

Multifunctional modifier for regulating the properties of concrete mixtures

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Abstract. The purpose of this work is the synthesis of new high-molecular surfactants polyalkylacrylates and the establishment of correlations between their colloidal chemical properties. Well-known methods for the synthesis and determination of the properties of surfactants were used. New high molecular surface-active substances (HMSAS) were obtained based on the reaction of polymer-analogous transformations. The resulting copolymers contain side hydrocarbon radicals of various lengths. Polyalkylacrylates were obtained by esterification with aliphatic alcohols (butyl, octyl, decyl) in a mixture of organic solvents and the presence of a catalyst, sulfuric acid. The surface activity and foaming ability of the obtained new HMSAS in aqueous solutions have been studied. The results obtained showed that with an increase in the length of the aliphatic hydrocarbon radical in the chain of macromolecules, the surface activity of polyalkylacrylates increases. An analysis of the results showed a good correlation between foaming and surface activity of the investigated HMSAS. Based on research, it was found that the stability of the foams is largely determined by the interaction of the HMSAS molecules in the monolayer.

1 Introduction

At present, plasticizers are widely used in the construction industry to improve the technological process of manufacturing concrete and to improve its quality [1-3]. Their use makes it possible to obtain highly mobile concrete mixtures without reducing the strength of concrete and to reduce the consumption of cement. Many processes cannot proceed without the participation of surfactants, for example, the processes of flotation of non-ferrous metal ores, dispersion and stabilization of emulsions, suspensions and foams, modification and protection of various surfaces, regulation and stabilization of cement mortars and concrete mixtures. The diverse action of surfactants (stabilizers, emulsifiers, dispersants, inhibitors, regulators of the structure formation of cement suspensions) in

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aqueous and non-aqueous media is based on the processes of their adsorption on the surface of solid particles [4-6].

In this regard, it is important to obtain new effective plasticizing additives based on polyalkylacrylate derivatives, which allows for solving environmental problems at the same time. Increasingly important is the introduction of organic additives (in particular, HMSAS) and mineral binders in cement suspensions, and concrete mixtures to give them the necessary structural and mechanical qualities and control the colloidal chemical and technological properties of these dispersed systems. Acceleration and retardation of the setting time and control of the flow regime of cement slurries can be achieved by treatment with appropriate chemical reagents, including surfactants [7- 10].

The development of the chemical industry and the growth in the production of synthetic products make it possible to widely use various methods and formulations to control the properties of binders.

There are several works devoted to the processes occurring during the interaction of cement clinker hydration products with chemical reagents [11- 14].

The influence of active additives is considered, and the mechanism for regulating the setting time, increasing the mobility and reducing the water loss of cement slurries is investigated. The action of surfactants and surface-active additives for cement mortars is determined by their surface activity, i.e. the ability of molecules and ions of such additives to be adsorbed (concentrated) under the action of inter- and intramolecular forces on the interface. In this case, adsorption can be both physical and chemical in nature. The resulting surface compounds block the active centres of the products of hydrolysis and hydration of clinker minerals and inhibit setting and hardening. The study of the properties of cement slurries with SAS additives showed the possibility of changing the general course of the setting process and subsequent hardening of the cement slurry [15- 17].

SAS molecules are adsorbed on the hydrophilic surface of cement particles and form an adsorption layer of oriented molecules on a separate cement grain. Due to the formation of protective films on the surface of cement particles, the interaction of cement with water and the hydration process, and hence the setting of the cement slurry, slow down. Many surfactants and surface-active additives to cement mortars reduce viscosity, and ultimate static and dynamic stress, which is explained by their chemisorption on cement particles and blocking of active centres of the crystal lattice.

2 Methods and Materials

To obtain high molecular weight surfactants (HMSAS), the esterification reaction of GPAA (hydrolyzed polyacrylamide) with aliphatic alcohols (ethyl, octyl and dodecyl) was carried out in a mixture of organic solvents and the presence of a catalyst - sulfuric acid at a temperature of 378 K, reaction time 3.5-4 .0 hours. The work involves modern physicochemical, analytical, colloid-chemical methods of directed synthesis and study of the properties of surfactants:

a) refractive indices of aqueous solutions of surfactants

An Easy Plus refractometer was used to determine the refractive index (n_D^{20}) of aqueous solutions of the obtained new surfactants. The refractive index of aqueous solutions was measured at a temperature of 293 K.

b) the density of surfactant samples

To determine the density (d_4^{20}) of new surfactants a density meter Easy Plus was used. The density of the obtained surfactants was measured at a temperature of 293 K.

c) Determination of surface tension

The surface tension of surfactant solutions was determined using a tensiometer DCAT-9T at different temperatures and concentrations. To obtain statistically significant results, each

measurement was repeated 5 times. Freshly prepared surfactant solutions were used for measurements.

d) Foaming ability

The foaming ability was determined at a temperature of 293K, while 100 ml of a freshly prepared surfactant solution with a certain concentration was shaken in a graduated container for 60 s. Then the height of the foam column at the initial moment in the graduated container was measured.

e) Hydrophilic-lipophilic balance

The hydrophilic-lipophilic balance (HLB) for the surfactants was calculated by group numbers according to the equation: $HLB = HLB_{gf} - nHLBCH_2 + 7$, where HLB_{gf} is the HLB of hydrophilic groups, $HLBCH_2$ is the HLB for the $-CH_2-$ group. The surfactants were purified by vacuum distillation and recrystallization methods.

3 Results and Discussions

To obtain high molecular weight surfactants (HMSAS), the esterification reaction of GPAA (hydrolyzed polyacrylamide) with aliphatic alcohols (ethyl, octyl and dodecyl) was carried out in a mixture of organic solvents and in the presence of a catalyst - sulfuric acid at a temperature of 378 K, reaction time 3.5-4 .0 hours.

The macromolecules of the obtained copolymers consist of two groups with opposite properties: hydrophilic and hydrophobic. The presence of a carboxyl group, which transforms into a carboxylate group, gives the copolymers the ability to dissolve in water, while hydrophobic aliphatic radicals of various lengths enhance hydrophobic interactions and surface activity at the interface between different phases.

The resulting copolymers are light yellow amorphous substances that dissolve in aqueous solutions of alkalis, dimethylformamide, insoluble in acetone, ethanol, ethers and hexane. Physico-chemical properties of the obtained surface-active derivatives of polyacrylates are presented in Table 1.

Table 1. Physical and chemical properties of the obtained surface-active derivatives of polyacrylates

Surfactants	length hydrocarbon radical	C, kg/m ³	$\sigma \cdot 10^{-3}$ N/m, 293K	HLB	n_D^{20}	d_4^{20} , kg /m ³
SDEASGMAK	-N(CH ₂ CH ₂ -OH) ₂ , C ₇ H ₁₅	10.0	30.0	14.25	1.294	1135.0
SDESDCMAK	-N(CH ₂ -CH ₂ -OH) ₂ , C ₁₀ H ₂₁	10.0	27.3	15.16	1.255	1125.0
SDEGEAAC	-(CH ₂ -CH ₂ -O) ₂ -	10.0	40.5	11.35	1.305	1150.0
SMEASGMAK	-NH-CH ₂ -CH ₂ -OH, C ₇ H ₁₅	10.0	27.0	13.25	1.274	1130.0
SASGMAK	C ₇ H ₁₅	10.0	38.0	10.36	1.331	1160.0

To study the surface-active properties of polyalkylacrylates, the surface tension of their aqueous solutions with a concentration of (0.01-3.0%) was measured.

In the process of measuring the surface tension of copolymer solutions, a significant difference was found between high-molecular surfactants and conventional surfactants. This difference, as in [18, 19], consists of the slow establishment of the equilibrium values of the surface tension. To complete this process for solutions of low molecular weight

surfactants, 2–5 minutes are sufficient, while in solutions of copolymers, equilibrium is reached within 10 hours.

The study of the kinetics of the formation of an adsorption layer in aqueous solutions of copolymers showed (Table 2) that the time for establishing equilibrium values of surface tension depends on the length of the introduced radical and ranges from 30 minutes to 10 hours. It can be seen from this table that, at different lengths of the side hydrocarbon radical of the macromolecule, the time required establishing equilibrium in the adsorption layer changes. The establishment of the equilibrium value of surface tension over a long time is explained by the differentiation of segments of macromolecules of different polarities in the adsorption layer, which requires a long time, not slow diffusion of macromolecular coils to the interface.

Table 2. Kinetics of adsorption layer formation in aqueous solutions of polyacrylates with a concentration of 10 kg/m³

Surfactants	length hydrocarbon radical	C, kg/m ³	$\sigma \cdot 10^{-3}$ N/m, 293K	τ , hour
SDEASGMAK	-N(CH ₂ CH ₂ -OH) ₂ , C ₇ H ₁₅	10.0	42.5	0
			39.1	2
			37.5	4
			36.5	6
			35.3	8
			35.3	10
SDESDCMAK	-N (CH ₂ - CH ₂ -OH) ₂ , C ₁₀ H ₂₁	10.0	40.0	0
			38.1	2
			37.0	4
			35.0	6
			33.0	8
			31.0	10
SDEGEAAC	-(CH ₂ -CH ₂ -O) ₂ -	10.0	60.5	0
			55.5	2
			53.3	4
			53.2	6
			53.0	8
			53.1	10

A certain role in this process is assigned to the hydrophobic interaction between side hydrocarbon radicals, which makes it difficult to differentiate polarity segments of macromolecules in the adsorption layer. As can be seen from Table 2, the time required establishing the equilibrium of conformations of macromolecules at the liquid-gas interface for copolymer solutions with a concentration of 10 kg/m³ depends on the length of the introduced side hydrocarbon radical. For the solution of the copolymer SDEGEAAC, it is equal to 4 hours SDEASGMAK -8 hours, SDESDCMAK -10 hours.

This is explained by the fact that the mass side hydrocarbon radicals of the macromolecule reduce its flexibility, and also, due to the manifestation of hydrophobic interactions among themselves, increase the packing density and stabilize the conformation of a dense coil, making it difficult to differentiate in the adsorption layer. Since the conformational state of macromolecules depends on the concentration, it was of great practical and theoretical interest to study the effect of concentration and structure on the surface-active properties of copolymers.

The largest decrease in σ was observed for samples of SDEASGMAK, SDESDCMAK and SMEASGMAA containing long-side radicals in the macromolecule chain. It has been

established that with an increase in the concentration of the studied copolymers, the values of the surface tension fall to a value of 27.0-33.7 mN/m.

In semi-logarithmic coordinates, the dependence $\sigma=f(c)$ is characterized by a break in the curves (Fig. 1).

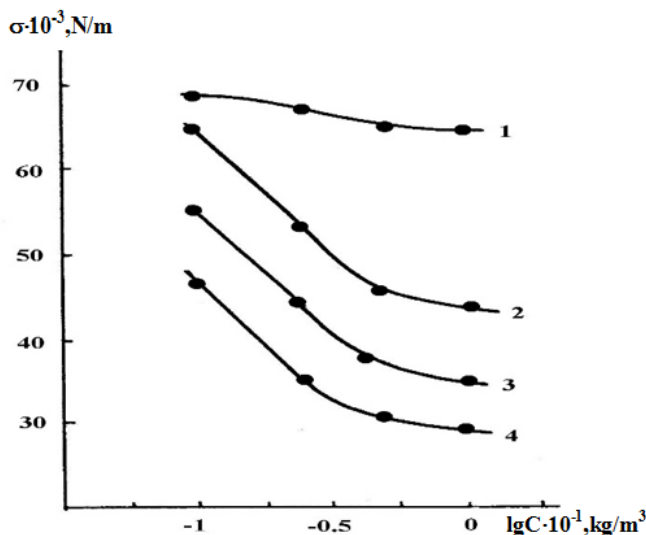


Fig. 1. Dependence of the surface tension of aqueous solutions of copolymers on the logarithm of concentration at 298K: 1-SDEGEAAA; 2-SDESDCMAK; 3-SDEASGMAK; 4-SMEASGMAK

These breaks, as in the case of low molecular weight surfactants, indicate the concentration of high molecular weight surfactants at which the formation of micelles in the bulk of the solution begins, which indicates saturation of the adsorption layer. However, for low molecular weight surfactants, a sharp break is characteristic, while for high molecular weight, a smoother one is observed. This difference is explained by the fact that macromolecules of high molecular weight surfactants in aqueous solutions at concentrations below CMC are in a folded conformational state and each macromolecule can be represented as an “associate” consisting of a large number of fragments of conventional low molecular weight surfactants. Hydrophobic interactions between side radicals of high molecular weight surfactants are preserved at low concentrations of copolymers in solution, which is confirmed by their high activity and high solubilizing ability.

The surface activity of water-soluble polymers is closely related to foaming properties, which largely determine their practical significance. Based on the study of the surface-active properties of aqueous solutions of copolymers, it can be concluded that a sufficient concentration of macromolecules of these compounds at the liquid-gas interface imparts mechanical strength to the surface and, in particular, to the adsorption layer, due to intermolecular interaction. Because of the foregoing, for the first time, polyacrylates were found to have foaming properties. An important role in foam formation is played by the structure and functional composition of polyacrylates. With an increase in the length of the aliphatic radical in the macromolecule of copolymers, the ability to foam their aqueous solutions increases.

For the studied copolymers, an increase in the volume of foam was observed with an increase in the concentration of solutions up to 5–10 kg/m³, after which the foaming somewhat decreased (Table 3). An increase in the volume of foam with an increase in

concentration is associated with the achievement of CMC, at which micellization occurs in the volume of the solution and a saturated adsorption layer is formed, which has the highest mechanical strength. A further increase in the concentration of the solution increases the viscosity of the system, which makes it difficult for molecules to move from the volume of the solution to the surface layer, as a result, foaming is reduced.

Table 3. Foaming ability of aqueous solutions of polyacrylates at pH = 6.0

Copolymers	Concentration <i>n</i> , kg/m ³	Foam volume, <i>V</i> ·10 ⁻⁶ , m ³ at a time (min)						Sustainability		Foam ratio (multiplicity)
		Start	V1	V5	V10	V30	V60	Y10	Y60	
SMEASGMAK	1.0	350	220	180	150	120	100	0.43	0.29	1.75
	2.5	510	380	320	310	240	180	0.61	0.35	2.55
	5.0	690	520	420	380	320	230	0.64	0.39	3.45
	10.0	610	540	300	280	250	200	0.57	0.41	3.05
SDESDCMAK	1.0	430	360	180	140	90	70	0.33	0.17	2.15
	2.5	480	450	350	250	220	140	0.52	0.29	2.40
	5.0	530	470	380	330	270	190	0.62	0.36	2.65
	10.0	460	420	380	250	210	150	0.54	0.33	2.30
SDEASGMAK	1.0	460	400	380	320	230	115	0.70	0.25	2.30
	2.5	500	380	320	300	285	210	0.60	0.42	2.50
	5.0	720	575	510	500	480	420	0.75	0.63	3.60
	10.0	670	645	550	530	490	430	0.74	0.60	3.35
SEGEAAC	1.0	350	225	185	185	150	75	0.53	0.21	1.75
	2.5	420	290	265	240	210	95	0.57	0.23	2.10
	5.0	640	430	390	360	310	120	0.55	0.18	3.20
	10.0	650	480	450	430	270	200	0.66	0.30	3.25
SDEGEAAC	1.0	435	290	265	250	180	80	0.57	0.18	2.18
	2.5	510	320	310	285	265	115	0.56	0.23	2.55
	5.0	620	510	470	465	410	140	0.69	0.21	3.10
	10.0	670	490	440	360	300	120	0.58	0.19	3.35

Further, the influence of the branching of the hydrocarbon radical on the foaming ability was revealed. The data obtained showed that the volume of the foam of copolymer solutions practically does not change upon branching of the radical, the minimum value of the copolymer concentration is necessary to induce foaming, and the rate of formation of stable foam decreases with the increasing length of the side hydrocarbon radical.

Foam stability is high enough for all concentrations of copolymer solutions. The most stable foam is formed by copolymers SMEASGMAK, SDESDTSMAC, and SDEASGMAK at 10.0 kg/m3, i.e. with an increase in the alkyl radical in the copolymer macromolecule. This is because with the growth of the hydrocarbon radical, the surface adsorption layers at the interface become more saturated and durable, and therefore the foaming ability and, especially, stability increases sharply.

The effect of new polyacrylates on the technological properties of cement mortars has been studied. Technological characteristics of cement slurries with VMPAV additives are presented in Table 4. Studies have shown that new surface-active polyacrylates are effective retarders of the setting time of cement slurries. At optimal concentrations of such surfactants, the setting time of cement mortars increases to 4.5-5.0 hours. An analysis of the

results obtained shows that the presence of hydroxyl and carboxyl groups and ester bonds in the structure of the studied surfactant molecules enhances their effectiveness in slowing down the setting of cement mortars. It was found that the presence of one hydroxyl group in the structure of surfactant molecules is optimal for slowing down the setting. An increase in the number of hydroxyl groups in the structure of surfactant molecules reduces their effectiveness. Apparently, this result is associated with the hydrophilization of cement particles with an increase in the content of hydroxyl groups. It is also interesting to note the influence of the length of the hydrocarbon radical of the studied surfactants on the setting time of cement mortars.

Table 4. Technological characteristics of cement mortars with surfactant additives at a temperature of 20 °C and Water/Cement 0.5

<i>SAS</i>	<i>Additive, mass%</i>	<i>Spreadability, cm</i>	<i>Density, kg/m³</i>	<i>Termsgrasping, hour/minutes</i>	
				Start	End
SMEASGMA K	0.0	22.5	1790	0-45	1-45
	0.1	19.0	1800	0-45	1-50
	0.3	18.0	1800	0-50	2-00
	1.0	27.0	1790	2-00	3-00
	2.0	25.0	1790	3-00	4-15
SDESDCMA K	0.0	22.5	1790	0-45	1-45
	0.1	22.5	1790	0-45	1-45
	0.3	22.5	1790	0-50	2-00
	1.0	18.0	1800	2-40	3-20
	2.0	19.0	1800	2-50	4-30
SDEASGMA K	0.0	24.0	1860	0-45	1-45
	0.1	25.0	1850	2-00	2-45
	0.3	25.5	1850	2-20	3-00
	1.0	26.5	1850	3-30	4-30
	2.0	27.0	1850	3-50	4-50

Studies have established that with an increase in the length of the surfactant carbohydrate radical, the effectiveness of slowing down the setting of cement mortars increases. The results obtained showed that at low concentrations, the retarding effect of surfactants increases linearly with an increase in their concentration and surface activity. At low concentrations of surfactants, the formation of adsorption layers is observed, which leads to a decrease in the hydration of cement particles. However, at higher concentrations of surfactants (above CMC), the effectiveness of slowing down the setting of cement slurries increases significantly. This result is associated with the sorption of micellar particles on the surface of the cement, which leads to increased aggregative stability of the dispersion, and, accordingly, a decrease in the setting rate of the cement mass.

4 Conclusion

Several new high-molecular surfactants have been synthesized - water-soluble polyalkylacrylates with a controlled composition of hydrophilic (COOH, COONH₄, CONH₂) functional groups and a controlled length of the hydrophobic side hydrocarbon radical (C₄-C₁₀). The dependence of the physical- and colloid-chemical properties of aqueous solutions of polyalkylacrylates on their structure has been studied.

The effect of new HMSAS on the technological properties of cement slurries has been studied. The data obtained showed that the new surface-active polyalkylacrylates are

effective retarders of the setting time of cement slurries. At optimal concentrations of such surfactants, the setting time of cement mortars increases to 4.5-5.0 hours.

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