eISSN: 2349-5715 pISSN: 2349-5707

Volume: 10, Issue 10, Okt-2023 SJIF 2019: 4.702 2020: 4.737 2021: 5.071 2022: 4.919 2023: 6.980

УДК 541(64+49):547(458.82+39)

COLLOID-CHEMICAL PROPERTIES OF POLY-COMPLEXES BASED ON 1,4-DIMALEATEDIOXYETHANACRYLATE HEPTYL ETHER MONOETHANOLAMINE SALT WITH POLYACRYL ACID

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Abstract. : The emulsifying and foaming ability of a poly-complex based on the monoethanolamine salt of 1,4-dimaleatedioxyethaneacrylate heptyl ester with polyacrylic acid was studied. A synergistic effect of the compositions 0.5:0.3; 0.4:0.7 in the stabilization of foams and emulsions has been established due to a decrease in the surface tension of solutions and mainly due to the formation of a spatial structure in the interfacial adsorption layer, which creates a structural-mechanical barrier.

Keywords: foam stabilization, emulsifying ability, foaming ability, complex, adsorption layer, synergistic effect, intermolecular interactions, foam resistance.

Introduction. One of the global tasks of modern chemistry is the purposeful creation of compounds with predetermined properties and the development of controlled technological processes for obtaining complex multicomponent systems. This is what today determines the progress of many areas of science and the national economy.

The amphiphilic structure of the studied polymers determines their surface-active properties. Macromolecules, as well as molecules of low molecular weight surface-active (nonionic surfactants) substances, being adsorbed at the phase boundaries, reduce the excess of interfacial surface energy. In the process of spontaneous physical adsorption, at the "liquid-gas" interface, the surface tension of solutions decreases, and the surface-active groups of macromolecules are localized at the interface, while the polar (surface-inactive) areas are associated with them in the solution. Hydrophilic (polar) groups of polymer macromolecules provide solubility in water, while hydrophobic (nonpolar) groups impart a known affinity for nonpolar phases [1–3].

In [4–6], the interaction of polymethacrylic acid (PMAA) with surfactants based on polyethylene glycol in aqueous solutions was studied by viscometry and potentiometric titration. It has been established that complex formation depends on the hydrophilic-hydrophobic balance and on the surfactant concentration. The presence in the elementary chain of a macromolecule of a large number of hydroxyl and carboxyl groups capable of forming intra- and intermolecular hydrogen bonds, along with the surface activity of macromolecules, promotes spatial structure formation in adsorption layers. And this gives mechanical strength to the films formed at the liquid-gas, liquid-liquid interfaces, this allows us to assume the presence of foaming and emulsifying properties of the studied polymer mixtures [7-12].

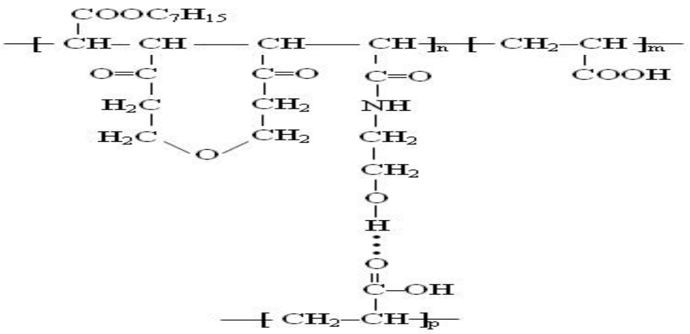
The foaming and emulsifying ability of mixtures of water-soluble polymers has not been practically studied, and therefore the study of foams stabilized by them is of particular interest.

Methods and Materials

Turbidimetric titration was used to obtain a poly-complex of the monoethanolamine salt of polyacrylic acid and the heptyl ester of 1,4-dimaleatedioxyethaneacrylate. When titrating a solution of a copolymer of monoethanolamine salt of heptyl ester of 1,4-dimaleatedioxyethane acrylate

(MASHEM) with a solution of polyacrylic acid (PAA), a poly-complex is formed containing an excess of non-ionic MASHEM, in a ratio of 1:1. The molecular weight of MASHEM, determined from the intrinsic viscosity of its aqueous solution at 250C according to the formula [η]= 4.1-10-4 M0.5, was 5.5×103, PAA with a molecular weight (MW) equal to 6.8×103, calculated according to [η]=4.9-10-4 M0.5 based on the data of viscometric studies at 25°C in 0.02 N aqueous solution of HC1.

Scheme of the formation of hydrogen bonds between MASHEM with PAA



Foaming capacity was determined by shaking for 30 seconds. A solution of a mixture of polymers of a certain concentration with a volume of 200 ml, in a cylinder with a capacity of 1000 cm3.

The emulsifying ability of solutions of the copolymer complex was studied by determining the dependence of the stability of direct emulsions of benzene - an aqueous solution of polymer complexes to coalescence over the time of release of ½ part of the hydrocarbon.

Results and Discussions

The data on the concentration dependence of the volume of foams, stabilized complexes of MASHEM with PAA shows (Fig. 1) that an increase in the concentration of individual components, as well as their concentration in the mixture, contributes to a monotonous increase in the volume of the foam due to the formation of a saturated adsorption layer with a high structural viscosity. The foaming ability of mixtures of MASHEM with PAA is much better than that of individual polymers, which is probably due to the formation of stronger mixed interfacial adsorption layers.

Tables 1 and 2 show the results of a study of the kinetics of destruction of foams, coefficients of foam resistance, as well as the multiplicity of foams. The table shows that the foams are quite stable for 30 minutes. An analysis of the data in Table 2 on the foaming ability of the MASHEM complexes with PAA shows that the complex exhibits a synergistic effect in stabilizing foams and foam volume. Also, the stability sharply increases for compositions 0.5:0.3; 0.4:0.7, which is associated with the formation of an intermacromolecular adsorption complex, which, apparently, makes the main contribution to the stabilization of foams.

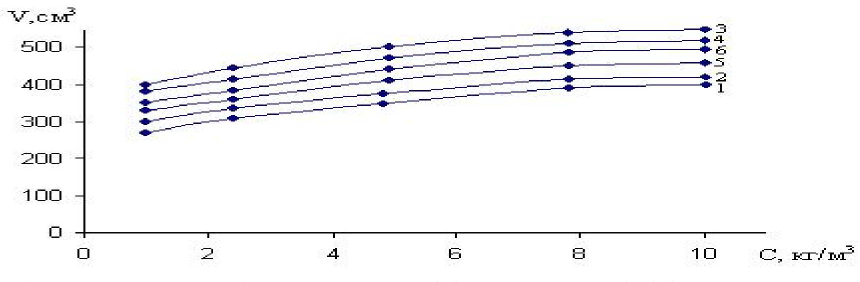


Fig.1. Dependence of the volume of foams at the initial moment on the concentration of solutions of MASGEMA complexes with PAA at 2980K and in the compositions: 1 - 1:1; 2-0.2:0.6; 3 - 1:0.2; 4-0.8:0.2; 6 - 0.6:0.4; 5-0.2:0.6.

Table 1

Foaming capacity of monoethanolamine salt of 1,4-dimaleatedioxyethaneacrylate heptyl ester (MASHEM) and acrylic acid (PAA) at 2980K

Polymer	C, kg/m^3	Foam volume (cms^3) per (minute)						Foam resistance coefficient		multiplicity
		V_0	1	5	10	30	60	Y_5	Y_{30}	
MASHEM	1,0	300	195	180	170	120	80	0,600	0,400	1,50
	2,5	335	225	215	195	160	130	0,641	0,478	1,62
	5,0	380	245	225	205	185	165	0,592	0,487	1,85
	10,0	435	365	330	290	265	220	0,758	0,379	2,18
PAA	1,0	0	0	0	0	0	0	0	0	0

Table 2

Foaming capacity of MASHEM +PAK complexes at 2980K

Polymer	C, кg/m^3		Foam volume (cm^3) per (minute)					Foam resistance coefficient		multiplicity
		V_0	1	5	10	30	60	Y_5	Y_{30}	
MASHEM +PAA 1,0:0,2	1,0	395	290	245	200	170	125	0,620	0,430	1,98
	2,5	435	325	290	250	205	155	0,667	0,471	2,17
	5,0	515	440	365	335	290	235	0,709	0,563	2,57
	10,0	545	460	420	375	345	295	0,771	0,633	2,72

The study of the influence of the pH environment on the foaming ability of polymer complexes (Fig. 2) showed that the maximum foaming occurs in the region of pH=5-6 for the studied complexes. An increase and decrease in pH leads to a decrease in foaming capacity due to an increase in the surface tension of polymers under the influence of low molecular weight electrolytes.

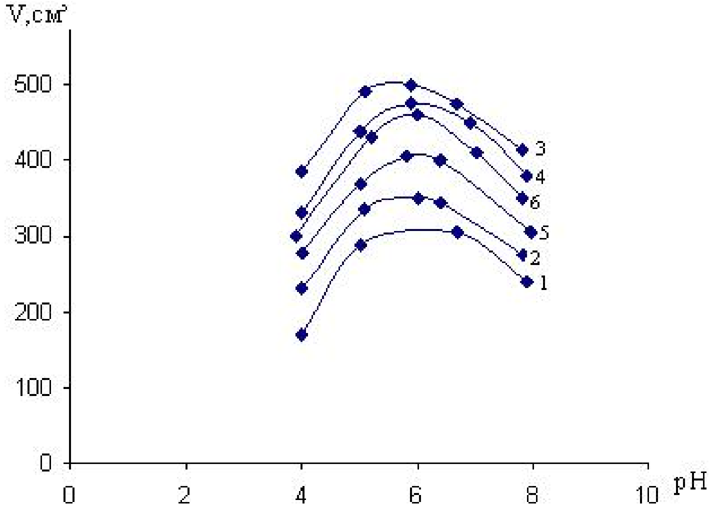


Fig.2. The dependence of the volume of foams at the initial moment on the pH of the MASHEM + PAA complexes at 2980 K and in the compositions:
1 – 1:1; 2-0,2:0,6; 3 – 1:0,2; 4- 0,8:0,2; 6 – 0,6:0,4; 5 – 0,2:0,6.

The study of the dependence of the stability of emulsions on the concentration of aqueous solutions of MASHEM, PAA, as well as their complexes showed that a sharp increase in the stability of emulsions (τ1/2) begins at a concentration of polymers in the amount of (10-3 kg/m3) due to an increase in the content of macromolecules on the interfacial surface, and strengthening of intermolecular interactions (Fig. 3). The studied polymers are characterized by an increase in the stability of emulsions stabilized by mixtures of MASHEM with PAA composition (0.5:0.3); and (0.4:0.7). The increase in the stability of emulsions stabilized by mixtures of polymers compared to the stability of emulsions stabilized by individual components is apparently associated with the stabilizing effect of polycomplexes on emulsions. The ratios of MASHEM and PAA formed in this region and causing the formation of mixed adsorption layers with additional intermolecular adhesion contacts, imparting mechanical strength to these adsorption layers. Apparently, the stabilizing effect of macromolecules, as well as their complexes, is not so much in changing the surface tension as in the formation of a structural-mechanical barrier that ensures the stability of emulsions. The strength of this barrier is due to the system of intermolecular (hydrogen) bonds between –OH and -COOH groups of macromolecules and the formation of a three-dimensional spatial structure in solution. The decisive role of H-bonds in the formation of a spatial structure is evidenced by the fact, known from the literature [13], that with an increase in temperature, the stability of an emulsion stabilized by both MASHEM and PAA drops sharply. Along with the formation of the spatial structure of the interfacial adsorption layer at the phase boundary, the spontaneous appearance of a microemulsion of oil microdroplets in water [13], which also creates a structural-mechanical barrier, is possible. Thus, the resistance to coalescence of benzene droplets is due to the adsorption layers of polymer complexes, these layers are strong due to the formation of H-bonds between segments of both homogeneous and heterogeneous macromolecules.

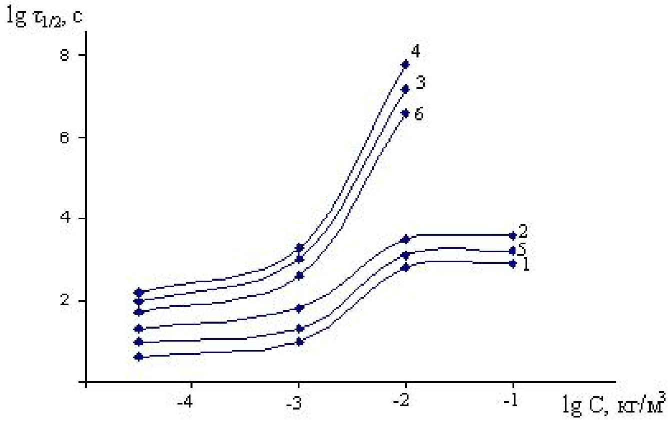


Fig. 3 Dependence of the half-life of the emulsion on the logarithm of the concentration of aqueous solutions of the MASHEMA + PAA complexes

Conclusion. Thus, the study of the foaming and emulsifying ability of MASHEM with PAA revealed a synergistic effect of the compositions 0.5:0.3; 0.4:0.7 (that is, according to the thermodynamically stable ratio of complexes in solutions) It is formed due to the stabilization of foams and emulsions by reducing the surface tension of solutions and mainly due to the formation of a spatial structure that creates a structural-mechanical barrier.

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