PHYSICAL CHEMISTRY

P. A. DEMCHENKO and Corresponding Member of the Academy of Sciences of the USSR A. V. DUMANSKY

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Abstract

Full Text

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DESOLUBILIZATION OF HYDROCARBONS FROM SOLUTIONS OF NAPHTHENIC ACID SOAPS AND POTASSIUM LAURINATE

Solubilized systems are formed in the production of synthetic detergents, in the alkaline refining of individual petroleum fractions, in emulsion polymerization of monomers, and in other branches of industry. Insufficient study of the various factors influencing the processes of solubilization and desolubilization hinders the development of theoretical foundations for separating solubilized systems into individual components and for obtaining pure surface-active substances in industry. Solubilization and desolubilization are among the least studied problems of colloid chemistry. A small number of works have been devoted to the study of solubilization ([1–5]), while the study of desolubilization apparently has not yet been carried out.

In the process of solubilization, hydrocarbons are located in the oleophilic part of the micelles ([1,2]). Their desolubilization is possible when micellar structures are disrupted and the oleophilic properties of detergent solutions are lowered. This assumption was confirmed in a study of the desolubilization of hydrocarbons from aqueous solutions of naphthenic acid soaps and potassium laurinate. Low-molecular oxygen-containing organic substances were used as desolubilizers: aliphatic alcohols, glycol, glycerin, formalin, acetone, dioxane, etc. In a solution containing soaps above the critical micelle-forming concentration ([6]), the limiting amount of hydrocarbon was solubilized by the method described previously ([7]). Then a measured amount of such a solution was transferred into the apparatus, a calculated amount of desolubilizer was added, and the separation of the solubilized hydrocarbon as a separate phase in the graduated tube of the apparatus was observed. The experimental data are given in Figs. 1–4.

Fig. 1. Effect of ethylene glycol *(1)* and glycerin *(2)* on the solubilization of

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

toluene in 0.3 *M* solutions of potassium laurinate (at 60°)

Additions of increasing amounts of glycol and glycerin to a 0.3 *M* solution of sodium laurinate reduce its solubilizing capacity with respect to toluene, the desolubilizing action of glycerin being greater than that of glycol (Fig. 1). Aliphatic alcohols exert a complex effect on the solubilization of hydrocarbons in detergent solutions: low-molecular alcohols decrease it, whereas high-molecular alcohols increase solubilization, the more so the longer their hydrocarbon radicals. Thus, for example,

From Fig. 2 it is evident that amyl and butyl alcohols sharply increase, while ethyl and methyl alcohols decrease, the solubilization of *n*-heptane in 0.3 M solutions of sodium naphthenate (molecular weight 297). Propyl alcohol has transitional properties. Small additions of propanol substantially decrease solubilization, but when its content exceeds 15 moles per mole of soap, solubilization increases noticeably. Acetone and dioxane proved to be more effective desolubilizers than low-molecular-weight alcohols. When about 3 mol/l of dioxane is added to a 0.3 M solution of sodium naphthenate, its solubilizing capacity is reduced almost 2.3-fold (Fig. 3).

Fig. 2. Effect of aliphatic alcohols on the solubilization of *n*-heptane in a 0.1 M solution of sodium naphthenate: 1 —*n*-amyl alcohol, 2 —*n*-butyl alcohol, 3 — ethyl alcohol, 4 —methyl alcohol.

In view of the important significance of desolubilization for the purification of naphthenic acids from unsaponifiable impurities, the system sodium naphthenate—heptane—acetone—water was systematically investigated. From the experimental data presented in Fig. 4 it is evident that, with increasing additions of acetone, the solubilization of heptane in a 0.3 M solution of sodium naphthenate (molecular weight 334) decreases sharply, and at an acetone concentration of about 3.0-3.5 mol/l the curve passes through a minimum. A further increase in the acetone concentration in the system increases the transfer of heptane into the volume of the solution. An analogous regularity was observed in mixtures of sodium soaps of naphthenic acids. An especially sharp decrease in the solubilization of the hydrocarbon is observed when 1.5-2.0 mol/l of acetone and dioxane is introduced into the soap solution. It was found that,

Fig. 3. Effect of additions of acetone (1) and dioxane (2) on the solubilization of toluene in a 0.3 M solution of sodium naphthenate (molecular weight 297) at 40°.

Figure 4

Figure 4: Figure 4

Fig. 4. Effect of acetone additions on the solubilization of heptane in a 0.3 M solution of sodium naphthenate (molecular weight 334).

that high-molecular hydrocarbon impurities are more fully desolubilized in the presence of readily boiling hydrocarbons.

On the basis of the experimental data obtained, a technique was developed for separating hydrocarbon impurities from solutions of naphthenic-acid soaps by the method of desolubilization, which consists of the following: technical naphthenic acids containing hydrocarbon impurities were dissolved in petroleum ether; acetone and an equivalent amount of an aqueous alkali solution, necessary for obtaining the naphthenic-acid soaps, were added. After saponification of the naphthenic acids, the system separates into two phases with a clear phase boundary: the upper phase consists of petroleum ether and the unsaponifiable impurities that have passed into it, while the lower phase is an aqueous-acetone solution of naphthenic-acid soaps. Additions of acetone were calculated so that, at the end of saponification, its content in the aqueous phase was about 3 mol/l. The indicated amount of desolubilizer is sufficient to prevent the formation of micellar structures with high oleophilic properties and to sharply reduce the solubilization of hydrocarbons.

It is interesting to note that desolubilizers are also effective demulsifiers; this ensures the simultaneous separation from the detergent solution, as a separate phase with a clear phase boundary, of the solubilized and emulsified portion of the hydrocarbons. The hydrocarbon phase is separated by distillation. The regenerated petroleum ether is reused for diluting crude naphthenic acids before saponification, while the high-boiling hydrocarbons extracted from the naphthenic acids can be used for producing greases, emulsols, and for other purposes. From the aqueous-acetone solution, the sodium soaps of naphthenic acids were salted out with a concentrated solution of sodium hydroxide. This gave a soap containing 60–62% naphthenic acids. The resulting "spent soap lye," in the form of an aqueous-acetone solution of sodium hydroxide, was reused for saponifying new portions of naphthenic acids. The light-colored naphthenic-acid soaps obtained, with a weak characteristic odor, can be used as independent detergents, emulsifiers, flotation reagents, thickeners, and for incorporation into detergent formulations. The naphthenic acids isolated by decomposition of the soaps with mineral acid have a light-yellow color, a weak odor, and contain hydrocarbon impurities in an amount of 0.6–0.9%. Naphthenic acids are high-quality products which, in a number of cases, can replace fats and fatty acids. All operations for purifying naphthenic acids from hydrocarbon impurities were carried out at ordinary temperature and with slight heating. The possibility has been shown of utilizing the acetone, petroleum ether, and alkali used for salting out. This makes it possible to consider that the proposed method for purifying naph-

thenic acids by desolubilization of hydrocarbon impurities will prove effective and economical when introduced into practice. Using potassium laurinate and sodium naphthenates as examples, the possibility has been shown of desolubilizing hydrocarbons from detergent solutions with the aid of low-molecular oxygen-containing substances.

Institute of General and Inorganic Chemistry
Academy of Sciences of the Ukrainian SSR

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Note: Figure translations are in progress. See original paper for figures.