times 10^{-2}$ M) [9]. Therewith, the authors believed that, at $C_{\text{Tr}} < \text{CMC}$, NS molecules hydrophobized the polymer, while the micellar form of Triton X-100 promoted its hydrophilization.

In the above-listed communications, the bulk characteristics of binary mixed solutions of polysaccharides and NSs were considered. At the same time, polysaccharide–NS mixed adsorption layers, which, to a substantial extent, govern the aggregation stability and properties of different disperse systems, including emulsions, have not actually been studied. Only a few communications are available. For example, guar-gum adsorption on the surface of manganese-dioxide particles with an average size of $6.8 \mu\text{m}$ was studied [25] in an aqueous medium in the presence of Triton X-100 ($C_{\text{surf}} = 1 \times 10^{-4}$ M, which is lower than CMC) and additives of an electrolyte (0.01 M NaCl or 0.003 M CaCl_2). The analysis of the data obtained taking into account the values of the electrokinetic potential, surface-charge density, and the thickness of adsorption layers enabled the authors to hypothesize that there is a layered structure of a mixed adsorption layer composed of polysaccharide molecules chemisorbed on a particle with NS and additional polysaccharide molecules successively attached to them [25]. In this situation, molecules of Triton X-100 and guar-gum macromolecules may interact with each other due to both the hydrophobic effect and hydrogen bonding [25].

The kinetic dependences obtained for the surface tension of aqueous solutions of hydroxypropyl cellulose (HPC, $M_w = 850$ kDa) and NS (a mixture of esters of saccharose and palmitic and stearic acids), as well as mixtures of NSs and HPC at a constant polymer concentration, were compared in [26]. The joint adsorption of both components was observed; at the same time, the possible interaction between the components was not discussed.

Thus, data on the association of nonionogenic polysaccharides and NSs in bulk solutions and adsorption layers are scarcer and contradictory. The question of whether uncharged surfactant and polymer molecules interact with each other remains open. In order to answer this question, the colloid-chemical properties of aqueous solutions of HPC, polyethoxylated NS (Tween 80), and binary mixtures thereof of

different compositions were comprehensively studied in this work.

OBJECTS OF STUDY

HPC with a linear structure was selected as a water-soluble polysaccharide. This biopolymer is used as an emulsifier, stabilizer, thickener, or binder when producing various drug-dosage forms, cosmetic remedies, food compositions, etc. The addition of HPC to dairy products makes them seem fatty [27], which makes it possible to improve the taste of foods with decreased fatness (ice creams, yoghurts, toppings, etc.). Aqueous HPC solutions may be used to prepare oil- and light-resistant films [28], as well as support films for crystallization of a protein, lysozyme [29].

HPC of Klucel EF commercial grade (Hercules, United States) with weight-average molecular mass $M_w = 80$ kDa was used in the work. HPC macromolecules are semirigid. It is known that the Kuhn segment length for cellulose ethers in aqueous media is ≈ 18.2 nm [30, 31], while the size of a cellulose monomer unit is 0.545 nm [30]. Hence, the Kuhn segment of HPC contains nearly 33 units. The degree of substitution that characterizes the average number of hydroxypropyl groups per one glucopyranose unit is $3.4 - 4.4$ [32]. Figure 1 schematically represents a fragment of HPC with the degree of substitution equal to 3.5. Assuming that the molecular mass of a unit of studied HPC is equal to 388.2 Da, the average polymerization degree of HPC was calculated to be ≈ 206 units; i.e., a macromolecule comprised, on average, 6 Kuhn segments. HPC is readily soluble in water at temperatures below 38°C [32, 33]. For example, its solubility at 10°C is ≈ 35 wt % [34]. Aqueous HPC solutions are transparent or slightly opalescent. HPC is known to exhibit surface-active properties at water–air interfaces [32, 33]. For example, the surface tension of water decreases by ≈ 29 mN/m in the presence of 0.1 wt % of HPC [32].

Polyethoxylated (20) sorbitan monooleate (Tween 80, Tw) (Sigma-Aldrich) with $M_w = 1308$ Da and the hydrophilic–lipophilic balance number of 15 [35] was selected as an NS. Its structural formula is depicted in Fig. 2. Tween 80 is biodegradable and nontoxic; it is used in pharmaceuticals, cosmetic and food industries as a solubilizer for oils and vitamins, and as an emulsifier and stabilizer. Tw is used to advantage for producing microemulsions and nanospheres, which can be applied as drug carriers. It is known [36] that the saturation of aqueous Tw solutions with toluene leads to the formation of type-1 microemulsions according to the Winsor classification. It has been shown [37] that Tw can form a complex with a protein, lysozyme, due to hydrogen bonding, with this complex being capable of stabilizing black foam films [38]. In addition, Tw can be used as a stabilizer of the native protein structure in the freezing–defrosting processes [39]. In

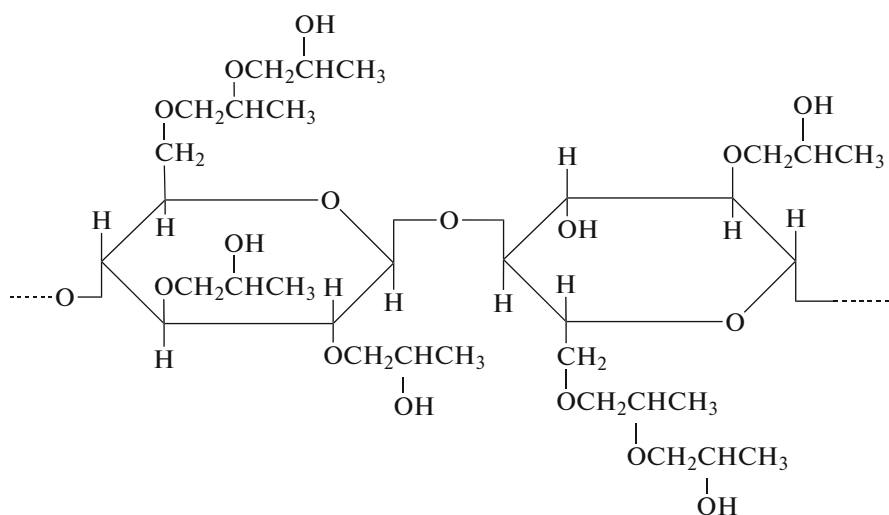


Fig. 1. Schematic representation of a fragment of a hydroxypropyl cellulose molecule with an average degree of substitution equal to 3.5.

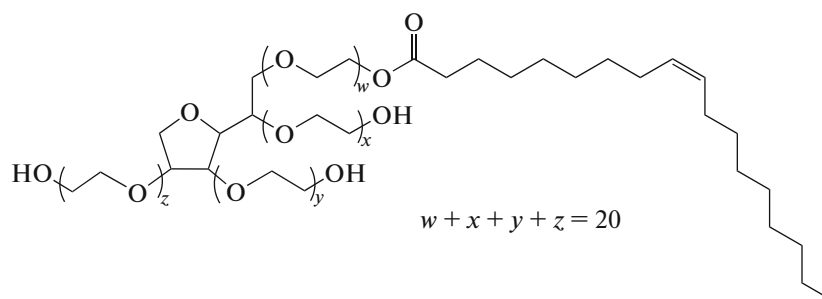


Fig. 2. The structural formula of a Tween 80 molecule. Total amount of ethoxy groups ($x + y + z + w$) is equal to 20.

combination with HPC, this NS stabilizes toluene oil-in-water emulsions, which possess film-forming properties [29].

Decane (reagent grade, Reakhim, Russia) served as a dispersed phase. The aforementioned compounds were used as received.

Triply distilled water with a specific electrical conductivity of 7.9×10^{-5} S/m at 25°C was used in the work.

Initial aqueous HPC solutions (1.25×10^{-4} and 3.78×10^{-4} M) were prepared as described in [40], allowed to stand for 24 h, and diluted to reach a necessary concentration. All solutions were stored in a refrigerator.

Solutions of HPC–Tw binary mixtures with a constant component ratio were prepared by mixing equal volumes of solutions of individual components with concentrations twice as high as the necessary ones. When preparing a series of solutions with a constant polymer concentration and different Tw concentrations, an aqueous HPC solution ($C_{\text{HPC}} = 3.1 \times 10^{-8}$ M) was used as a solvent.

Oil-in-water decane emulsions with a constant volume fraction of the dispersed phase equal to 0.2 were obtained in a water-cooled cell using a UZDN-A ultrasonic disperser (Russia). The dispersing time was no longer than 1 min. Aqueous solutions of Tw ($C_{\text{Tw}} = 3.9 \times 10^{-2}$ M), HPC ($C_{\text{HPC}} = 1.9 \times 10^{-4}$ M) and a binary mixture of them ($C_{\text{Tw}} = 3.9 \times 10^{-2}$ M and $C_{\text{HPC}} = 1.9 \times 10^{-4}$ M), in which the molar concentration ratio between the components was such that one Tw molecule corresponded 1 HPC monomer unit, were used as dispersion media.

INVESTIGATION METHODS

Surface tension σ was measured by the pendant-drop method, according to which the drop was photographed using a horizontal microscope equipped with a DCM-130 digital video camera. The σ values were calculated with the help of the Drop Shape Analysis software (Krüss) by numerically integrating the Young–Laplace equation. To avoid solvent evaporation, an examined drop was formed on the tip of a cap-

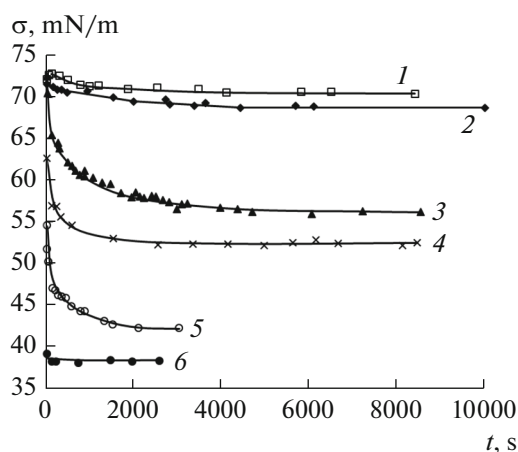


Fig. 3. Time dependences of surface tension for aqueous Tw solutions with different concentrations: (1) 8.0×10^{-7} , (2) 1.2×10^{-6} , (3) 5.0×10^{-6} , (4) 8.3×10^{-6} , (5) 5.0×10^{-5} , and (6) 1.1×10^{-3} M.

illary in the atmosphere of saturated vapors in a cell equipped with a hermetical cover having an orifice for the capillary. The kinetics of variations in the surface tension was monitored for a long time (from a few seconds to 25 h), thereby reaching equilibrium σ values with an accuracy of ± 0.5 mN/m. The measurements were performed at $23 \pm 0.5^\circ\text{C}$ the day after solution preparation.

Particle-size distributions in the studied solutions and emulsions were determined by dynamic light scattering with a ZetatractTM NPA152 high-speed analyzer (Microtrac Inc., United States) operating on the basis of laser diffraction. The data obtained were processed using the Microtrac FLEX software. This software enables one to obtain differential distribution curves characterizing the percentage of scattered light intensity for particles of every diameter (the Intensity mode). The dispersion analysis of the solutions did not require a preliminary dilution of the samples, while the samples of the emulsions were 17.7-fold diluted with water. Water was used as a reference medium.

The rheological properties of the emulsions were studied with a RheoStress 1 rheometer (Thermo Haake, Germany) equipped with a thermostated cone–plane measuring unit having a cone diameter, an angle between the cone generatrix and the plane, and a working gap between the truncated cone vertex and the plane of 60 mm, 2° , and 0.104 mm, respectively. The rheometer could operate with the control over both shear rate and shear stress. The tests were carried out in the latter mode at 20°C .

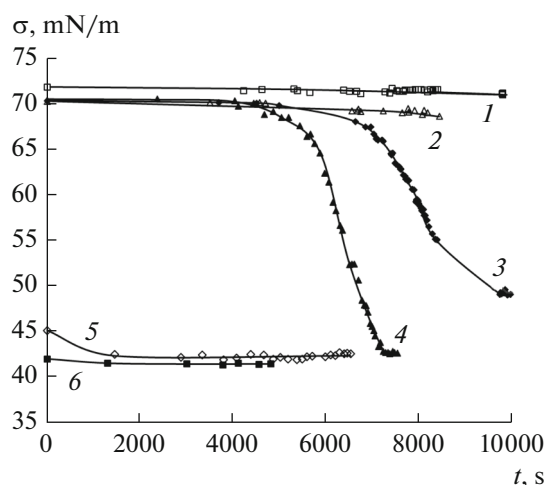


Fig. 4. Time dependences of surface tension for aqueous HPC solutions with different concentrations: (1) 2.1×10^{-8} , (2) 3.1×10^{-8} , (3) 4.0×10^{-8} , (4) 5.1×10^{-8} , (5) 5.0×10^{-7} , and (6) 5.1×10^{-5} M.

RESULTS AND DISCUSSION

Equilibrium Surface Tension Isotherms

Equilibrium $\sigma(\ln C)$ surface tension isotherms were plotted on the basis of $\sigma(t)$ kinetic dependences, with some of them being presented in Figs. 3–5 as an example. Isotherms of σ for aqueous solutions of the individual components were plotted in wide concentration ranges ($C_{\text{Tw}} = 8.0 \times 10^{-7}$ – 1.1×10^{-3} M and $C_{\text{HPC}} = 1.5 \times 10^{-8}$ – 5.1×10^{-5} M). The $\sigma(\ln C)$ dependences for solutions of Tw–HPC binary mixtures were obtained under the following conditions:

(1) while varying Tw concentration ($C_{\text{Tw}} = 2.8 \times 10^{-6}$ – 1.1×10^{-3} M) at a constant HPC concentration ($C_{\text{HPC}} = 3.1 \times 10^{-8}$ M); and

(2) while varying concentrations of both components within ranges of $C_{\text{Tw}} = 1.6 \times 10^{-6}$ – 5.3×10^{-5} M and $C_{\text{HPC}} = 0.8 \times 10^{-8}$ – 2.5×10^{-7} M, but maintaining a constant $C_{\text{Tw}}/C_{\text{HPC}}$ ratio between the molar concentrations of the components at which nearly one molecule of Tw corresponded to one unit of the polymer.

For aqueous Tw solutions, the $\sigma(\ln C_{\text{Tw}})$ surface tension isotherm exhibited an inflection (Fig. 6, curve 1), which corresponded to the critical micelle concentration ($\text{CMC} = 3.2 \times 10^{-5}$ M). The value that we obtained for the CMC agreed with the published data [41]. The Gibbs equation ($\Gamma = -\frac{1}{RT} \frac{d\sigma}{d \ln C}$) and the value of the $-d\sigma/d \ln C$ derivative determined as the slope of the linear pre-micellar region of the isotherm were used to calculate maximum Tw adsorption value Γ_m at the solution–air interface. This enabled us to calculate the surface area per molecule of this NS in an ultimately filled monolayer ($s_0 = 1/N_A \Gamma_m$, where N_A

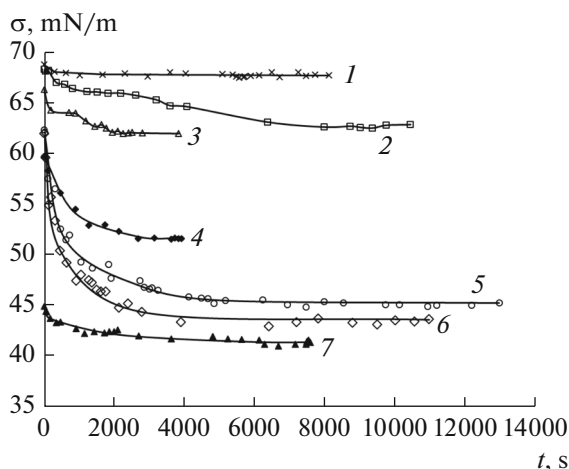


Fig. 5. Time dependences of surface tension for aqueous solutions of Tw/HPC mixture with a constant component ratio (≈ 1 Tw molecule/HPC unit) and different concentrations: (1) 1.6×10^{-6} M/ 0.8×10^{-8} M, (2) 2.1×10^{-6} M/ 1.0×10^{-8} M, (3) 3.1×10^{-6} M/ 1.5×10^{-8} M, (4) 5.2×10^{-6} M/ 2.5×10^{-8} M, (5) 6.3×10^{-6} M/ 3.0×10^{-8} M, (6) 8.3×10^{-6} M/ 4.0×10^{-8} M, and (7) 5.3×10^{-5} M/ 2.5×10^{-7} M.

is Avogadro's number). The values of Γ_m and s_0 appeared to be 3.31×10^{-6} mol/m² and 0.5 nm²/molecule, respectively.

Surface activity $G = \lim_{C \rightarrow 0} (d\pi/dC)$, where π is the two-dimensional pressure, which is equal to the difference between the surface tensions of water (σ_0) and an NS solution, was determined from the linear $\pi(C_{Tw})$ isotherm. The value of G for Tw turned out to be $\approx 1.4 \times 10^6$ (mN L)/mmol. The standard Gibbs free energy of adsorption was calculated from the following relation: $\Delta G^\circ = -RT \ln G$ [42]. The values of ΔG° and the increment of free energy of adsorption calculated for one CH₂ group ($\Delta G_{CH_2}^\circ$) were -34.8 and -2.05 kJ/mol, respectively.

The surface tension isotherms for HPC solutions (Fig. 7, curve 1) are similar to the isotherms typical of aqueous solutions of micelle-forming surfactants, thereby being in agreement with the published data. For example, a similar pattern of the $\sigma(\ln C)$ dependence was observed for aqueous solutions of HPC with molecular mass $M_w = 106$ kDa in [43], where the inflection was detected at $C^* \approx 2.0 \times 10^{-8}$ M, i.e., at a lower concentration than that for our HPC with a lower molecular mass ($C^* = 5.1 \times 10^{-8}$ M). However, the authors of [43] did not analyze the reasons for the observed inflection. A decrease in the molecular mass of the surface-active polymer is accompanied by a growth of its solubility in water and the degeneration of the inflection in the $\sigma(\ln C)$ isotherm [4]. Therefore, we may suppose that the inflection in the isotherm corresponds to the maximum possible concentration

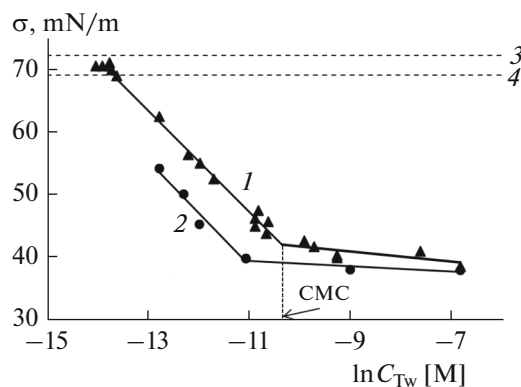


Fig. 6. Surface tension isotherms for aqueous Tw solutions (1) without additives and (2) in the presence of HPC (3.1×10^{-8} M) HPC. The dashed lines correspond to the surface tensions of (3) water and (4) aqueous 3.1×10^{-8} M HPC solution.

of the molecular form of HPC in a solution. When this concentration is exceeded, association of molecules takes place, which is confirmed by the dispersion analysis data (see below).

Since the question of the reversibility of polymer adsorption at interfaces still remains debatable, the applicability of the Gibbs equation is doubtful in this case. At the same time, the surface activity of HPC may be approximately estimated by the relation that is used for micelle-forming surfactants [44]: $G \approx (\sigma_0 - \sigma_{CMC})/CMC \approx (\sigma_0 - \sigma_{C^*})/C^*$. The value of HPC surface activity at a solution–air interface has appeared to be $G = 5.8 \times 10^8$ (mN L)/mmol; i.e., HPC exhibits a much higher surface activity than does Tw.

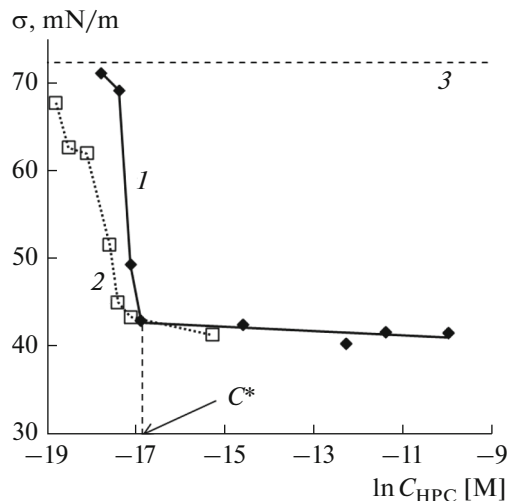


Fig. 7. Dependences of surface tension on polymer concentration for (1) aqueous HPC solutions and (2) solutions of Tw/HPC binary mixture. Component ratio in the mixture is constant (≈ 1 Tw molecule per 1 HPC unit). Dashed line 3 corresponds to water surface tension.

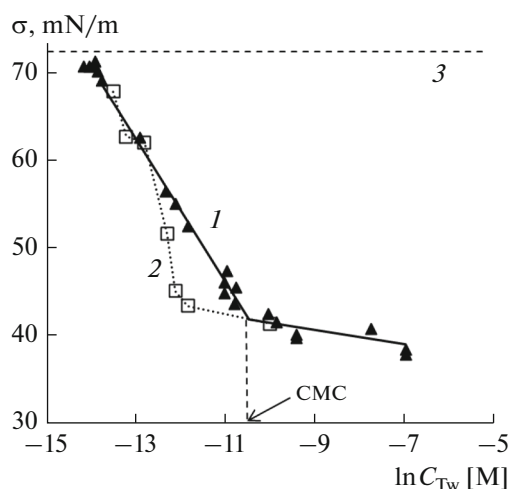


Fig. 8. Dependences of surface tension on NS concentration for (1) aqueous Tween 80 solutions and (2) solutions of Tw/HPC binary mixture. Component ratio in the mixture is constant (≈ 1 Tw molecule per 1 HPC unit). Dashed line 3 corresponds to water surface tension.

Figure 6 enables one to compare the isotherms of the surface tension for aqueous Tw solutions with different concentrations in the presence of HPC ($C_{\text{HPC}} = 3.1 \times 10^{-8}$ M, curve 2) and in the absence of this polymer (curve 1). As can be seen from Fig. 6, the polymer decreases the CMC of Tw seemingly due to the hydrophobic effect caused by the promotion of the formation of hydrogen bonds between water molecules in the presence of the polymer. This agrees with the literature data on decreasing CMC of micelle-forming surfactants in aqueous media in the presence of hydrophobic additives that cause water structuring [42, 45]. In the pre-micellar concentration range, the addition of the polymer leads to a greater decrease in the surface tension (by ≈ 9 mN/m) than that observed in the case of the individual NS (Fig. 6, curves 1, 2). Since, at this polymer concentration, the σ value of water decreases only by ≈ 3 mN/m (Fig. 6, curves 3, 4), it may be concluded that, for the studied binary compositions, a synergistic effect takes place. In the pre-micellar concentration range, the isotherms are almost parallel to each other (Fig. 6), thereby, with allowance for the Gibbs equation, indicating that the polymer has no effect on the value of the limiting adsorption. Hence, a saturated adsorption layer of Tw is formed on the surface, and the observed synergistic effect may be explained only under the assumption that HPC macromolecules are attached to adsorbed Tw molecules via hydrogen bonding between ethoxy groups of the NS and hydroxyl groups of the polymer, with this phenomenon leading to the hydrophobization of the adsorption layer and a more efficient reduction in the surface tension at the solution–air interface.

It should be noted that the pre-micellar region of concentrations in which the synergistic effect is

observed corresponds to variations in the molar concentration ratio between the binary mixture components at which the amount of Tw molecules per one unit of HPC varies from 0.45 to 2.5. Subsequent studies were performed at a $C_{\text{Tw}}/C_{\text{HPC}}$ ratio, at which one Tw molecule corresponded to nearly one HPC unit. Hereafter, the term “binary mixture” signifies a mixture with this composition. It is reasonable to represent the results of the tensiometric measurements performed for aqueous solutions of a binary mixture with the selected $C_{\text{Tw}}/C_{\text{HPC}}$ ratio in two different coordinate systems, i.e., as depending on the concentrations of HPC or Tw. This enables us to compare the surface tension isotherms for the binary mixtures with the isotherms for the solutions of the individual components (Figs. 7, 8). It can be seen (Fig. 7) that the $\sigma(\ln C_{\text{HPC}})$ dependences for the solutions of the binary mixture and the polymer are similar. At the same time, the inflections in the isotherms are detected at almost the same polymer concentration. Hence, the presence of the NS has no effect on the limiting concentration of the molecular form of HPC in a solution. Seemingly, HPC macromolecules associate at concentrations higher than C^* irrespective of the presence or absence of the NS. At HPC concentrations in a binary mixture of no higher than C^* ($C_{\text{HPC}} = (1.7\text{--}4.0) \times 10^{-8}$ M), the binary mixture reduces the surface tension more efficiently than the individual polymer does (Fig. 7).

As can be seen in Fig. 8, the patterns of the $\sigma(\ln C_{\text{Tw}})$ isotherms for the solutions of the binary mixtures and NS are different. Within a narrow concentration range, when C_{Tw} in a binary mixture is in a range of $(3.5\text{--}8.3) \times 10^{-6}$ M, the mixture reduces the surface tension more efficiently than the NS does. It is of interest to compare the experimental data on the two-dimensional pressure with those calculated under the assumption of the additive contributions of the components by the following equation:

$$\pi_{\text{cal}} = X_{\text{HPC}}\pi_{\text{HPC}} + X_{\text{Tw}}\pi_{\text{Tw}} = X_{\text{HPC}}\pi_{\text{HPC}} + (1 - X_{\text{HPC}})\pi_{\text{Tw}},$$

where X_{HPC} and X_{Tw} are corresponding molar fractions of HPC and Tw in the binary mixture, respectively, and π_{HPC} and π_{Tw} are the two-dimensional pressures of the solutions of the individual components at concentrations equal to the total concentration of the binary mixture.

The calculation results are presented in Table 1. It can be seen that the two-dimensional pressure grows with the total concentration of the components. The experimental values of π for the binary mixture are, in all cases, higher than the calculated ones, thereby confirming the synergetic effect of HPC and Tw with respect to a reduction in the interfacial energy. The observed effect likely confirms that there is hydrogen bonding of the components in the adsorption layers.

Dispersion Analysis

Particle-size distribution was studied in solutions of the individual components and binary mixtures thereof. The measurements were performed at polymer concentrations higher than C^* . The results are presented in Fig. 9. Micellar solutions of Tw with concentrations $C_{\text{Tw}} = (0.58-1.2) \times 10^{-2}$ M are characterized by a narrow monomodal distribution with average hydrodynamic diameter D_{av} of micelles equal to 8.1 ± 0.2 nm (Fig. 9a). For HPC solutions ($C_{\text{HPC}} = (2.8-5.5) \times 10^{-5}$ M), a bimodal particle-size distribution has been found (Fig. 9b). The D_{av} values for the fractions were 20 ± 2 and 550 ± 50 nm. The smaller and larger particles are probably individual HPC molecules and their associates, respectively. It is of interest that the diameter of the small particles is comparable with the length of the Kuhn segment for a semirigid HPC macromolecule. The presence of the submicron particles confirms the association of HPC macromolecules at concentrations higher than C^* , which agrees with the tensiometric data (Fig. 7).

A bimodal particle-size distribution has also been revealed for solutions of the binary mixture (Fig. 9c). The presence of Tween 80 has almost no effect on the sizes of submicron particles; therewith, the contribution of this fraction to the scattered light intensity increases with the concentration (Fig. 9c). The sizes of small particles ($D_{\text{av}} \approx 9.2 \pm 0.5$ nm) have appeared to be almost equal to the sizes of micelles and two times smaller than the sizes of individual polymer macromolecules. Since, in the binary mixture, the molar concentration of NS micelles calculated under the assumption that a Tw micelle contains, on average, 34 molecules [36] exceeds the molar concentration of HPC by more than six times, it may be assumed that the contribution of the micelles to the scattered light intensity is markedly higher than the contribution of nonassociated HPC macromolecules. The data

Table 1. Experimental values of two-dimensional pressure (π) and those (π_{cal}) calculated under the assumption of the additive action of the components for solutions of binary mixtures with different concentrations ($C_{\Sigma} = C_{\text{Tw}} + C_{\text{HPC}}$) at the selected $C_{\text{Tw}}/C_{\text{HPC}}$ ratio corresponding to HPC molar fraction in the binary mixture $X_{\text{HPC}} = 0.0048$

$C_{\Sigma} = 5.23 \times 10^{-6}$ M		
X_{HPC}	X_{Tw}	π , mN/m
0	1	15.6
1	0	30.6
0.0048	0.9952	20.7 ($\pi_{\text{cal}} = 15.7$)
$C_{\Sigma} = 6.33 \times 10^{-6}$ M		
X_{HPC}	X_{Tw}	π , mN/m
0	1	17.2
1	0	30.7
0.0048	0.9952	27.2 ($\pi_{\text{cal}} = 17.3$)
$C_{\Sigma} = 8.34 \times 10^{-6}$ M		
X_{HPC}	X_{Tw}	π , mN/m
0	1	19.5
1	0	30.7
0.0048	0.9952	28.9 ($\pi_{\text{cal}} = 19.5$)

obtained will be used to calculate the diffusion coefficients of macromolecules for the analysis of the kinetics of surface tension.

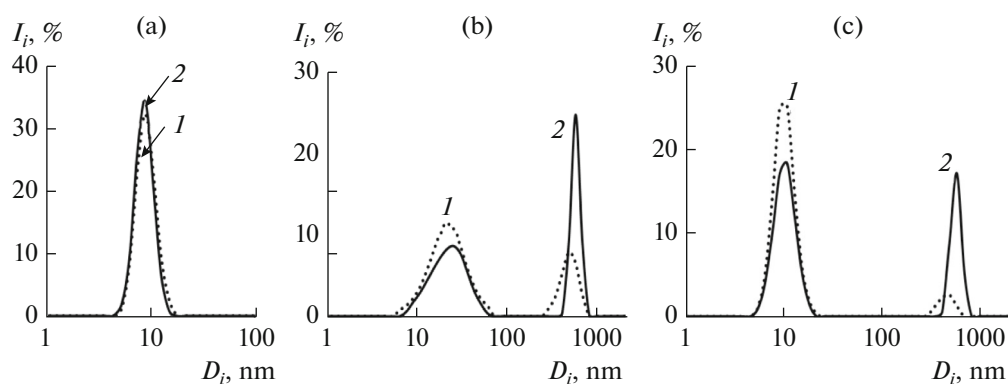


Fig. 9. Differential particle-size distribution curves characterizing intensity (I_i , %) of light scattered by particles with each diameter (D_i) in aqueous solutions with different concentrations. Panel (a): Tw ($C_{\text{Tw}} > \text{CMC}$): (1) 5.8×10^{-3} and (2) 1.2×10^{-2} M, panel (b): HPC ($C_{\text{HPC}} > C^*$): (1) 2.8×10^{-5} and (2) 5.5×10^{-5} M, and panel (c): Tw-HPC binary mixture at a constant component ratio (≈ 1 Tw molecule /HPC unit): (1) 5.8×10^{-3} M Tw + 2.8×10^{-5} M HPC and (2) 1.2×10^{-2} M Tw + 5.5×10^{-5} M HPC.

Analysis of Time Dependences of Surface Tension

The time dependences of the surface tension for aqueous Tw solutions with different concentrations are presented in Fig. 3. It can be seen that, as C_{Tw} increases, the time required to reach equilibrium values of σ markedly decreases (from 2–3 h to 5 min). This agrees with data published on diverse surfactants at fluidic interfaces between phases of different natures [46–49]. It is known that the time required to reach the adsorption equilibrium may be governed by different factors, namely, surfactant diffusion from a bulk solution into a near-surface layer with a thickness of a few molecular radii [50], the existence of an energy barrier [51] that a molecule being adsorbed has to overcome upon the passage from this layer to the surface, and both of these factors [49, 52, 53]. At early stages of surfactant adsorption at fluidic interfaces, diffusion is, as a rule, the rate-limiting step of the process; then, a mixed mechanism is realized; and the overcoming of the energy barrier appears to be the limiting step upon a long-term observation. To verify the hypothesis that the diffusion of NS molecules plays a rate-limiting role, experimental time dependences of two-dimensional pressure were analyzed using an equation derived on the basis of the Fick law and the assumption that the ideal gas equation of state is applicable to an adsorption layer [54]:

$$\pi_t = 2CRT(Dt/3.14)^{1/2}, \quad (1)$$

where π_t is the two-dimensional pressure at time moment t ; C and D are the concentration (mol/m^3) and diffusion coefficient (m^2/s) of a solute, respectively; R is the gas constant; and T is the absolute temperature (K).

The diffusion coefficients that we have calculated for Tw are one to two orders of magnitude lower than the diffusion coefficient for NS molecules in an aqueous medium ($\sim 10^{-10} \text{ m}^2/\text{s}$) [55]. Hence, Tw diffusion does not control the rate of adsorption. Note that the authors of [41] arrived at an opposite conclusion, seemingly due to the fact that σ values for aqueous Tw solutions were measured at times of no longer than 80 s, i.e., at earlier stages of the formation of adsorption layers than those considered in this work.

Under the assumption that the energy barrier plays a key role in the establishment of the adsorption equilibrium, the π_t versus t dependences for Tw solutions in the premicellar concentration range were analyzed on the basis of a kinetic analog of the Langmuir adsorption equation [51]:

$$\ln\left(1 - \frac{\pi_t}{\pi_\infty}\right) = -(\alpha C_{Tw} + \beta)t = -Zt, \quad (2)$$

where π_∞ is the equilibrium two-dimensional pressure and α and β are the adsorption- and desorption-rate constants, respectively.

Note that Eq. (2) is valid for the Henry region, which is characterized by an ideal state of a surfactant

monolayer ($\pi = RT\Gamma$). For different NS concentrations, the values of constant $Z = (\alpha C_{Tw} + \beta)$ were calculated from the dependences of $\ln(1 - \pi_t/\pi_\infty)$ on t in accordance with Eq. (2). The $Z(C_{Tw})$ plot was used to determine the values of the adsorption- and desorption-rate constants, which appeared to be $75 \pm 8 \text{ L}/(\text{mol s})$ and $(5.1 \pm 0.5) \times 10^{-4} \text{ s}^{-1}$. These data enable us to determine adsorption-equilibrium constant $K = \alpha/\beta$ in the Langmuir equation $\Gamma = \Gamma_{\text{max}}KC/(KC + 1)$. The value of K has appeared to be $(1.47 \pm 0.025) \times 10^5 \text{ L}/\text{mol}$. As is known [42], the adsorption-equilibrium constant may also be determined from the value of the surface activity: $K = RTG/\Gamma_m$. Our calculations have yielded $K = (1.70 \pm 0.17) \times 10^5 \text{ L}/\text{mol}$. The satisfactory coincidence between the values of the adsorption-equilibrium constant confirms that the energy barrier plays a limiting role in the kinetics of Tw adsorption.

The $\sigma(t)$ dependences for aqueous HPC solutions of different concentrations are shown in Fig. 4. As the HPC concentration increases, the pattern of the dependences changes drastically. At $C_{\text{HPC}} = (2.1\text{--}3.1) \times 10^{-8} \text{ M}$ (Fig. 4, curves 1, 2), the surface tension remains almost unchanged during the observation (to $\approx 25 \text{ h}$) and appears to be only slightly lower than that of pure water. At $C_{\text{HPC}} = (4.0\text{--}5.1) \times 10^{-8} \text{ M}$, σ values close to the surface tension of the solvent are observed for a rather a long time; then, σ dramatically decreases to reach equilibrium values (Fig. 4, curves 3, 4). Analogous $\sigma(t)$ dependences were observed for solutions of polymers in [26, 40, 43, 56, 57]. Therewith, the time corresponding to the end of the initial portions of the $\sigma(t)$ curves is commonly referred to as an “induction period” (delay time), which, as a rule, diminishes with an increase in the polymer concentration [26, 40, 43, 56, 57], this phenomenon being also observed for our systems. At $C_{\text{HPC}} \geq 5.0 \times 10^{-7} \text{ M}$, the equilibrium values of the surface tension are established actually at once (Fig. 4, curves 5, 6).

Induction periods may be present in the $\sigma(t)$ kinetic dependences for polymer solutions due to both the slow diffusion of macromolecules from a bulk solution to an interface and conformational transformations of adsorbed polymer molecules [43, 56, 57]. Based on the study of the time dependences of the surface tension and the rheological properties of the adsorption layers of HPC ($M_w = 850 \text{ kDa}$) at the interfaces of aqueous solutions with air and oils (triglycerides of caprylic and capric acids), it was concluded that the induction period is caused by the diffusion of macromolecules, while the dramatic decrease in σ is due to conformational transformations of adsorbed macromolecules [26, 40]. The authors of [26, 40] have proposed an original “brush” model of HPC adsorption layers, with this model being consistent with the rigid-chain structure of polymer macromolecules.

The obtained values of the average hydrodynamic radius of HPC macromolecules ($r = 10 \pm 1$ nm) and the Stokes–Einstein equation ($D = kT/6\pi\eta_0r$, where k is the Boltzmann constant and η_0 is the viscosity of the dispersion medium) were used to calculate the diffusion coefficient of HPC macromolecules in an aqueous solution ($D = (2.1 \pm 0.2) \times 10^{-11}$ m²/s), the value of which turned out to be in good agreement with published data. For example, the diffusion coefficient of HPC macromolecules ($M_w = 60$ kDa) determined in an aqueous solution by the interferometric method [56] was 2.7×10^{-11} m²/s. Assuming that the process kinetics is governed by diffusion, the $\sigma(t)$ dependence can be described by Eq. (1). The satisfactory agreement observed between the experimental and calculated $\sigma(t)$ curves for the lowest examined concentration of HPC (2.0×10^{-8} M) indicates that diffusion plays a limiting role. In all other cases, the experimental curves did not correspond to the calculated ones. Moreover, immediately after droplet formation (~ 10 s), the values of surface tension were markedly lower than that of water, and the difference grew with HPC solution concentration. It should be emphasized that the time required to reach equilibrium values of the surface tension for HPC solutions turned out to be markedly longer than that for Tween 80 solutions.

Since the $\sigma(t)$ dependences for the studied systems are governed by the component concentrations, to correctly compare the kinetic curves obtained for solutions of individual components and binary mixtures thereof, it is necessary to properly select their concentrations. For the polymer, a concentration of 4.0×10^{-8} M was chosen at which its specific behavior at a surface is most pronounced (Fig. 4, curve 3). The concentration of the Tw solution was 8.3×10^{-6} M, because it corresponded to the selected C_{Tw}/C_{HPC} ratio in the binary mixture.¹ The corresponding kinetic dependences of the surface tension are presented in Fig. 10. It can be seen that the time required to reach the equilibrium σ values increases in the series Tw (curve 1) < binary mixture (curve 3) < individual polymer (curve 2). Hence, in the case of the binary mixture, Tw molecules are first to be adsorbed. At the same time, the equilibrium σ values for the studied solutions decrease in the series Tw > HPC > binary mixture, thereby confirming the existence of the synergistic effect. Thus, it may be assumed that the solution–air interface is covered with a monolayer of NS molecules, with the diffusing macromolecules being attached to them subsequently. The components of the adsorption layer interact with each other via the hydrogen bonding between the ethoxy units of Tw molecules and hydroxyl groups of HPC (Fig. 11).

¹ In all cases, the selected concentrations of the components corresponded to the limiting filling of the adsorption layers.

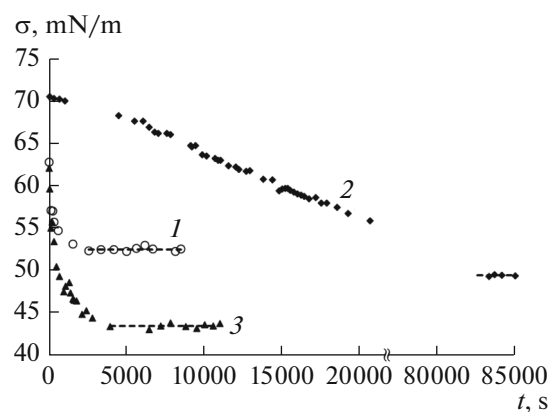


Fig. 10. Time dependences of surface tension for different solutions: (1) Tw (8.3×10^{-6} M), (2) HPC (4.0×10^{-8} M), and (3) their binary mixture (8.3×10^{-6} M Tw + 4.0×10^{-8} M HPC).

Emulsions

The emulsifying ability of the individual components and the Tw–HPC binary mixture (≈ 1 Tw molecule per HPC unit) was studied with respect to decane in an aqueous medium. Freshly prepared oil-in-water emulsions had a monomodal particle-size distribution and a high dispersity (Fig. 12): the values of D_{av} were 200 ± 20 , 250 ± 20 , and 600 ± 50 nm in the cases of Tw, Tw–HPC, and HPC, respectively.

All of the emulsions were unstable with respect to sedimentation. When the dispersion medium contained only HPC, the sedimentation (cream formation) was observed for 10–15 min. For the subsequent ≈ 30 min, a thin decane layer was separated, thereby confirming the occurrence of coalescence. The emulsions stabilized with Tw and the binary mixture remained resistant to sedimentation for 4 and 2 h, respectively. The data obtained suggest that HPC acts as a flocculant both in the presence and (more pronounced) absence of Tw.

Figure 13 shows the flow curves for emulsions stabilized with the individual NS and the Tw–HPC binary mixture, as well as for their dispersion media. An aqueous Tw solution ($C_{Tw} = 3.9 \times 10^{-2}$ M) and a decane emulsion in it exhibited Newtonian behavior, with their viscosities being equal to 2.7 and 3.9 mPa s, respectively. The viscosity of the emulsion calculated by the Einstein equation ($\eta = \eta_0(1 + 2.5\phi)$, where η is the emulsion viscosity and ϕ is the volume fraction of the dispersed phase), appeared to be 4.1 mPa s, which agrees with the experimental value of η .

An aqueous solution of the binary mixture (3.9×10^{-2} M Tw + 1.9×10^{-4} M HPC) was also characterized by Newtonian properties in accordance with the results of rheological tests performed for Tw and HPC solutions previously [29]. However, for the emulsion stabilized with the binary mixture, an anomaly of vis-

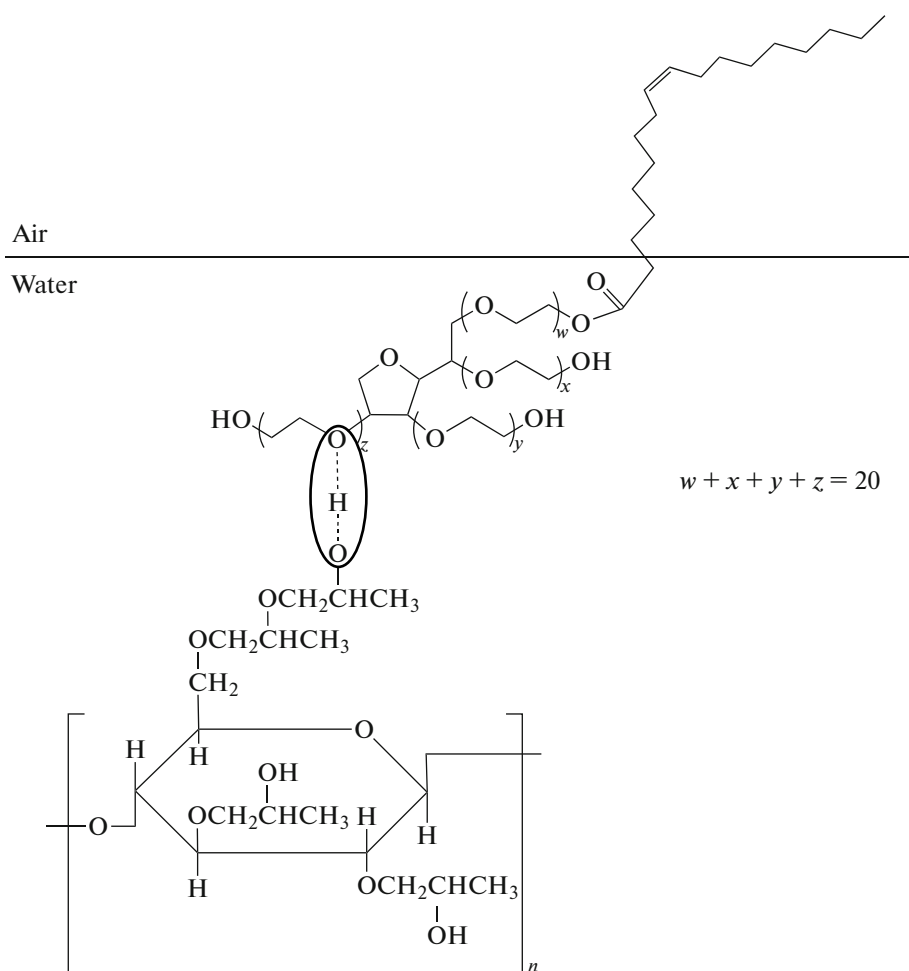


Fig. 11. Schematic representation of a fragment of a Tween 80–HPC mixed adsorption layer at an aqueous solution–air interface.

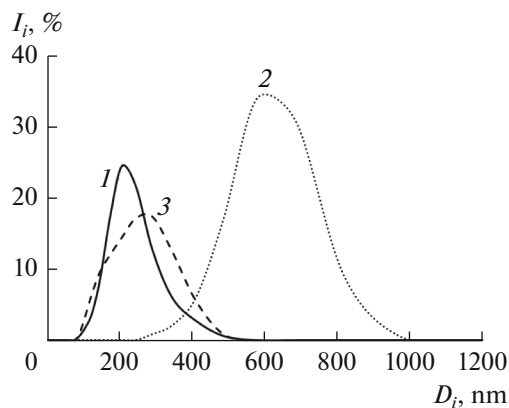


Fig. 12. Differential particle-size distribution curves characterizing intensity (I_i , %) of light scattered by particles with each diameter (D_i) in oil-in-water decane emulsions stabilized with (1) Tw ($C_{Tw} = 3.9 \times 10^{-2}$ M), (2) HPC ($C_{HPC} = 1.9 \times 10^{-4}$ M), and (3) Tw–HPC binary mixture ($C_{Tw} = 3.9 \times 10^{-2}$ M, $C_{HPC} = 1.9 \times 10^{-4}$ M).

cosity was observed, with the apparent viscosity decreasing from 754 to 16 mPa s upon an increase in the shear stress. A drop in apparent viscosity as great as this cannot be associated with the orientational effect alone, and all the more so because the dispersion medium has a constant viscosity value ($\eta = 6.8$ mPa s). The data obtained attest to structuring occurring in the emulsion due to the flocculating action of HPC via the bridge mechanism. Decane droplets stabilized with Tw adsorption layers are probably bonded via “bridges” of HPC macromolecules, with these bridges arising upon the formation of hydrogen bonds between hydroxyl groups of HPC and ethoxy units of Tw.

CONCLUSIONS

Colloid-chemical properties of aqueous solutions of hydroxypropyl cellulose, Tween 80, and binary mixtures thereof with different compositions have been comprehensively studied. The efficiency of a reduction in the interfacial energy under dynamic and static

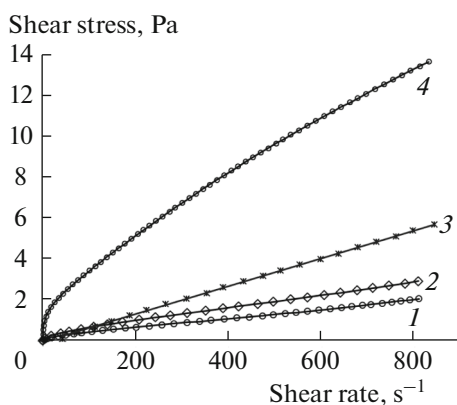


Fig. 13. Flow curves for oil-in-water decane emulsions and their dispersion media: (1) aqueous Tw solution ($C_{Tw} = 3.9 \times 10^{-2}$ M), (2) emulsion in it, (3) solution of Tw-HPC binary mixture ($C_{Tw} = 3.9 \times 10^{-2}$ M, $C_{HPC} = 1.9 \times 10^{-4}$ M), and (4) emulsion in it.

conditions, the surface activity, the capability for self-organization in the bulk and on a surface, and the emulsifying efficiency of the studied systems have been analyzed. In a narrow concentration range and at a certain ratio of the components in the binary mixture, they exhibit a synergistic effect with respect to a decrease in the interfacial energy, with this effect being due to the formation of a Tween 80-polymer bilayer via the hydrogen bonding between the hydroxyl groups of hydroxypropyl cellulose and ethoxy units of Tween 80. The polymer flocculating action, which is realized via the bridge mechanism and leads to a loss in the sedimentation stability of oil-in-water decane emulsions stabilized with Tween 80, also results from the hydrogen bonding between the NS and the polymer.

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