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## THE EFFECT OF SUPERPLASTICIZER HYDROPHILIC GROUP NATURE ON ITS PLASTICIZING ACTIVITY

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### Abstract

Generalized and systematized The results of known developments in the field of concrete mortar and concrete modification are presented concerning the research of superplasticizer (SP) hydrophilic group nature on their plasticizing activity, showing that SP plasticizing activity depends on their chemical structure. The adsorption of superplasticizers on dispersed phase particles increases the aggregate stability of the suspension, which becomes very possible after the formation of an adsorption monolayer.

Thus, the peptization of aggregates to primary particles takes place and immobilized water is released. It was shown that the hydroxyl groups increase plasticizing SP activity at the expense of lower molecular weight and higher hydrophilicity as compared to the activity with sulfonic groups. Experimental data are presented which show that a synergistic effect is presented at a certain ratio of SP and sulfonic and hydroxyl groups in a multifunctional modifier (MFM) due to the interaction of molecules on the surface of the dispersed phase particles. On the basis of experimental research and literature data analysis stated the statements about the necessary qualities of SP are formulated.

**Keywords:** Concrete modifiers, multifunctional modifiers, plasticizing activity, adsorption-active groups, aggregate stability, rheological properties, adsorption, peptization, monomolecular layer, electrokinetic potential, synergy effect.

### Introduction

Concrete and reinforced concrete among a wide variety of building materials occupied and continues to occupy a leading role in construction industry. With the development of monolithic concrete in recent years concrete technology moved to the open construction sites from factories, where it is much more complicated due to the lack of

steady-state conditions concerning the processes of structure formation and curing. Nowadays, almost all used concrete is produced using various chemical additives. SP and MFM on its basis are the most widely spread ones. Today MFM occupies a leading position on the market of additives, as their use allows you to control the whole complex of concrete properties simultaneously within specified operating conditions [1-5].

The management of physical and chemical processes concerning the structure formation of concrete at nanoscale by the regulation of colloid-chemical properties of cement dispersions and crystallization using MFM refers to the promising nanotechnologies in construction industry.

The correct choice of a SP in the production of concrete and reinforced concrete for the specific conditions of its production and operation is based on a deep understanding of its action mechanism. Furthermore, a synergistic and antagonism effect can be manifested at the joint use of individual SP different by nature and properties in MFM composition.

Numerous studies of SP mechanism effect, carried out by different researchers and research schools for decades do not provide a general unified theory of this process. In this context, in order to study the mechanism of plasticizing action more completely, the authors studied the colloid-chemical properties of mineral suspensions, plasticized SP with different adsorption-active groups by nature [6-11].

A working hypothesis was put forward that the combined use of different SP may show a synergistic effect. The theoretical assumptions of SP studies and the compositions on their basis as the effective SP in concrete technology were the basic positions concerning synergistic surfactant composition synergy theory according to which surfactants and hence the properties of concrete mixtures and concretes can be controlled not only by the change of chemical structure, and by qualitative and quantitative combination of active additives for organic polar substances of different molecular weight [12]. The purpose of this paper is the highlighting of experimental study results concerning the influence of SP hydrophilic group nature on its plasticizing activity, the development of MFM increased activity, the study of supplement effect on the physical and mechanical properties of concrete and concrete compounds.

### **Methods:**

This paper studied the colloid-chemical properties of mineral suspensions plasticized by different SP, used most widely in the construction industry.

Due to the fact that the plasticizing activity, and hence the mechanism of SP action is determined by nature, composition and structure at the performance of tests SP were used with different adsorption-active groups: diluent S-

3, LST, containing sulfo groups in its composition as hydrophilic ones –  $\text{SO}_3^-$ , SP SB-3, comprising hydroxyl groups and the mixtures thereof in its composition.

In order to eliminate the instability factor of the dispersed phase and the dispersed medium at the interaction of cement with water, in order to study the influence of SP on colloid-chemical properties the chalk suspension was used as a model one.  $\text{CaCO}_3$  has a low solubility ( $PR 1 \cdot 10^{-8}$ ) and contains the cations that make the part of the majority of cement clinker minerals. The study of SP impact mechanism was carried out according to the results of standard tests for colloidal-chemical properties of SP and modified mineral suspensions.

The studies of suspension rheological parameters were performed using the rotational viscometer "Reotest 2". The concentration of SP ( $C_m$ ) was calculated in wt. % in a dry substance from the dispersed phase amount. During the studies the relationship between the values of shear stress and a shear rate was measured. According to obtained results rheological curves were developed, according to which the limiting shear stress  $[\tau]_0$  and the plastic viscosity  $[\eta]_{pl}$  were determined.

The aggregate stability of chalk suspensions was evaluated by the most probable particle radius using the sedimentation analysis.

In order find the electrokinetic properties of the surface they used the streaming potential method taking into account the surface conductivity, which allows to determine the  $[\zeta]$  potential in concentrated suspensions.

In order to determine the composition and structure of the oligomer molecules they used liquid-gas and liquid chromatography, ultraviolet and infrared spectroscopy, spectroscopy, nuclear magnetic resonance, conductometry and potentiometry. The molecular weight of the synthesized oligomers was determined by cryoscopy.

Main part. The study of SP hydrophilic group nature influence on their plasticizing activity showed that SP has the best plasticizing properties with hydroxyl groups. They also showed that MFM containing plasticizing components with different hydrophilic groups by nature may manifest a synergistic effect, expressed in plasticizing activity increase as compared with the individual components, and concrete properties improvement due to the attraction interaction.

The study of SP influence on the surface tension at the solution-air boundary showed that SP-3 has no surface activity, almost without an effect on a surface tension. SP SB-3 is a weak air attractor, which reduces the surface tension slightly from 72 to 60  $\text{mJ/m}^2$ . LST supplement makes a strong air attraction, as it reduces the surface tension to 45  $\text{mJ/m}^2$ . A complex supplement comprising SP S-3 and SP SB-3 at their optimum ratio occupies an intermediate

position. The reduction of the surface tension at the boundary of solution-air improves the wetting of hard surfaces with a liquid, and hence, the dissolution of the dispersed phase by the dispersion medium (the dispersion of cement particles by water).

The aggregate stability, rheology and other properties of disperse systems is influenced significantly by the surface tension value at the solid body-solution boundary, which determines the effective Gammaker constant characterizing the forces of intermolecular attraction between dispersed phase particles. The surface tension on the boundary solid body-solution at the modification of SP chalk surface was assessed indirectly by Young famous equation

$$\cos \theta = \frac{\sigma_{\tau-\Gamma} - \sigma_{\tau-\kappa}}{\sigma_{\kappa-\Gamma}}$$

$[\sigma]_{\kappa-\Gamma}$  and the contact angles of wetting  $[\theta]$  were measured on  $\text{CaCO}_3$  surface in the area of balanced concentrations corresponding to a monomolecular layer filling (Table 1). Due to the fact that during the experiment performance, the surface tension at the boundary solid body - gas remained a constant one,  $[\sigma]_{\tau-\kappa}$  was determined by the change of adhesion tension value ( $[\sigma]_{\tau-\Gamma} - [\sigma]_{\tau-\kappa}$ ), which was determined from Young equation.

**Table 1: The effect of SP SB-3 concentration on the contact angle of chalk wetting and surface tension.**

C, %	$\theta, ^\circ$	$\cos \theta$	$\sigma_{\tau-\kappa}, \text{мДж/м}^2$	$\sigma_{\tau-\Gamma} - \sigma_{\tau-\kappa}, \text{мДж/м}^2$
0	46,1	0,693	72,0	49,9
0,01	38,4	0,784	71,7	56,2
0,02	34,8	0,821	71,5	58,7
0,03	34,2	0,827	71,4	59,0
0,05	34,4	0,825	70,9	58,5

The experimental results showed that SP SB-3 concentration increase the surface tension at the boundary solid body-solution is decreased as the increase of ( $[\sigma]_{\tau-\Gamma} - [\sigma]_{\tau-\kappa}$ ) at a constant value of  $[\sigma]_{\tau-\Gamma}$  can be conditioned only by the decrease of  $[\sigma]_{\tau-\kappa}$ . This indicates the increase of chalk hydrophilic surface during the formation of SP adsorption layer and the reduction of intermolecular attraction forces between dispersed phase particles. A similar pattern of  $[\sigma]_{\tau-\kappa}$  change is observed for other SP.

The study of SP adsorption using chalk showed that adsorption isotherms have a typical character of the monomolecular adsorption. At small equilibrium concentrations almost complete removal of adsorbate is observed from solution. At the further increase of concentration the curves become saturated and the adsorption reaches its maximum value. The maximum adsorption is reached at close values of balanced concentrations for the studied SP:

0.05% for SP SB-3, 0.052% for SP S-3 and 0.05% for SB-3 + S-3. This indicates that the change of hydrophilic group nature in SP makes a slight impact on its adsorption activity, and apparently is determined by the dispersion forces of interactions between the system of related SP molecule aromatic rings and chalk surface.

At the same time the values  $\Gamma_{max}$  vary considerably depending on SP type and make  $2,8 \cdot 10^{-4}$ ;  $5,5 \cdot 10^{-4}$ ;  $3,0 \cdot 10^{-4}$  g/m<sup>2</sup> for СБ-3, С-3, СБ-3+ С-3, respectively (Table 2).

**Table 2: Adsorption parameters of monomolecular layer.**

$$m_{meia} = 60\Gamma, m_{H_2O} = 33\Gamma$$

Parameter	Supplement type		
	СБ-3	С-3	СБ-3+С-3
C <sub>p</sub> , %	0,05	0,052	0,05,
$\Gamma_{max}$ , g/m <sup>2</sup>	$2,8 \cdot 10^{-4}$	$5,5 \cdot 10^{-4}$	$3,0 \cdot 10^{-4}$
C <sub>M</sub> , % from chalk weight	0,082	0,14	0,085

The reduction of  $\Gamma_{max}$  SB-3 in comparison with S-3 is conditioned, as we mentioned previously, by lower molecular weight of hydroxyl groups as compared with sulfogroup. At the same time, the experimental value of  $\Gamma_{max}$  for PFM is less than the value of  $3,61 \cdot 10^{-4}$  g/m<sup>2</sup>, obtained by calculation on the basis of additivity. This suggests that during the adsorption of molecules with different hydrophilic groups one must take into account the interaction "adsorbate-adsorbate" or the so-called attraction interaction. This is indicated during the study of ionogen dye adsorption on hydrophilic surfaces [13]. The attraction interaction was evaluated by the following equation

$$B \cdot C = \frac{\theta}{1 - \theta} \cdot e^{-2A\theta},$$

where  $\theta = \frac{\Gamma}{\Gamma_{max}}$ ;  $\Gamma$ ,  $\Gamma_{max}$  - equilibrium element and maximum adsorption by chalk g/m<sup>2</sup>; B - adsorption equilibrium constant; C - equilibrium concentration, kg/m<sup>3</sup>; A - attraction constant.

During PFM adsorption the constant A is shifted to negative area, indicating the adsorbate-adsorbate interaction increase and reduces  $\Gamma_{max}$ . For individual SP the value A within experimental data error is significantly different from zero, while the value A decreases to -50 for PFM SB-3+C-3. The increase of attraction interaction in this case may be related to the increase of electrostatic interaction and to spatial difficulties at combined adsorption of SB-3 and S-3. The synergistic effect is manifested at the weight ratio of SB-3 and S-3, equal to 3:7 and 7:3. Taking into account the

average molecular weights SB-3 and S-3 (800 and 2000, respectively) the molar ratio of SP is equal to 1.07:1 and 5.8:1.

The first case corresponds to the equivalent SP ratio, which explains the presence of maximum at this ratio. In the second case, the maximum appears when one molecule S-3 is surrounded by six SB-3 molecules. A similar effect of a massive central molecule influence on the landing areas of adjacent molecules with low molecular weight for liquid-gas boundary was described by Adam [14].

During the calculation of SP dosage necessary to form a monomolecular layer, one needs to take into account  $\Gamma_{\max}$  and the corresponding equilibrium concentration (Table. 2).

The calculation was performed according to the following formula:

$$C_M = \frac{(\Gamma_{\max} \cdot m \cdot S_{y\partial} \cdot C_p \cdot V_p) \cdot 100\%}{m},$$

where  $C_M$  - the percentage from chalk weight - SP dosage required to form a monolayer;  $C_p$ , g/l - equilibrium concentration of SP during the formation of a monolayer;  $\Gamma_{\max}$ , g/m<sup>2</sup> - the maximum SP adsorption;  $m$ , g - chalk weight;  $S_{y\partial}$ , m<sup>2</sup> - chalk specific surface;  $V_p$ , l - solution volume.

The obtained values of  $C_M$  are presented in Table 2. These data show that SP SB-3 has the smallest value of 0.082%, SP S-3 has the highest value of 0.14. For PFM  $C_M$  is equal to 0,085%, which is 16% less than the value calculated according to additivity principle equal to 0,099%.

The balance in coagulation and peptization processes is determined by the ratio between coagulation contact energy  $U_k$  and the energy of particle thermal motion. SP adsorption changes  $U_k$  on the surface of particles and shifts the equilibrium coagulation  $\leftrightarrow$  peptization in one direction or another.

The study of differential distribution curves according to chalk particle radii at various SP dosages showed that SP dosage increase leads to a narrower distribution of particles and the maximum distribution shift towards smaller values of a radius. The studies showed that at the dosage increase the most probable range is reduced by an order, reaching a minimum value equal to 1 ... 1.5 mcm. The latter value coincides with the size of chalk primary particles according to electron microscopy data and confirms that the peptization of aggregates takes place prior to primary particles.

In order to calculate the number of primary particles involved in the formation of a unit, let's use the following calculations.

The volume of the unit is the following:

$$V = 4/3 = 3,14 \cdot 13^3 = 9,2 \cdot 10^3 \text{ mcm}^3$$

The volume of the dispersed phase in the unit is the following (taking into account a random packing):

$$V_{\text{д.ф.}} = 0,56 \cdot 9,2 \cdot 10^3 = 5,152 \cdot 10^3 \text{ mcm}^3$$

The volume of a primary particle is the following:

$$V = 4/3 \cdot 3,14 \cdot 1^3 = 4,19 \text{ mcm}^3$$

The amount of primary particles in a unit is the following one:

$$n = \frac{5,125 \cdot 10^3}{4,19} = 1230 \text{ part/unit}$$

During the peptization of units immobilized water is released, which leads to the centrifugate increase, separated from suspension after centrifugation and which reaches a maximum when the minimum size of particles is reached.

The obtained results show that SP adsorption on the chalk surface increases the aggregate stability of chalk particles.

At certain dosages the system becomes completely stabilized and aggregates are peptized to primary particles.

The limit shear stress and plastic viscosity, determined from the rheological curves obtained at various dosages of SP, showed that during SP dosage increase the limit shear stress is decreased sharply at first, then the reduction rate  $[\tau]_0$  slightly decreases and when a certain dosage is reached  $[\tau]_0$  becomes almost equal to zero. Plastic viscosity is also decreased dramatically at first, but then it reaches a certain minimum value, and a minimum occurs at the same dosages, at which  $[\tau]_0$  becomes equal to zero.

SP efficiency in terms of their impact on the maximum shear stress increases with the transition from SP-3 to SP SB-3. The increase of impact is observed for PFM in comparison to individual components.

The value of the limit shear stress concerning a concentrated suspension is caused by the set of cohesive forces for particles in the places of their contact with each other: the strength  $P$  of individual contacts between the particles and their number  $[\alpha]$  per surface unit. In this approximation  $\tau_0 = P \cdot \alpha$ , where the value  $[\alpha]$  is determined by particle size and packing density and during SP introduction it varies only within certain limits due to peptization or coagulation processes. Thus, that the reduction of the limit shear stress nearly to a zero at optimal SP dosages is conditioned by the fall of an individual contact strength to the values comparable with thermal motion energy [10-11]. In the first approximation the value  $[\alpha]$  may be estimated according to [15] according to the most probable range of particles obtained by sedimentation analysis.

$$\alpha = \frac{1}{(2r)^2},$$

where  $r$  – particle radius, m.

For the particles with the size of  $\alpha = 2 \cdot r = 2 \text{ mcm}$  the number of contacts per surface unit will be as follows:

$$\alpha = \frac{1}{(3 \cdot 10^{-6})^2} = 1,11 \cdot 10^{11} \text{ cont/m}^2$$

The strength of the coagulation contact is determined by the forces of intermolecular interaction. At that the adhesion energy can be found according to the following formula

$$U_{\kappa} = P \cdot h$$

where  $U_{\kappa}$  - cohesion energy in contact, J;  $h$  – the distance between particles, m;  $P$  – individual contact strength, H.

The distance between the particles which are in the coagulation contact (i.e., through a dispersion medium layer) according to the literature data [16] makes 0.5-1 nm.

Based on the above stated information, one may estimate the energy of the coagulation contact according to the shear stress values

$$U_{\kappa} = P \cdot h = \frac{\tau_0 \cdot h}{\frac{1}{(2r)^2}} = \tau_0 \cdot h \cdot (2r)^2,$$

The substitution of specific values for chalk suspension without additives ( $\tau_0 = 300 \text{ Па}$ ,  $h = 0,75 \text{ nm}$ ,  $r = 1,5 \text{ mcm}$ ) provides the following value of  $U_{\kappa}$ :

$$U_{\kappa} = 300 \cdot 0,75 \cdot 10^{-9} \cdot (2 \cdot 1,5 \cdot 10^{-6})^2 = 2,02 \cdot 10^{-18} \text{ Дж} \approx 505 \text{ kT},$$

which greatly exceeds the energy of thermal motion and causes the structured nature of the suspension. The SP adsorption on the chalk particles reduces the coagulation contact energy to the thermal energy and the reduction of the limit shear stress almost to a zero.

The reduction of plastic viscosity is related primarily to the release of immobilized water and, therefore, the increase of the dispersion medium relative content. The increase of water layer thickness between the particles reduces the friction between moving layers and plastic viscosity drop.

The studies of SP dosage effect on the electrokinetic potential of chalk particles showed that the surface of unchanged chalk has a slight excess negative charge, as evidenced by a slight negative potential value. The increase of SP dosage results in the change of electric kinetic potential, from -4 mV to -35 ÷ -40 mV. At that the values of [zeta]-potential for C-3 is somewhat less than for SB-3 and PFM. The progress of [zeta]-potential dependency curves on the dosing of additives is similar to the course of supplement adsorption, and the output of [zeta]-potential to the minimum value corresponds to the completion of a monomolecular layer.

Based on the experimental study results, we can cite the following assumptions concerning SP action mechanism.

The aggregate stability and disperse system rheology with the particles of a solid dispersed phase and a liquid dispersion medium are determined by their nature, dispersion and particle concentration. Each particle is a micro-volume of a condensed phase, the dimensions of which are large in comparison with molecular ones. So the forces of attraction between particles are determined mainly by the dispersion interactions. The forces of repulsion can be of different nature, the coagulation strength of a structure is determined by the depth of the secondary minimum on a potential curve, i.e., by the relation between the forces of attraction and repulsion.

Let's consider the role of various factors of stabilization concerning disperse systems using the example of a chalk suspension. The calculation of dispersion attraction forces was carried out according to a well-known formula [17].

$$U_M = -\frac{A^*}{12 \cdot \pi \cdot h^2},$$

where  $U_M$  is the molecular attraction energy;  $A^*$  - Hamaker's constant;  $h$  - the distance between particles. Hamaker's constant was taken equal to  $5 \cdot 10^{-20}$  J similar to the data for the mineral oxides [14, 17]. The calculation results are presented in Table 3.

Entropic stabilization factor is in the pursuit of a dispersed phase to a uniform distribution along the system volume under the influence of the thermal motion. The value of the surface tension is determined by the Rebinder-Shukin ratio at the solid body-solution boundary in which the stability of a dispersed system is provided

$$\sigma_{\tau-ж} \leq \frac{k \cdot T}{4 \cdot \pi \cdot r^2},$$

The substitution in this equation of  $T = 298$  °K, and  $r = 1$  mcm provides the value  $[\sigma]_{\tau-ж}$ , equal to  $3,6 \cdot 10^{-11}$  J/m<sup>2</sup>.

Comparing this value with Young's equation

$$\cos \theta = \frac{\sigma_{\tau-\Gamma} - \sigma_{\tau-ж}}{\sigma_{ж-\Gamma}},$$

we see that in this case we should observe a complete wetting of the chalk surface, as  $[\sigma]_{\tau-ж}$  can be ignored due to its small value, and  $[\sigma]_{\tau-\Gamma}$  is more than  $[\sigma]_{\tau-ж}$  for the studied systems. However, experiments showed that during the introduction of additives a contact angle decreases (Table 1), but a complete wetting is not observed. This indicates that the thermal energy of the particles is much less than the energy of interaction between them and it does not affect the suspension mobility.

The structural and mechanical factor of suspension stability occurs during the adsorption of surfactant molecules, which are the surface-active ones for this boundary of phase division and are capable to develop a gel-like structured layer at the a phase boundary. The thickness of a gel layer should be 5-10 nm [18] to prevent the rapprochement of the particles within the ranges where the molecular forces of attraction are great. The analysis of adsorption isotherms for the supplements at the solid body-solution boundary indicates the formation of a monomolecular layer only on the dispersed phase surface. The thickness of an adsorption layer makes no more than 1 nm, which is not enough to create a steric repulsion between particles.

**Table-3: Interaction energy between chalk particles.**

Energy type	Interaction energy for the distance between particles, nm					
	1	2	5	10	20	30
$U_M \cdot 10^6 \text{ J/m}^2$	-1330	-332	-53,1	-13,3	-3,32	-1,47
$U_e \cdot 10^6 \text{ J/m}^2$	531	322	71,9	5,9	0,0388	0,000268
$U_s \cdot 10^6 \text{ J/m}^2$	10700	7700	2830	535	19,1	0,681
$(U_M+U_e+U_s) \cdot 10^6 \text{ J/m}^2$	9420	7370	2780	522	15,8	-0,793

The hydrodynamic stability factor is in the reduction of speed and particle collision frequency at dispersion medium viscosity and density change. At the introduction of additives the solution viscosity and density changes insignificantly, and therefore the influence of hydrodynamic factor is absent.

The electrokinetic factor of stability is based on the electrostatic repulsion of diffuse ion particle layers. The calculation for electrostatic repulsion forces in accordance with DLVO theory was conducted according to the equation [17]

$$U_e = 2 \cdot \epsilon_0 \cdot \epsilon \cdot \chi \cdot \zeta_s^2 \cdot e^{-\chi h},$$

where  $U_e$  is the electrostatic repulsion energy;  $\epsilon_0 = 8,85 \cdot 10^{-12} \text{ F/m}$  – electric constant;  $\epsilon = 81$  - the relative dielectric constant of water;  $[\zeta]_s$  - the diffusion layer potential, taken equal to  $[\zeta]$  potential;  $[\kappa]$  - reverse diffusion layer thickness;  $h$  - the distance between particles.

The value  $[\kappa]$  was calculated according to the following equation

$$\kappa = \sqrt{\frac{2F^2 I}{\epsilon \epsilon_0 k T}},$$

where  $F = 9,65 \cdot 10^4 \text{ C/g-eq}$  is Faraday number;  $\epsilon_0 = 8,85 \cdot 10^{-12} \text{ F/m}$  – electric constant;  $[\epsilon]$  - relative dielectric permittivity;  $I$  – ionic solution strength.

The value of electrokinetic potential for the chalk suspension with supplements was taken equal to -35 mV.  $U_e$  calculation results for different distances between the particles are shown in Table 3. As can be seen from the comparison of  $U_m$  and  $U_e$  values in the entire range of distances between the particles the energy of molecular attraction is greater than electrostatic repulsion energy.

The adsorption-solvation stability factor is in surface tension reduction at the boundary a solid body - solution after the adsorption of the stabilizer molecules and the occurrence of developed hydrate layers. At the approach of particles hydrate layers are intersected, the osmotic pressure increases, and the repulsion pressure that prevents coagulation also increases. The development of rather large hydration shells is unlikely for disperse systems with a lipophobic dispersed phase due to a weak energy interaction of environment with a dispersed phase. During the adsorption of additives which have a large number of ionic hydrophilic groups the phase to phase interaction is increased leading to surface tension reduction and hydrate layer development. An important role of structural forces conditioned by the existence of a boundary layer of water on hydrophilic surfaces is confirmed by the works of many authors [14, 19]. In accordance with these works, the energy of structural interaction was calculated according to the following formula

$$U_s = k \cdot l \cdot e^{-h/l},$$

where  $U_s$  – the structural interaction energy;  $k$  - the constant of structural forces characterizing the surface hydrophilicity;  $l$  - the characteristic length of structural forces.

For hydrophilic surfaces, which include chalk,  $k$  varies between  $10^6 \div 10^7$  J/m,  $l$  varies  $1 \div$  within 10 nm according to [20]. The average values of  $k$  and  $l$  were used for calculation, the calculation results are presented in Table 3. The comparison of  $U_m$  and  $U_s$  values shows that a secondary minimum is observed at the distances between 20 nm particle. Thus, the coagulation of particles is more favorable thermodynamically than peptization.

The analysis of table 3 shows that one may overcome the action of the molecular attraction forces only by the joint action of the electrostatic and the adsorption-solvation factors as the amount of  $U_e$  and  $U_s$  is more than  $U_m$  for all the distances between particles. The theoretical calculation is confirmed by the following experimental facts. During the washing of chalk suspension with distilled water stabilized by SP-SB 3, pH is reduced to the values of 7-7.5 that is less than pK values for the phenolic hydroxyl groups [20]. At that the balance of dissociation is shifted towards the formation of not dissociated molecules. SB-3 molecules become electrically neutral ones and electrostatic stabilization factor decreases sharply. At the same time there is the loss of aggregate stability and the transition to the Bingham nature of chalk suspension flow. The increase of pH suspension to the values exceeding the pK of the

*Mikhail Mikhailovich Kosukhin\* et al. International Journal of Pharmacy & Technology*  
hydroxyl groups, leads again to the dissociation of molecules, the increase of stability electrostatic factor and, consequently, to the full aggregate stability and Newtonian nature of the suspension flow. This transition from one state of a system to another one can be carried out repeatedly.

On the other hand, the study of stabilized chalk suspension rheology at different temperatures showed that with the temperature increase the plastic viscosity is decreased monotonously, while a considerable increase in the maximum shear stress is observed within the temperature range of 60-65 °C. The loss of water dispersion stability in this temperature range is related by the authors [21] with the destruction of the boundary hydrate layers of water by the increase of water molecule thermal motion intensity and a sharp decrease of the adsorption-solvation stability factor role.

Thus, in our opinion, the mechanism of plasticizing action concerning studied SP is in the following. SP molecules are adsorbed on the particle surface, developing a monomolecular layer. SP adsorption on the particle surface is provided by the dispersion forces of interaction between the system of SP aromatic rings and a particle surface. At that, since SP are anionic substances, the charge of particle surface becomes more negative, resulting in repulsive force increase. This also contributes to the formation of hydrate layers around the particles due to the presence of hydrophilic groups in SP molecules.

Thus, the repulsive forces start to predominate over the molecular forces of attraction, resulting in reduced coagulation contact to the values comparable with the thermal movement energy. At that the transition to the full aggregate stability of a system, the peptizing of units to the primary particles, the change in the rheological nature of suspension flow from Bingham one (yield strength is greater than zero) to Newton one (yield strength is zero). SP efficacy is largely determined by the nature of hydrophilic groups. At that hydroxyl groups are the most effective ones.

According to our research, one cannot ignore the interaction "adsorbate-adsorbate" on the surface of a dispersed phase during SP adsorption. The account of this phenomenon and the correct selection of the individual components allows to obtain PFM, which have a pronounced synergistic effect.

On the basis of performed experimental studies and literature data one can formulate the following provisions about the necessary qualities of SP:

1. SP adsorption is carried out by the dispersion forces of attraction. In order to localize SP molecules on a particle surface it is necessary that SP molecule contains a system of related aromatic rings or conjugated double bonds.

2. The adsorbed molecules of SP must hydrophilize a disperse phase surface, and contain the hydrophilic groups along the entire length.
3. SP plastifying activity is determined by surface activity at the boundary of a solid body-solution and a landing site of SP molecule.
4. SP molecules must create the same charge on particle surface, while the electric kinetic potential of the modified particles should not be less than 30 mV.

## **Summary**

This article is an attempt to summarize and systematize the known developments in the field of concrete mixture and concrete modification. The results of SP hydrophilic group nature research on their plasticizing activity are provided. The theoretical prerequisites of SP studies in concrete technology are the basic positions of synergism theory concerning the compositions of surfactants whereby the surfactant materials, and consequently, the properties of concrete mixtures and concretes can be controlled not only by chemical structure change but also by the qualitative and quantitative combination of active ingredients in organic polar substances of different molecular weights. The experimental data are provided which allow to formulate the following provisions:

- The study of hydrophilic SP group nature influence on its plasticizing properties showed that, in comparison with sulfogroups the hydroxyl groups at the expense of higher molecular weight and high hydrophilicity increase SP plasticizing activity;
- PFM and SP SB-3; in contrast to SP-3, they have some surface activity at the solution-air boundary, thus increasing the frost resistance for casts and equally moveable compounds by air intake increase at 0.5 ÷ 1.5% without making a negative impact on the concrete strength;- It was shown that at a certain ratio of SP with sulfonic and hydroxyl groups in PFM a synergistic effect is produced due to the attraction interaction of molecules on the particle surface. PFM SB-3 + C-3 ("Renaplast") and SB-3 + LST are developed with an improved plasticizing activity; - They showed that the increase of mineral suspension aggregate stability and their transition into a liquid-like state at optimal SP dosages is conditioned by the action of electrostatic adsorption-solvation factors;

## **Conclusions**

1. Research showed that SP have surface activity on the solid-solution boundary, reducing the surface tension of  $[\sigma]_{T-\text{ж}}$ . At the same time, the surface tension on the solution-air boundary may remain a constant one or it is decreased slightly, depending on SP chemical structure.

2. SP adsorption during the disperse phase of the suspension is conditioned by the dispersion forces, and, regardless of hydrophilic group nature it has a monomolecular character. The capacity of a monolayer and the corresponding equilibrium concentration of SP depend on the nature of hydrophilic groups and have the lowest values for the hydroxyl groups.
3. At the joint SP adsorption with various hydrophilic groups as the result of "adsorbate-adsorbate" interaction on the particle surface at certain ratios of the individual components a synergistic effect is produced.
4. SP adsorption on the dispersed phase particles leads to suspension aggregate stability increase, which is very possible after the development of an adsorption monomolecular layer. Thus, the peptization of aggregates to primary particles takes place and immobilized water is released.
5. At the optimum dosages of SP ultimate the maximum shear stress of the suspension becomes equal almost to a zero, and this is conditioned by the energy decrease of an individual contact to the thermal motion energy. The plastic viscosity of the suspension is reduced to a certain value, which is associated with the immobilized water release.
6. It was shown that the increase of aggregate stability and the suspension transition from a structured to a liquid-like state at SP optimal dosages is conditioned by the combined action of an electrostatic and an adsorption-solvation factor.

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