



## Technology of Production of Surfactants

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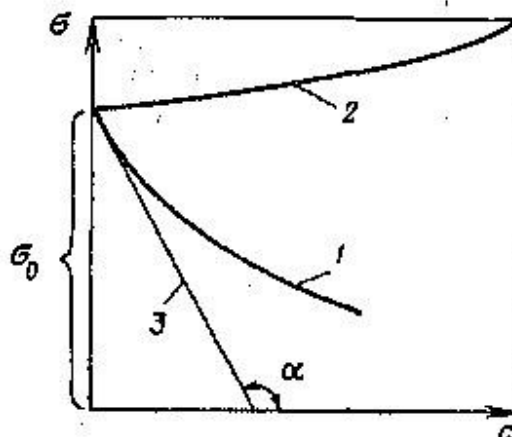
**Abstract:** The results of the use of surface-active substances (surfactants) in the process of oxidative demercaptanization of hydrocarbon raw materials are presented. It is shown that the use of surfactants increases the efficiency of the demercaptanization process and makes it possible to extract from processed hydrocarbons not only the simplest, but also higher molecular weight mercaptans, as well as organosulfur compounds of other classes.

**Keywords:** Surfactants (surfactants), synthetic detergents (SMS), micelles, ionic surfactants, nonionic surfactants, hydrophilicity, hydrophobicity, detergency, biodegradability. One of the large-capacity areas of the petrochemical industry is the production of surface-active substances (surfactants).

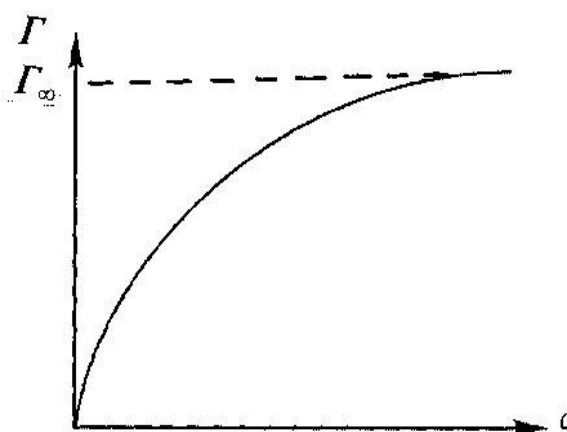
The first historically known detergent, the main component of which is surfactant, was soap, obtained by treating fats with an aqueous ash extract containing potassium carbonate. This soap was very bad because of the high content of neutral fats in it. Much later, its quality was improved by treating fats with potassium hydroxide, and then pouring soap with sodium chloride and turning soft potassium soaps into hard sodium soaps. The depletion of resources led to the need for substances that would perform the functions of soap more efficiently and in a variety of conditions. The development of organic synthesis made it possible by this time to find ways to obtain such synthetic detergents. The raw materials for the production of surfactants and synthetic detergents are currently the products of oil, gas and coal processing. Later it was found that the useful properties of the latter can be enhanced by adding a number of other organic and inorganic compounds to them: complexing agents, pH regulators, etc. The optimal choice of these and surfactants has led to the creation of modern synthetic detergents (SMS), in which, as a rule, the most rational is a combination of two or three.

### **Surfactants with various target additives.**

Substances whose introduction into the system leads to a decrease in surface tension ( $d\sigma/dc < 0$ ) are called surfactants (surfactants) (Fig. 1.). In accordance with the Gibbs equation, adsorption for such substances is positive, i.e. their concentration in the surface layer is higher than the volume concentration (Fig. 2). So, for the water-air and water-hydrocarbon boundary, organic compounds with a hydrocarbon (non-polar) part and a polar group (- OH, - COOH, - NH<sub>2</sub>, etc.) are surfactantly active. Such an asymmetric (diphilic) structure of surfactant molecules leads to the fact that they turn out to be related to both contacting phases: a well-hydrating polar group determines the affinity of surfactant molecules with respect to water, and the hydrocarbon chain with respect to the non-polar phase. At the boundary with air, surfactants have a surface tension ( $\approx 25$  MJ/m<sup>2</sup>) significantly lower than water (72.75 MJ/m<sup>2</sup>).



**Rice-1. Isotherm of surface tension for surfactants and surfactants.**



**Rice-2. Surfactant adsorption isotherm.**

As a measure of surface activity, Rebinder proposed using the value  $G$ , equal to and measured in

$$G = \lim_{c \rightarrow 0} \left( -\frac{d\sigma}{dc} \right)$$

Inorganic electrolytes, when dissolved in water, only very slightly increase its surface tension. According to the Gibbs equation, this means that the adsorption of electrolytes is negative - the surface layer of the solution is depleted of dissolved matter compared to the volume ( $c(s) < c$ ). Such depletion of the surface layer when the electrolyte is dissolved in water is quite understandable: the ions are hydrated, and it is unprofitable for them to approach the surface closer than the thickness of the hydrate shell (the ion output directly into the surface layer is thermodynamically unprofitable due to the energy costs of ion dehydration).

### Adsorption work

Along with the surface activity ( $-d\sigma/dc$  at  $c \rightarrow 0$ ), another thermodynamic parameter is used to characterize surfactants - the adsorption work ( $W_{ads}$ ), which is equal to the work performed by the system when transferring 1 mole of surfactant from the internal volume of the solution to its surface bordering the neighboring phase at a constant temperature. To calculate the adsorption work, we will again consider the simplest case - a dilute aqueous surfactant solution at the gas



boundary. Then the chemical potential of surfactants in the volume of the solution with a concentration of  $c$  is equal to:  $\mu = \mu^0 + RT \ln c$ .

$$\mu = \mu$$

For dilute solutions, the specific adsorption ( $G$ ) is significantly less than the maximum adsorption ( $G_{mah}$ ) corresponding to a saturated monolayer of surfactants on the surface of the solution. Under the condition  $G \ll G_{mah}$ , the surface layer with a thickness  $\delta$  is a dilute surface solution. Then the chemical potential of surfactants in the surface layer of the substance can be determined by the usual ratio:  $\mu_s = \mu_s^0 + RT \ln c_s$

where  $c_s$  is the surface concentration;  $\mu_s^0$  is the standard chemical potential of surfactants in the surface layer of the solution. The condition of thermodynamic equilibrium between the surfactant solution and the surface layer is the equality of their chemical potentials:  $\mu = \mu_s$ . We emphasize that the standard potentials of surfactants in the solution volume ( $\mu^0$ ) and the surface layer ( $\mu_s^0$ ) differ ( $\mu^0 \neq \mu_s^0$ ).

After substituting expressions for the specified chemical potentials  $\mu$  and  $\mu_s$ , we obtain:

$$\frac{c_s}{c} = \exp\left[\frac{(\mu^0 - \mu_s^0)}{RT}\right]$$

The difference in the standard chemical potentials of this surfactant ( $\mu^0 - \mu_s^0$ ) by definition is equal to the operation of a perfect system when transferring 1 mole of surfactant from the volume to the surface of the solution under standard conditions. It is this difference that determines the work of adsorption:

$$W_{adc} = \mu^0 - \mu_s^0$$

From equation (1) we obtain

$$W_{adc} = RT \ln \frac{c_s}{c}$$

For dilute surfactant solutions, the excess adsorption  $G$  for a surface layer with a thickness  $\delta$  is equal to  $G = (c_s - c) \delta$ . For dilute solutions,  $c_s \gg c$  is valid, so the expression for  $G$  can be simplified:  $G = c_s \cdot \delta$ ,

where  $\delta$  is the thickness of the surface layer.

This equation is used to calculate the adsorption work of various surfactants according to experimental data. In the homologous series of surfactants, during the transition to the next homologue, the adsorption work increases by about 3 kJ/mol. This result allows us to explain the reason for the increase in surface activity by about 3 - 3.5 times with the elongation of the hydrocarbon chain in the surfactant molecule by one group - CH<sub>2</sub>.

### Hydrophilic-lipophilic surfactant balance

The ability of surfactants to be adsorbed on various surfaces is determined primarily by the specifics of the structure of their molecules, namely, their diphilicity. The surfactant molecule consists of polar and nonpolar parts. The surface activity and other properties of surfactants depend on the ratio of the properties of these parts. The following example is indicative. In the homological series of low molecular weight surfactants (wetting agents and foaming agents), the surface activity of homologues (alcohols, fatty acids) at the solution-gas interface increases with increasing length of the hydrocarbon radical according to the Duclos-Traube rule. At the same time, the lower homologues (CH<sub>3</sub>H, C<sub>2</sub>H<sub>5</sub>H) do not show surface activity. Due to the predominant influence of the hydroxyl group, they dissolve very well in water and therefore there



is no thermodynamic incentive for them to concentrate on the surface (adsorption). At the same time, alcohols and carboxylic acids with a very low  $\log K_{ow}$ .

Thus, the optimal action of surfactants corresponds to a certain balance of the polar and non-polar parts of the surfactant molecule. A quantitative measure of the colloidal-chemical properties of surfactants is the hydrophilic-lipophilic balance (GLB), determined by the action of the polar (hydrophilic) and nonpolar (lipophilic) parts of the surfactant molecule. There are several empirical methods for determining GLB. The most common method is the use of group numbers. Each group that is part of the surfactant molecule is assigned a certain group number ( $q_i$ ). The hydrophilic-lipophilic balance is defined as the sum of the group numbers:  $GLB = 7 + \sum q_i$

For hydrophilic groups  $q_i > 0$ ; for hydrophobic  $q_i < 0$ . Accordingly, at  $GLB > 7$ , the action of polar groups prevails, and such surfactants dissolve mainly in water. On the contrary, at  $GLB < 7$ , the solubility of surfactants in a nonpolar liquid ("oil") prevails. In this regard, the values of GLB are used in the selection of surfactants to stabilize direct emulsions (drops of "oil" in water) and reverse emulsions (drops of water in "oil"). It is surfactants with high GLB values that are used to produce direct emulsions. On the contrary, surfactants with low GLB values are effective for obtaining reverse emulsions.

The physical meaning of the GLB numbers is that they determine the work of adsorption during the transfer of polar groups of surfactant molecules to the non-polar phase and non-polar groups to the polar phase. Depending on the number of GLB surfactants are used for one purpose or another. So, if surfactants have GLB numbers from 7 to 9, they are used as wetting agents, from 13.

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