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

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Abstract

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

THE INFLUENCE OF THE STRUCTURE OF HYDROCARBONS ON THEIR SOLUBILIZATION IN SOLUTIONS OF SODIUM SOAPS OF SATURATED FATTY ACIDS

In investigating the solubilizing capacity of individual detergents, differing colloidal dissolution of hydrocarbons in their solutions was observed (^{1}, ^{2}). In the present work we give the results of a systematic study of the solubilization of hydrocarbons of various structures in aqueous solutions of sodium soaps of saturated fatty acids. The soap samples for the investigation were prepared by neutralizing pure fatty acids with an equivalent amount of alkali according to the method described earlier (^{3}). The compared effects of solubilization of various hydrocarbons were studied by a direct method (^{4}), which gives good reproducibility of the experiments. Experimental data on the limiting solubilization of certain aromatic and aliphatic hydrocarbons in 0.1 M solutions of sodium caprylate, caprate, laurate, myristate, palmitate, and stearate are presented in Fig. 1.

From consideration of the curves showing the dependence of the solubilization effect on the length of the hydrocarbon radical of the soap, it is seen that the solubilization of octane, isooctane, heptane, ethylbenzene, *o*-xylene, styrene, toluene, and benzene changes regularly. Sodium enanthate, which contains 7 carbon atoms, and solutions of lower-molecular homologs of sodium soaps of saturated fatty acids practically do not solubilize the indicated hydrocarbons. With an increase in the length of the soap radical above 7, the solubilization of hydrocarbons in their aqueous solutions becomes appreciable. For soap homologs from sodium caprylate (C_8) to sodium laurate (C_{12}), a nonuniform increase in solubilization is observed, expressed by the gently sloping portions of curves *AB* (Fig. 1). With a further increase in the soap radical from laurate to sodium stearate (C_{12}–C_{18}), a sharper increase in hydrocarbon solubilization occurs, which is represented by the almost straight portions of curves *BC*. An analogous regularity was observed earlier in the study of the solubilization of chlorinated hydrocarbons (^{5}, ^{6}). The solubilization effect of hydrocarbons in solutions of the soaps studied is strongly influenced by the structure and length of their hydrocarbon chain. Aromatic hydrocarbons are solubilized to a considerably greater extent than aliphatic hydrocarbons of similar molecular weights, while ethylbenzene, which has a mixed structure, occupies an intermediate position between them in the value of solubilization (Fig. 1, 5). Comparing the solubilization of styrene with that of ethylbenzene, it is seen that the presence of a double bond in the aliphatic part of the hydrocarbon molecule (styrene) sharply increases its solubilization in soap solutions, evidently owing to the hydrophilicity of the double bond, previously studied in the hydrocarbon radicals of soaps of oleic and ricinoleic acids (7).

From consideration of the curves expressing the dependence of hydrocarbon solubilization on the structure of the radicals of soaps of saturated fatty acids, it may be concluded that the solubilization of the monomer (styrene) obeys the general regularity established in the study of the solubilization of aromatic hydrocarbons. When an ethyl group (ethylbenzene), or one or two methyl groups (toluene and xylene), are present in the benzene ring, the ability of the hydrocarbon to be solubilized in the corresponding solutions

of the soaps studied decreases sharply. Isooctane and heptane are solubilized in greater amounts than octane (Fig. 1, 8), which indicates an increase in the solubilization of a hydrocarbon homolog when the molecule is shortened by a CH_2 group and when branching is present in the hydrocarbon chain.

In terms of their ability to be solubilized in solutions of soaps of saturated fatty acids, the hydrocarbons studied are arranged in the following decreasing series: benzene > toluene > styrene > *o*-xylene > ethylbenzene > heptane > isooctane > octane.

The observed regularity of solubilization can be explained by the fact that soap homologs, with increasing length of their hydrocarbon radicals, form more oleophilic micellar structures capable of binding larger amounts of hydrocarbons in the volume of the aqueous solution.

This view is confirmed by the course and by the analogous arrangement of the hydrocarbon solubilization curves. The quantitative difference in solubilization depends on the structure and binding energy of the hydrocarbons with the soaps (3). Soap micelles have a smaller effective volume for the solubilization of aliphatic hydrocarbons than for aromatic ones.

The partial pressure of solubilized hydrocarbons is substantially lower than that of those emulsified in an aqueous medium (2). This indicates the establishment of a close connection between the oleophilic part of soap micelles and the solubilized hydrocarbons. The determining factor in the colloidal dissolution of hydrocarbons is apparently the energy of their binding with the soap (3). The higher solubilization value of aromatic hydrocarbons and of the monomer is explained by their greater binding energy with the micellar structures of soap in solution. During solubilization they are apparently located not only between the terminal groups of the hydrocarbon chains of the soap associated into micelles, but also in the space between their long lateral sides.

Fig. 1. Solubilization of hydrocarbons of different structure in 0.1 M solutions

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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.