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ACTIVITY OF POLYMERIC SURFACTANTS IN AQUEOUS SOLUTIONS AND PROSPECTS OF THEIR APPLICATION AS PAINT DISPERSANTS

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Abstract. *The article analyses literature sources and general classification of surface-active substances (surfactants). The analysis explains the scientific interest in the development of new high molecular weight and polymeric compounds changing the surface tension on the prase boundaries. The article gives examples of the use of polymeric surfactants in various areas for the chemical industry and in construction (modified additives in concrete, protective compositions and paint compositions) itself. Despite the market of synthesised polymeric surfactants has not undergone global changes in recent years, the modern stage of scientific development has revealed a range of promising modifiers. Adding these modifiers to the systems provides a predictable effect of creating tenacious compositions with good adhesion to the surface of building materials and structures, as well as obtaining water-resistant coatings on the basis of such compositions.*

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Introduction

Nowadays, the use of surfactants is becoming more popular in various fields of industrial production, economics, biology, etc.

The peculiarity of their application is the reduction of tension on the surface. It is caused by their ability to adsorb on the prase boundaries. As a rule, surfactant molecules include both hydrophilic and hydrophobic fragments [1]. Surfactants have the leading position along with rubbers and dyes in terms of production volume worldwide. In particular, more than 250 thousand tonnes of surfactants were produced in the Russian Federation in 2020. At the same time, more than a quarter of the output is consumed in the field of household chemicals, while the main part is used in industry and agriculture [2]. Medicine is also a very extensive area of their practical application.

The involvement of the medical aspect largely explains the intensity of new surfactants implementation. For example, polymeric surfactants have the ability to form micelles. These are the structures consisting of groups of different complex molecules or ions. Therefore, the field of their use is expanding annually.

However, surfactant applications are generally associated with the study of their physical properties, i.e., their adsorption capacity. Nevertheless, the physical properties of polymeric surfactants have not been fully investigated. Moreover, their application is not always theoretically justified [3]. This provides an opportunity to include a range of new research in this area. Therefore, the issue of pigments and filler dispersion improvement in organic medium is of special interest. It can reveal the possibilities of achieving new qualitative characteristics of high molecular weight compounds, as well as for painting in construction.

General classification of surfactants by group or chemical nature

The classification according to the charge of hydroxyl groups or the chemical nature of surfactant molecules is recognised as the most well-known in the world scientific community. According to this classification, it is possible to subdivide:

- cationic surfactants (CSAS);
- anionic surfactants (ASAS);
- amphoteric surfactants (ampholytic, AmSAS) can perform the functions of both proton donor and acceptor depending on the pH of the solution;
- non-ionogenic surfactants (NSAS).

We consider the characteristics of each type of surfactants. Cationic surfactants are characterised by the presence of a relatively large, positively charged hydrophobic group. They are used to improve dispersion of pigments and fillers in organic media due to their ability to adsorb on solid surfaces, displacing air, and moisture while forming a strong bond. Most surfactants contain positive charged nitrogen atom.

CSAS may include:

- salts of alkyl substituted ammonium bases, e.g. hexadecyltrimethylammonium bromide;
- salts of aliphatic amines;
- salts of aromatic amines;
- salts of alkyl-substituted pyridine.

The effective combination of surface-active properties with increased biological activity is a peculiarity of CSAS. As a result, they are used as disinfectants, bactericides, and corrosion inhibitors.

Table 1 characterises applications of CSAS in industry and national economy.

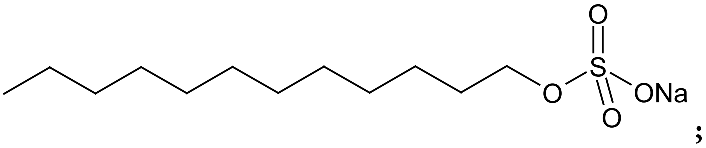
Table 1. Practical applications of CSAS for chemistry and biochemistry

Surface area	Field of application
Surface of steel	Anticorrosive agents
Inorganic pigments	Paint dispersants
Plastic	Antistatic agents
Bacterial cell walls	Germicide chemicals

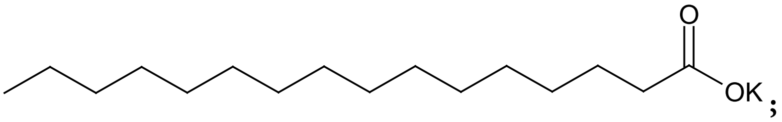
Anionic surfactants are characterised by the presence of a large negatively charged group. The hydrophilic part of the anionic surfactant usually contains a $NaSO_3^-$ or $NaOSO_3^-$ group.

Typical examples of ASAS are:

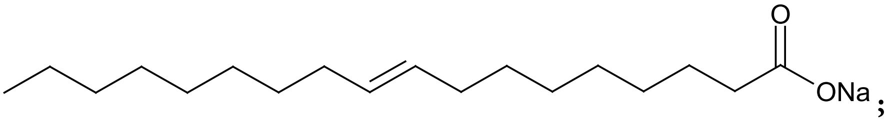
- salts of incomplete sulphuric acid esters, e.g. sodium dodecyl sulphate:



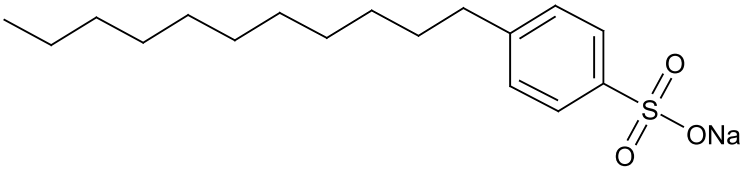
- carboxylic acids and salts with the general formula RCOOMe, where Me is a metal, e.g. potassium palmitate:



- sodium oleate:

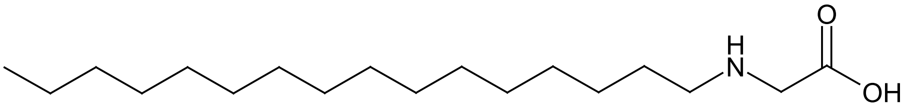


- salts of the related RSO2OM sulfonic acids containing an alkyl radical, e.g., dodecyl sulfonate:



ASAS is commonly used in the field of latex and synthetic rubber production [4].

Amphoteric or ampholytic surfactants (AmSAS) contain two functional groups. They differ in their properties and can demonstrate both anionic and cationic ones depending on the acidity of the medium. An amino group is capable to acquire a positive charge. Proteins and natural amino acids are the classic representatives of AmSAS. Their synthetic analogue is alkylamino acid or acetylaminoacetic acid:



The high cost of alkylamino acids production has been the reason for their rare industrial and medical implementation.

Non-ionogenic surfactants are not dissociate into ions in aqueous solutions. Their molecules consist of hydrophobic radicals (e.g. alkyl radicals) and hydrophilic atomic groups. Meanwhile, the hydrophilic portion of the NSAS typically includes hydroxyl (OH^-) groups or ether (C-O) bonds. It requires their significant amounts in the molecule to achieve the required level of hydrophilicity.

One of the obvious advantages of NSAS is their compatibility with ionogenic surfactants. Table 2 shows the different classes of surfactants.

Table 2. Examples of different classes of surfactants

Name	Abbreviated name	Formula
Cationic surfactants		
Octadecylamine	ODA	$C_{18}H_{37}NH_2$
Dodecylamine	DDA	$C_{12}H_{25}$ NH_2
Cetyltrimethylammonium bromide	CMAB	$[C_{16}H_{33}N(CH_3)_3]Br$
Anionic surfactants		
Sodium octyl sulphate	OS	$C_8H_{17}OSO_3Na$
Sodium dodecyl sulphate	SDS	$C_{12}H_{25}OSO_3Na$
Non-ionogenic surfactants Oxyethylated alkylphenol derivatives $C_nH_{2n+1}C_6H_4O(C_2H_4O)_mH$		
Emulsifier OP-7	OP-7	where n = 8–10, m = 6–7

Peculiarities of surfactant activity in aqueous solutions

There are two large groups of diphilic surfactants. They are divided according to their ability to self-organise in solutions, namely absolute soluble and micelle-forming surfactants [5, 6].

The group of absolute soluble substances includes lower alcohols, acids, and their salts. These substances remain in a molecularly dispersed state in solution until concentrations corresponding to their saturated solutions are reached. The system then separates into two macrophages.

The second group of surfactants is able to form heterogeneous disperse systems. Colloidal surfactant molecules, containing both hydrophilic and hydrophobic moieties, tend to migrate independently to the phase boundaries. When hydrophilic groups are isolated from water (totally or partially), an adsorption layer is formed, reducing the free energy at the interface. Furthermore, the rate of ultimate adsorption increases with increasing of surfactant concentration [7].

As the surfactant concentration in solution increases, structural aggregates (micelles) are formed. Micelles are formed when surfactants have long hydrocarbon chains and strong polar groups.

Furthermore, the concept of ‘critical micelle formation concentration’ (CMC) – the minimum surfactant concentration – is introduced. The thermodynamic equilibrium of ions and molecules with surfactants is reached at this concentration. Significant changes in the physical and chemical properties of the surfactant solution can be observed in the region of critical micelle concentration values [8-12].

To assess the effect of surfactant composition on the CMC values, we should consider the following patterns described in [13-16]:

- values of CMC strongly decrease with increasing of alkyl chain length of the surfactant. Moreover, the drop in CMC with increasing of alkyl chain length by one methylene group is 50% for ionic surfactants and up to 70% for non-ionic surfactants;
- the CMC for ionic surfactants is significantly higher than for NSAS. The ratio depends on the alkyl chain length, but the difference is about two orders of magnitude;

- displacement of ionogenic groups from the extreme boundary of the hydrocarbon radical to the middle of the alkyl chain causes an increase in the CMC;
- the increase of the counterion charge causes decreasing of the CMC.

The increase in the polarity of the hydrophobic part of the molecule also contributes to the growth of CMC.

Temperature is another important factor affecting the CMC. As the temperature increases, the CMC decreases. It is primarily due to the breaking of hydrogen bonds between water molecules and oxygen atoms, as well as a decrease in aggregation.

The presence and concentration of additional substances in solution also significantly affect the CMC, taking into account the following key principles:

- the adding of salt to the solution causes a decrease in the CMC. The CMC changes are higher at high salt concentrations as the number of carbon atoms in the surfactant chain increases;
- ionic charge in solution is relevant. The charge of the counterion has a particularly significant effect on the CMC;
- low molecular weight substances affect the CMC individually, depending on the polarity of the dissolved compounds;
- substances dissolving in water have some influence on the upward change of CMC.

CMC is one of the most important characteristics of surfactants. The CMC analysis is the main stage of surfactants use. The critical micelle formation concentration (CMC) is determined by measuring the surface tension and solubilisation process. The conductometric method also can be used for the determination of ionic surfactants [7].

Polymeric surfactants demonstrate ‘surface activity’. It is important for material production technology. This indicates their ability to adsorb at phase boundaries with a decrease in surface energy due to a certain orientation of molecules in the surface layer. Surface tension is required to create a unit of surface area (1 m^2).

Numerous amphiphilic and water-soluble surfactants are very effective in reducing the surface tension of solutions (especially at the air contact), often to values not exceeding 30-40 mN/m. Moreover, the view of the surface tension isotherm (see Fig. 1) provides a rather qualitative illustration of the correlation between the surface tension and the concentration of the dissolved substance at constant temperature.

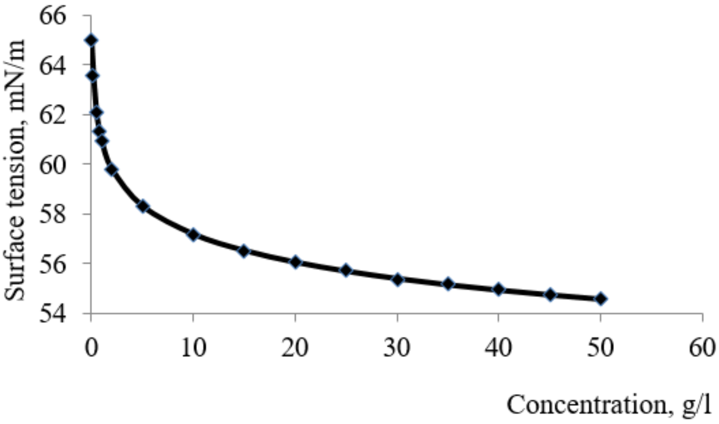


Fig. 1. General view of surface tension isotherm

The surface activity of surfactants in aqueous systems at a certain temperature depends on their concentration and the shape and size of the micelles. Generally, the surface tension decreases as the micelle mass increases. In water, micelles can be as spherical, cylindrical, or even have bilayer configurations.

Surface tension in solutions is determined by the characteristics of the solvent and dissolved substance, their concentration and temperature.

Solubilising ability of surfactants

Solubilisation is a process of significant increase of solubility of weakly polar organic compounds (solubilisates) in water in the presence of surfactants (solubilisers).

The ability of micellar systems to solubilise compounds is one of the most important properties. This process is closely related to hydrophobic interaction and causes the formation of equilibrium almost transparent solutions. Solubilisation can be direct (in aqueous solutions) and reverse (typical for hydrocarbon systems) [6, 17].

Non-polar hydrophobic substances and polar organic compounds are able to integrate into the micelle structure in various ways. Non-polar substances such as aromatic and paraffinic hydrocarbons are integrated into the hydrocarbon nuclei of the micelles. Polar substances such as acids and alcohols, on the contrary, are located between the surfactant molecules. Their polar groups are orientated/adapted to the surrounding water, while their hydrophobic parts line up parallel to the hydrocarbon chains of the surfactant.

Moreover, solubilisate molecules can attach to the surface of the micelles. These molecules are located between the curved chains without penetrating into the micelle core structure. This behaviour is characteristic of NSAS [6].

Initially, the solubiliser dissolves in solution. Afterwards, solubilisate molecules diffuse to the surface boundary of the micelle. At the final stage, the solubiliser is introduced into the micelle structure [18].

Peculiarities of surfactants synthesis for production of high-molecular compounds and polymer composites

Modification of pigments and fillers for polymer composites and coatings to improve their technological properties is most effective when chemisorption layers of modifying substances are formed on their surface. However, a significant decrease in the specific surface energy of the pigment and filler particles is undesirable. It reduces the energy of their surface wetting by polymer solutions or melts that make up the matrix. The surface of pigments often demonstrates a mosaic structure of acid-alkaline properties containing groups. These groups are capable of chemical interaction with acidic functional groups such as the carboxyl groups of organic modifiers.

Reactive and polar groups must be additionally integrated into the surfactant molecule during synthesis in order to facilitate chemisorption of the modifier while maintaining the ability of the adsorption layer to interact with the environment through a specific polarity (Fig. 2).

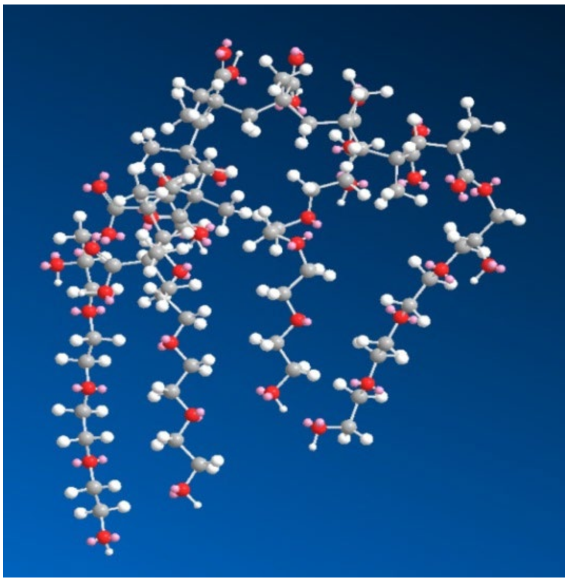


Fig. 2. 3D model of the copolymerisation product of oxyethylated glycyl methacrylate with methacrylic acid; atoms colour is grey (carbon), white (hydrogen), red (oxygen), and pink (unseparated electron pairs)

The model of molecule structure is presented in Fig. 2. It implies that part of the atoms (carbon, hydrogen) can remain chemically inert under the conditions of modification and composite formation.

Application of polymer surfactants based on polycarboxylates in the construction industry

Polymeric surfactants are widely used in various industrial, economic, and medical spheres.

We consider the process of producing oxidised bitumen and improving its properties. Modifying additives (surfactants) are introduced into the system during their production. These have a positive effect on the properties of the resulting material and their reactivity. In terms of reduction the costs, the use of surfactants in this case is reasonable [19, 20].

The advantage of using modifying additives containing surfactants is their ability to improve the characteristics of bitumen. The use of these additives improves wetting of mineral materials with bitumen due to the formation of an adsorption layer. Polar groups in this layer are orientated to the mineral surface, and hydrocarbon chains are included in the structure of bitumen matrix.

The main advantage of using such additives is reduction of the temperature and time required for the mixing process and homogeneous mixture. Furthermore, surfactants provide the formation of a monomolecular chemisorption layer at the interface ‘mineral material – bitumen’. It significantly increases the adhesion between the components of the mixture [21-23].

One of the priority tasks for the construction industry is to speed up the process of erecting monolithic structures. Therefore, the focus is on increasing the flowability of concrete mixtures capable of self-compaction. Various ways to improve the flowability of cement mortars and high molecular weight compounds for construction have been developed. Particularly, in the 1960s and 1970s, polymers based on condensation products of formaldehyde with sulfated melamine and naphthalene were obtained and are still in use [24].

New types of polymeric surfactants (superplasticisers) based on simple polycarboxylate esters were developed at the end of the 20th century. Their effect on flowability depends on their polymer structure and the cement characteristics. Their polymer properties vary considerably with the high percentage of alumina in the cement. The number of carboxyl groups in the chain and the chain length itself also play an important role. It determines the amount of adsorbed polymer [25].

Nowadays, plasticisers based on polycarboxylates are the most effective industrial plasticisers among all water-soluble additives known in the construction industry. When added to freshly prepared concrete, they significantly change its rheological properties, sharply reducing the viscosity of cement mixtures and facilitating pouring even into compact or heavily hardened moulds. The high flowability of concrete ensures its filling of all parts of the mould.

The action of polycarboxylate superplasticisers is based on a combination of electrostatic and spatial effects. They are achieved due to hydrophobic polyester side chains of tpolycarboxylate molecule complex. This mechanism provides a water-soluble effect several times higher than for conventional superplasticisers. The advantages of using polycarboxylate superplasticisers are lower viscosity and low water consumption required for mixing concrete mixtures compared to superplasticisers based on naphthalene sulphonate, melamine sulphonate or lignosulphonate [26-32].

Use of polymeric surfactants as paint dispersants

Modern dispersants are substances added to suspensions to improve particle separation and prevent agglomeration or precipitation. They must fulfil rather stringent requirements. Surfactants based on polymers with multiple functional groups, such as polycarboxylates, have significant perspectives as pigment surface modifiers. Their use prevents sintering during drying, improves dispersibility, reduces the moisture content of aqueous pastes after filtration, and decreases polydispersity.

Pigmented materials are microheterogeneous colloidal systems. Their physical, chemical, and technical properties are primarily determined by the dispersion of pigments and fillers. These factors impact the rheological properties of pigment dispersions, their aggregation and kinetic stability, optical properties (e.g. hiding power, colour and tinting power), and the protective and mechanical properties of coatings.

Stabilisation is essential for pigmented materials and is ensured by the structural and mechanical characteristics of adsorption layers. They form spatial barriers preventing the particles from approaching the distance at which the forces of attraction become significant. This interaction reduces the surface energy reserves at active sites on the pigment surface. Key functions of dispersants include wetting, dispersing, and stabilisation. An effective dispersant molecule should include both hydrophilic and hydrophobic moieties [33, 34].

Polymeric surfactants used as dispersants for paints include:

- maleic acid anhydride copolymers [35];
- polymeric dispersants based on urethane and urea derivatives [36, 37];
- copolymers of styrene with amino groups [38, 39];
- copolymers with hydrophilic and hydrophobic acrylic fragments containing side carboxyl or amino groups [39];

- low molecular weight alkyd resins with an acid content of more than 30 mg KOH/g;
- low molecular weight polyester resins with high acid and hydroxyl content and their mixtures with ionic and non-ionic surfactants derived of fatty acids [34];
- soya lecithin [34];
- organometallic compounds capable of reacting at room temperature with oxygen-containing groups on the surface of pigments and functional groups, such as in epoxy resins [39].

Polymeric surfactants and rheological properties of pigment and filler dispersions

The viscosity of the pigment dispersion has a great impact on the dispersibility of pigments and fillers. It depends both on the fluidity of the medium itself and on the amount and type of dispersed phase.

For example, the study of the flow of dispersions with the inclusion of latex, pigments, and fillers [40] revealed the certain content of the solid phase, and gel network formation. However, the filler particles still continue to interact through the liquid interlayers [41]. An extremum is observed on the graph of the shear stress dependence at constant latex content [42]. It corresponds to the densest packing of particles. As the concentration of the solid phase (e.g. red iron oxide pigment based on goethite) exceeds a critical value, the composition lacks latex to form an adsorption layer on the pigment and filler particles. When the amount of dispersed phase in the system does not exceed the threshold value, latex gives stable adsorption layers. They ensure the stability of the system and viscosity constancy, fulfilling the function of a surfactant [40]. The study of the flow of a mixture of a non-ionogenic surfactant (e.g., OP-10) and vinyl chloride-butadiene latex combined with hydroxyethylcellulose already four decades ago [43] can be considered as another striking example. Typically, a protective material suitable for obtaining coatings on surfaces of any type and characterised by increased water resistance and durability was obtained after curing of such a composition. If the pigment is not iron oxides but zinc oxides, we can already talk about creating primers with anti-corrosion properties. The doping of styrene-acrylate latexes with NH_2-groups, in turn, should be expected to impart antistatic properties [44, 45] to special coatings. This is especially important in the operation of certain types of technological equipment.

The introduction of small amount of polycarboxylate surfactants causes an increase in the viscosity of pigment pastes, and in some cases – a change in the nature of their flow. Moreover, these surfactants in the systems under study do not always demonstrate themselves as effective dispersants. The pigment surfaces are pre-modified in this case. Therefore, it is recommended to test the effect of such additives as polyol [46], albumin, and glycerin [47], as well as the effect of polyethylene glycol ethers (expected effect - strengthening of compositions and coatings), urotropine in the amount ≤ 5 wt% (expected effect – water-resistant composition) [48], polyisocyanate [49], and olypha-oxol (expected effect – increased adhesion to the surface of the building material) [50]. In general, to obtain stable mixtures using the tested surfactants we should use the relatively low concentration and include non-ionogenic compounds into the system [51, 52], (sulfated OP-10 (C-7), oxyethylated isooctylphenol, unsymmetrical block copolymer of ethylene, and propylene oxides (NBS-2)).

Conclusions

Hence, due to their specific properties, surfactants can be used as essential components for a wide range of applications.

Polymeric surfactants with a high content of carboxyl groups are recommended for use in the chemical industry, in particular, when modifying the surface of chromatic iron oxide pigments and fillers. They are used to improve the wettability and dispersibility, increase the strength and adhesion of colouring compositions, and obtain water-resistant coatings on their basis.

In construction, the concrete mobility index largely determines its ability to fill various forms and cavities when spreading under its own weight. Therefore, it is reasonable to use polymeric surfactants as superplasticisers of concrete mixtures. The resulting concrete samples are expected to have a low shrinkage.

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