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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Synthesis and Surfactant Properties of Esters of Tall Oil Fatty Acids and Hydroxyl-Containing Polymers

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Abstract—Esters of tall oil fatty acids and hydroxyl-containing polymers were synthesized in the presence of trichloroacetic acid and pyridine. The surfactant properties of the macromolecular esters obtained were evaluated.

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Surface-active polymers came into wide use in the past decades. These polymers are used for controlling rheological properties of dispersions and for stabilizing them. Growing interest in such polymers is due to their high affinity to phase boundaries, irrespective of physicochemical conditions.

One of synthetic routes to surface-active polymers is grafting of hydrophobic chains to a hydrophilic backbone. Among polymers with a hydrophilic backbone are polysaccharides and polyvinyl alcohol (PVA). Among natural surface-active polymers are so-called lipopolysaccharides, e.g., Emulsan. Products based on starch and cellulose with grafted alkyl chains are used as “associating thickeners.” Polymers in which segments with high and low degrees of substitution alternate exhibit the highest surface activity. With respect to the structure, the products obtained can be classed with so-called polymeric brushes, namely, with comb-shaped polymers [1] capable of forming stable self-organizing nanostructures. Modifica-tion of cellulose fibers by esterification not also makes them hydrophobic but also allows addition of various functional groups via the introduced double bonds, so as to impart to the fabrics ion-exchange, bactericidal, fire-retardant, and other properties [2–4].

A suitable way of introducing hydrophobic units into a polymer molecule is esterification with higher fatty carboxylic acids or their derivatives. A promising renewable source of such compounds is tall oil, a by-product from kraft cellulose production. The major components of tall oil fatty acids (TOFAs) are polyunsaturated C_{18} acids: oleic, linoleic, and linolenic.

Esters can be prepared by reaction of free acids with alcohols in the presence of acid catalysts, by reaction of acid anhydrides or halides with alcohols in the presence of catalysts, or by ester interchange of methyl or ethyl esters of acids with the corresponding alcohols in the presence of a base catalyst. The commonly used acid catalysts, sulfuric, perchloric, and arenesulfonic acids, are unsuitable for preparing esters of higher unsaturated acids by direct esterification. In this case, substituted acetic acids in the form of anhydrides are often used. Their action is based on formation in the reaction mixture of mixed anhydrides acylating the hydroxy groups of alcohols, with the subsequent ester interchange. This activation method, though being efficient, requires thorough preparation of the experiments and special precautions. Furthermore, the chemicals used are expensive and difficultly available [5].

Polyvinyl alcohol esters are prepared by reactions with carboxylic acid anhydrides or chlorides in the presence of pyridine or corresponding metal salts [6], or by the treatment with an aliphatic acid in the presence of a metal salt [7].

The goal of this study was preparation of esters of hydroxyl-containing polymers (polyvinyl alcohol and water-soluble starch) and tall oil fatty acids and evaluation of surfactant properties of the esters obtained.

EXPERIMENTAL

The physicochemical properties and composition of TOFAs (Segezha Pulp-and-Paper Combine, Joint-Stock Company; extra grade) met the requirements of GOST (State Standard) 14845–79. Tall oil fatty acids are a pale yellow oily liquid with a specific odor. The fatty acid content was 97.5 wt %; moisture content, less than 0.03 vol %; acid number, 197 mg KOH/g; iodine number, 160 g I_2/100 g; weight fraction of resin acids, 1%; weight fraction of unsaponifiables, 1%; coloration (iodine scale), 7. The polyvinyl alcohol was partially saponified polyvinyl acetate, PVA 18/11. We also used water-soluble potato starch (GOST 10163–76), trichloroacetic acid (chemically pure grade), and pyridine (chemically pure grade, dried over KOH and distilled). All the substances were dried by keeping in a vacuum (1 mm Hg, 48 h, 50°C). The spectra of the starting substances and modified products were recorded on a Shimadzu FTIR-8400S spectrometer (Nujol mulls). The surfactant properties of the initial polymers and synthesized fatty acid esters in aqueous solutions (decrease in surface tension, foam-forming and emulsifying properties) were evaluated by appropriate standard procedures.

Determination of the mean size of dispersed phase particles by the method of turbidity spectra is widely used for studying complex polymeric systems of heterogeneous structure [8, 9].

The optical density D of disperse systems was measured with a KFK-3 photocolorimeter (cell length l–2 cm) in the wavelength range 414–864 nm. The measurement error was 4.8%. The surfactant adsorption was studied gravimetrically [10]. As adsorbents we used coniferous bleached kraft cellulose and AGS-4 activated coal.

A weighed portion of cellulose (2 g) was preliminarily allowed to swell in 50 ml of water for 24 h. Activated coal was sieved to remove the fine fraction.

The adsorbent was treated with 50 ml of a surfactant solution for the time required to attain the adsorption equilibrium (usually 24 h). Then the adsorbent was separated from the solution by filtration and air-dried to a constant weight. The specific adsorption A (g surfactant/g adsorbent) was calculated by the formula

$$A = \frac{M_2 - M_1}{M_1},$$

where M_1 and M_2 are the adsorbent weights before and after adsorption, respectively.

To study the desorption, air-dry adsorbent samples were placed into 100 ml of water and left for 24 h, after which they were treated by the procedure described above. The amount of the surfactant retained on the adsorbent after desorption, Q (g surfactant/g adsorbent), was determined by the formula

$$D = \frac{M_3 - M_1}{M_1},$$

where M_3 is the adsorbent weight after desorption.

The emulsifying power as the capability to disperse an insoluble liquid and ensure aggregative stability of the resulting emulsion can be characterized by the emulsion type (oil/water, O/W; water/oil, W/O) and its resistance to coalescence. An emulsion was prepared by vigorous shaking in a volumetric cylinder of equal volumes of water, oil, and surfactant solution [11]. The emulsion type was determined by several procedures (dye solubility, phase dilution, wetting of filter paper). The foaming power was determined by beating up 10 ml of a surfactant solution of a definite concentration in a volumetric cylinder for 10 min. The resulting foam was evaluated by the foam volume, stability, and foam ratio [11, 12].

As shown previously [13], hydroxyl-containing polymers can be esterified not only with chlorides or anhydrides of fatty acids, but also with the acids themselves in the presence of readily available reagents: trichloroacetic acid and pyridine. As starting polymers we chose polyvinyl alcohol and water-soluble starch, which are widely used in industry. The esterification conditions are similar to those previously described above. Because of higher lability of interunit bonds in starch, the reaction temperature in this case did not exceed 50°C, and with polyvinyl alcohol it was 70°C. We prepared products of starch modification with the degree of substitution (DS) of 0.45, and those of polyvinyl alcohol modification with DS 0.03 and 0.06 (MPVA, run nos. 1 and 2, respectively).

The occurrence of the esterification is proved by comparison of the IR spectra of the initial and modified polymers. The peak at 1730 cm^{-1}, corresponding to stretching vibrations of ester C=O groups, appears in the case of starch and becomes stronger in the case of PVA (in the initial polymer, it corresponds to residual acetyl groups). In addition, in the spectra of the modified products, bands in the range 1680–1620 cm^{-1}, corresponding to stretching vibrations of double bonds

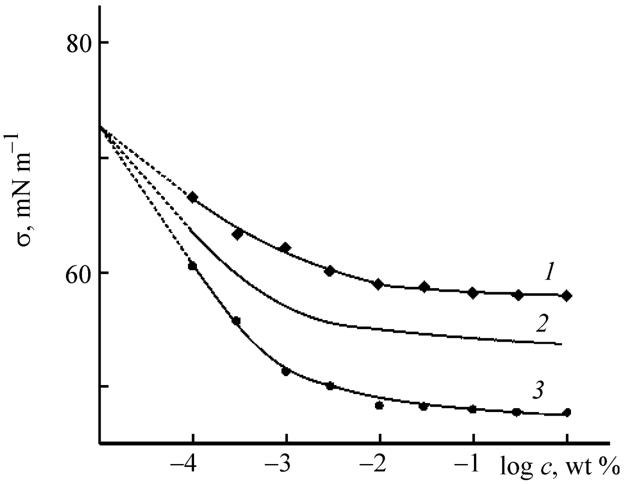

Fig. 1. Isotherms of surface tension σ of PVA and its esterification products: (*1*) PVA; (*2*) PVA, run no. 1 (DS 0.03); and (*3*) PVA, run no. 2 (DS 0.06). (*c*) Concentration; the same for Fig. 2.

in nonconjugated alkenes, increase in the intensity, which may be due to unsaturated nature of TOFAs. At the same time, there are no bands characteristic of auxiliary reagents used in the synthesis, such as C–Cl stretching bands (800–600 cm^{-1}).

To evaluate the surfactant properties of the esters obtained, we plotted the isotherms of the surface tension σ on the surfactant aqueous solution–air phase boundary, which was determined by the Du Nouy method, in the coordinates σ = *f*(*c*) and σ = *f*(log *c*), where *c* is the concentration of the surfactant solution. It should be noted that the film of the macromolecular surfactant adsorbed on the liquid surface can be readily removed by single dipping and withdrawal of a ring. Restoration of the equilibrium on the liquid–gas phase boundary requires much time, and with an increase in the length of pendant hydrocarbon groups the rate of formation of the adsorption layer decreases. This may be due to slow diffusion of macromolecules to the phase boundary and to relaxation processes occurring in the adsorption layer, as well as to a combined effect of both factors.

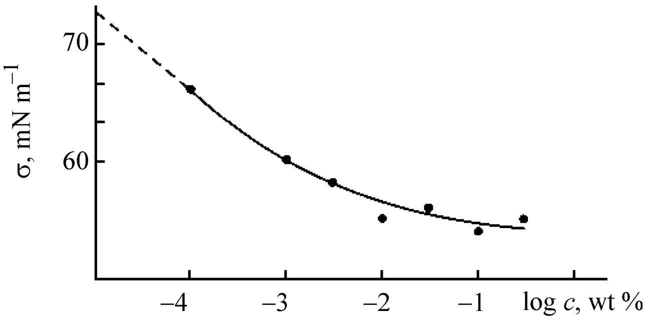

Fig. 2. Isotherms of surface tension σ of esterified starch.

As seen from Figs. 1 and 2, with an increase in the concentration the surface tension initially decreases, and in this concentration range the solutions are homogeneous. Starting from a definite solution concentration, the surface tension does not noticeably change, which is due to micelle formation, with the solution becoming heterogeneous. This transition is fairly smooth even when surface tension isotherms are plotted in the semilog coordinates, i.e., there is a relatively broad region of transition from the homogeneous state to the heterogeneous solution state. To determine the point of this transition more accurately, we constructed tangents to the branches of the surface tension isotherm. The point of their intersection corresponds to the critical micelle concentration. As in the surface tension isotherm in the homogeneous region there is no clear transition from the curvilinear to linear portion, it is impossible to determine the point at which the limiting adsorption Γ_m is reached.

The surface activity is evaluated most frequently by the adsorption and adsorption energy [8]. The basic equation is the Gibbs adsorption equation characterizeing the dependence of a decrease in the surface tension on the saturated vapor pressure and mutual solubility of the liquids, and also on the dynamics of surfactant molecules on the phase boundary surface, caused by the surfactant solubility. Using this equation, we calculated the adsorption Γ at 295.15 K.

Then we determined from the Langmuir equation the adsorption energy *W*, i.e., the energy gain from transfer of a molecule from the bulk of the phase to its surface, assuming the surface layer thickness δ to be equal to 1×10^{-9} m.

The calculated values of the limiting adsorption Γ_m and work of adsorption *W* are given in Table 1. As the adsorption of macromolecular compounds is irreversible, the calculated values of Γ and *W* are relative.

From Γ_m, it is possible to calculate the landing area and length of the molecule. For macromolecular compounds, Γ_m is determined by the monomeric unit size, and in more concentrated solutions, by the globule size. There are no grounds to speak of a definite orientation of a molecule on the surface, because the same value of Γ_m can be obtained at both vertical and horizontal orientation.

The absence of a minimum in the surface tension isotherm in the region of the critical micelle concentration (CMC) suggests the absence of impurities in the substances.

Introduction of pendant alkyl groups into the molecule leads not only to a decrease in CMC, but also to a more pronounced decrease in the surface tension compared to the initial polyvinyl alcohol. The effect grows in proportion with the degree of substitution with fatty acid residues. This fact is apparently due to diphilic nature of polymeric molecules and to alternation of segments lyophilic and lyophobic with respect to the dispersion medium. For the same reason, modified starch, in contrast to the initial starch, becomes surface-active.

Of the two PVA modification products, we chose for further comparative studies the sample with a higher degree of substitution (MPVA, run no. 2), because of its highest surface activity.

To estimate the mean size of colloidal particles in the solution of the modified PVA, we calculated the parameter $m = 1.19$ and experimentally determined the parameter $n = 1.757$. The parameter α determined from characteristic tables was 2.7, and r was 217 nm. Hence, the particle size is comparable with the wavelengths in the visible range.

An important characteristic of the substances obtained, determining their possible applications, is adsorption on the surface of solids, because adsorption layers strongly affect the interaction of the contacting phases.

Table 1. Experimental colloid-chemical parameters of surfactants

Substance	$\Gamma_m \times 10^6$ mol m^{-2}	CMC, wt %	G, mJ m kg^{-1}	W, kJ mol^{-1}
PVA	0.81	0.01	15.9	30.86
MPVA:				
run no. 1	1.58	0.003	61.5	34.59
run no. 2	2.46	0.003	117.0	36.52
Starch ester	2.72	0.01	44.1	33.78

The adsorption value sharply increases even at low concentrations (Figs. 3–6), which reflects high affinity of the adsorbate for the surface. As can be seen, the adsorption of the products is higher than that of the initial substances, which is due to an increase in the molecular weight on introducing long-chain acid residues.

The adsorption of starch on cellulose and activated coal and of PVA on coal reaches saturation at a concentration close to CMC. Adsorption of esterified starch on these adsorbents and of modified PVA on coal continues to uniformly increase after saturation of the adsorbent with the first layer of the polymer macromolecules, which may be due to aggregative mechanism of adsorption [14]. At the same time, the adsorption isotherms of PVA and its ester on cellulose pass through a maximum. This fact is attributable to specific features of adsorption of separate macromolecules and their aggregates on the adsorbent surface, and also to the conformation of macromolecules in solution.

Activated coal is characterized by a polydisperse pore structure with a polymodal pore volume distribu-

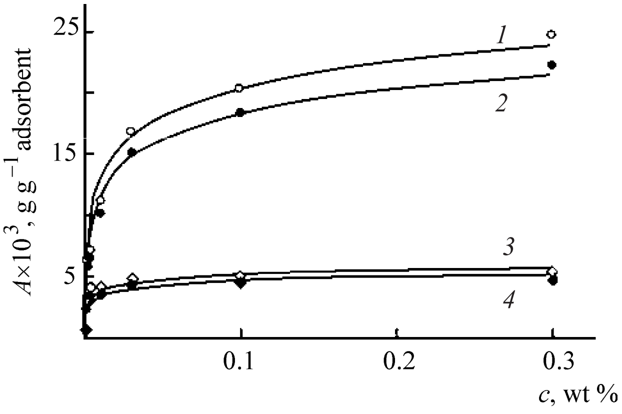

Fig. 3. (*1, 3*) Adsorption and (*2, 4*) desorption of (*3, 4*) PVA and (*1, 2*) MPVA (run no. 2) on coal. (*A*) Sorption and (*c*) concentration; the same for Figs. 4–6.

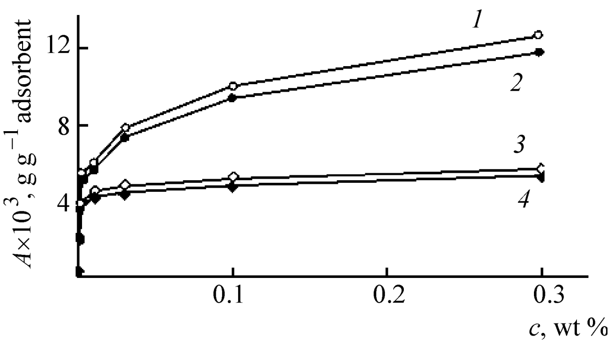

Fig. 4. (*1, 3*) Adsorption and (*2, 4*) desorption of (*3, 4*) starch and (*1, 2*) its modification product on coal.

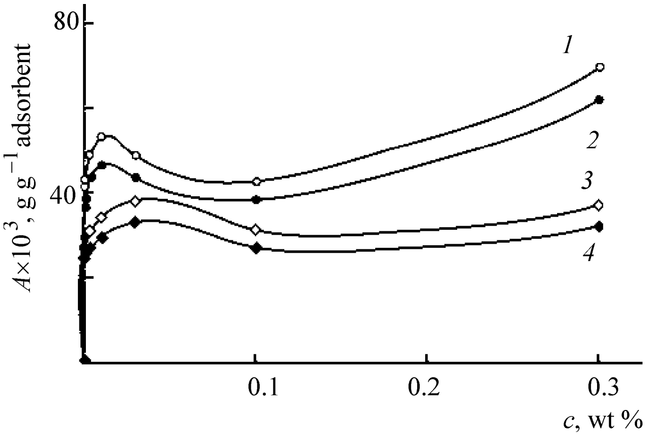

Fig. 5. (*1, 3*) Adsorption and (*2, 4*) desorption of (*3, 4*) PVA and (*1, 2*) MPVA (run no. 2) on cellulose.

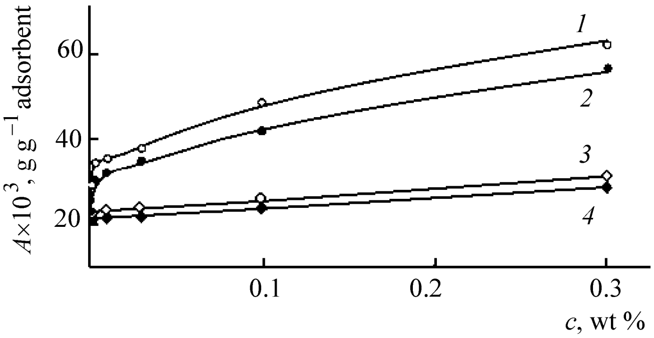

Fig. 6. (*1, 3*) Adsorption and (*2, 4*) desorption of (*3, 4*) starch and (*1, 2*) its modification product on cellulose.

tion. As a rule, it contains chemically bound oxygen forming basic or acidic surface compounds [15]. AGS-4 coal used in this study contains on its surface so-called acidic surface oxide C adsorbing basic substances from solution. In this case, the adsorbent surface does not interact specifically with the adsorbates under consideration. Therefore, the adsorption isotherms of the examined substances on activated coal are similar in shape.

Apparently, in the case of activated coal the decisive factor in adsorption is the character of the interaction between the adsorbate and adsorbent surface. For the adsorption on cellulose, the conformation of adsorbate macromolecules in solution plays a more significant role. Macromolecules of PVA in solution can occur as coils. Amylose molecules in solution are flexible helices. The helix size decreases with an increase in pendant chains. Therefore, amylopectin of equal molecular weight is more compact [16]. In our case, the number of the introduced pendant chains is not very large. Therefore, appearance of a maximum in the adsorption isotherm of modified starch can be expected only at increased degrees of substitution.

It is known that the adsorption becomes to a greater extent irreversible with a decrease in the solvent strength and with an increase in the molecular weight of the polymer and in the strength of bonding with the adsorption centers. The desorption is low for all the substances under consideration, which may be due to strong intermolecular bonds between the adsorbent and polymer, as well as between separate macromolecules and aggregates of the adsorbate.

Stable adsorption of the products obtained and the possibility of adding various functional groups via double bonds of fatty acid residues, so as to impart to the adsorbate surface ion-exchange, bactericidal, fire-retardant, and other properties, will make these products promising for various applications, e.g., in medicine.

At the same time, the adsorption properties of the surfactants obtained allow their use in processes associated with the preparation and treatment of cellulose fibers: in forming of paper sheets and in purification of printer's ink in the course of paper waste processing by preventing redeposition of impurities (tars, ink particles, etc.) on the fiber surface. In addition, the effect of adsorption layers of polymers on the surface of colloidal and dispersed particles is an important factor governing the stability of disperse systems or their tendency to flocculation.

In this study we examined the emulsifying power of the initial hydroxyl-containing polymers and their esters in the water–organic solvent systems, with octane, chloroform, 1-butanol, and cyclohexanol taken as the organic phase.

At low surfactant concentrations (*c* 0.00005%) in the water–organic solvent system, a small number of fine oil drops are observed in the bulk of the aqueous phase. With an increase in the surfactant concentration, the amount and stability of these drops increase considerably, and starting from a concentration of 0.005% the products form stable O/W emulsions. It should be taken into account, however, that nonionic surfactants with large polar and nonpolar molecular segments in ternary systems can give phases of different structures.

Starch in the systems under consideration does not exhibit emulsifying properties. At the same time, its ester exhibits dispersing properties with respect to chloroform and octane, and with butanol a poorly stable emulsion is formed.

The results of studying water–organic solvent–surfactant systems are given in Table 2.

Comparison of the volume and stability of emulsions formed with the same organic phase by solutions of PVA and its ester of equal concentrations shows that the modified PVA is a stronger emulsifying agent. The emulsions formed with PVA were stable for 20 days, whereas the emulsions formed with the modified PVA were stable for a longer period.

In accordance with Rebinder's rule of polarity equalization [8], the capability to form emulsions is directly related to the solvent polarity. Therefore, the stability of aqueous–organic emulsions formed with the modified PVA increases in the order octane, 1-butanol, cyclohexanol. With chloroform, mixing of the organic phase and aqueous solution is accompanied by formation of a gelatinous structure. Probably, with an increase in the amount of fatty acid substituents in PVA and starch to a definite level of the hydrophilic–lipophilic balance their emulsifying power will increase.

Table 2. Emulsifying power of surfactants in water–organic solvent systems

Surfactant concentration in aqueous phase, wt %	Volume, vol %					
	organic phase		O/W emulsion		aqueous phase	
	1 min	10 min	1 min	10 min	1 min	10 min
Octane solvent						
Modified polyvinyl alcohol						
0.005	32	32	3	3	66	66
0.015	29	30	13	7	58	63
0.05	0	2	58	42	42	57
0.15	0	0	83	48	17	52
Polyvinyl alcohol						
0.05	1	17	56	25	43	58
1-Butanol solvent						
0.005	3	23	97	68	0	8
0.015	10	10	90	82	0	8
0.05	1	17	99	83	0	0
0.15	0	1	100	99	0	0
Polyvinyl alcohol						
0.05	2	22	98	74	0	4
Modified starch						
0.015	4	33	86	2	10	66
Cyclohexanol solvent						
Modified polyvinyl alcohol						
0.005	0	5	96	82	4	13
0.015	0	12	100	88	0	0
0.05	0	0	100	100	0	0
0.15	0	0	100	100	0	0

Table 2. (Contd.)

Surfactant concentration in aqueous phase, wt %	Volume, vol %					
	organic phase		O/W emulsion		aqueous phase	
	1 min	10 min	1 min	10 min	1 min	10 min
Chloroform solvent						
Modified polyvinyl alcohol						
0.005	0	0	40	37	60	63
0.015	0	0	47	39	53	61
0.05	0	0	52	37	48	63
0.15	0	0	58	35	42	65
Polyvinyl alcohol						
0.05	0	0	52	40	48	60

Table 3. Foam volume at various concentrations for esterified (in parentheses, for initial) PVA

c, wt %	V_f, ml, at indicated time, min							
	0.02	0.5	1.0	2.0	4.0	5.0	7.0	10.0
0.001	1.8 (1.5)	1.2 (0.9)	0.8 (0.4)	0.3 (0.2)	0.1 (–)	– (–)	– (–)	– (–)
0.003	3.6 (3.0)	2.6 (2.4)	2.2 (2.0)	1.8 (1.6)	1.5 (1.1)	1.3 (0.9)	1.1 (0.8)	1.1 (0.8)
0.01	6.5 (5.8)	5.0 (4.2)	4.2 (3.8)	3.8 (3.5)	3.2 (2.8)	3.0 (2.6)	2.7 (2.4)	2.6 (2.0)
0.03	14.8 (14.0)	8.4 (8.2)	8.0 (7.7)	7.4 (7.3)	7.0 (6.7)	6.7 (6.5)	6.0 (5.8)	4.4 (4.0)
0.1	17.0 (15.0)	14.6 (14.0)	13.2 (13.0)	12.3 (11.2)	11.2 (10.2)	10.1 (8.9)	8.0 (7.4)	7.5 (4.4)

As the modified products form more stable aqueous emulsions with polar solvents than do the initial substances, these products can find wide applications in fields where such emulsions are used. Combination of good emulsifying and adsorption properties with the possibility of grafting of new functional groups opens wide prospects for using the esters obtained in cosmetic and pharmaceutical industry.

Table 4. Characteristics of the foam-forming power of PVA and its ester

c, wt %	Foam volume, ml		Foam ratio	
	PVA	MPVA, run no. 2	PVA	MPVA, run no. 2
0.001	1.5	1.8	3.0	3.7
0.003	3.0	3.6	3.6	4.0
0.01	5.8	6.5	4.5	5.0
0.03	14.0	14.8	4.7	5.3
0.1	15.0	17.0	5.5	6.5

The results of evaluating the foam-forming power are given in Tables 3 and 4.

With an increase in the surfactant concentration, the foaming of solutions increases (Table 4) even after reaching CMC, up to the maximal examined concentration. For low-molecular-weight surfactants, in the CMC region the formation of the adsorption layer is complete, and it acquires the maximal mechanical strength. As noted above, for esterification products the surface layer formation continues with a further increase in the surfactant concentration in solution (above CMC), which is confirmed by the

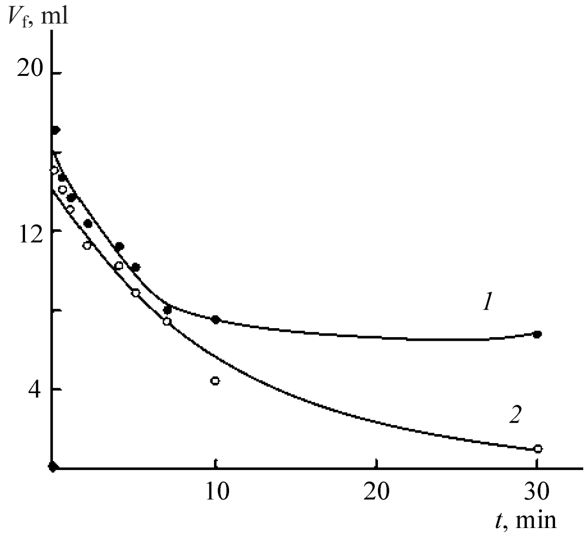

Fig. 7. Foam volume V_f as a function of time t (surfactant concentration 0.1%). (*1*) MPVA, run no. 2 and (*2*) PVA; the same for Fig. 8.

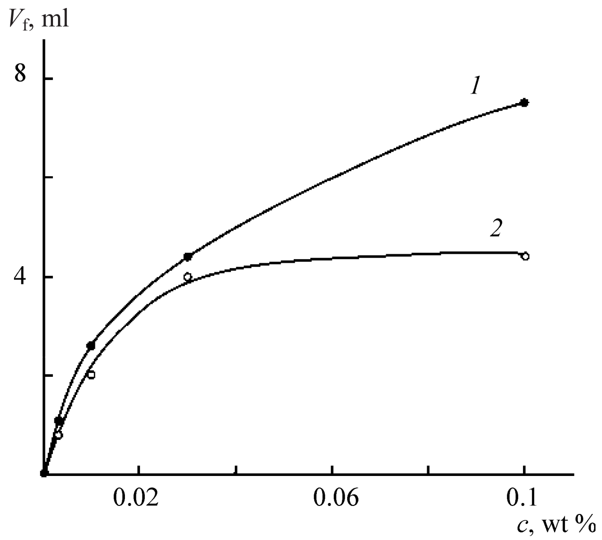

Fig. 8. Foam volume V_f as a function of concentration c (time 10 min).

results of studying the surface tension and adsorption of surfactants on solid adsorbents.

Table 3 shows that the volume of the foam obtained with the modified PVA is larger than that of the foam obtained with the initial PVA. The stability of foams in 10 min in the surfactant concentration range 0.001–0.03% is close in both cases. However, at a surfactant concentration of 0.1%, after the lapse of 7 min the foam obtained with the modified PVA becomes considerably more stable than that obtained with the initial PVA. This is clearly seen from Figs. 7 and 8.

The starch ester in all the concentrations gives a poorly stable foam (its life is several seconds) of a small volume. Probably, with an increase in the amount of fatty acid substituents in starch to a definite level of the hydrophilic–lipophilic balance, its foam-forming power will increase.

Although the modified PVA, like the initial PVA, exhibits a moderate foam-forming power, it can be used to enhance foaming in combination with other surfactants, especially anionic.

CONCLUSIONS

(1) Esters of hydroxyl-containing polymers (polyvinyl alcohol and starch) were synthesized by esterification with tall oil fatty acids in the presence of trichloroacetic acid and pyridine.

(2) The synthesized esters of tall oil fatty acids and hydroxyl-containing polymers exhibit surfactant properties. The critical micelle concentration of these products is lower than that of the initial polymers.

(3) The surface activity of the synthesized esters is not high, but they can be used, along with the known macromolecular surfactants, as stabilizers of moderately concentrated disperse systems such as emulsions and foams.

(4) The synthesized esters combine good emulsifying and adsorption properties. With polar organic solvents they form more stable aqueous emulsions than with nonpolar solvents.

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