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Solubilities of Toluene and *n*-Octane in Aqueous Protosurfactant and Surfactant Solutions

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The solubilities of toluene and *n*-octane in aqueous protosurfactant and surfactant solutions were determined at 25 °C. The protosurfactants studied are sodium salts of cyclohexanecarboxylic acid, 2,5-diisopropylbenzenesulfonic acid, and 3,5-diisopropylsalicylic acid. Each of them has six alkyl carbons ($S_{AC} = 6$) and does not form micelles in water. The two micelle-forming surfactants used are sodium *n*-hexanoate with six alkyl carbons ($S_{AC} = 6$) and sodium *n*-octanoate with eight alkyl carbons ($S_{AC} = 8$). In three-component systems of toluene or *n*-octane with water and organic salt (either protosurfactant or surfactant), the solubility of the hydrocarbon in the aqueous phase increases as the number of alkyl carbons of the organic salt and as the aqueous concentration of the organic salt increases. However, in this study we found that sodium 3,5-diisopropylsalicylate causes much more pronounced increases in hydrocarbon solubility than these two surfactants. Sodium 2,5-diisopropylbenzenesulfonate, although not as effective in solubilization as the salicylate, has much stronger hydrotropic properties for hydrocarbons than either of these two surfactants. Sodium cyclohexanoate, with a compact arrangement of the six alkyl carbons, shows a higher hydrotropic effect than sodium *n*-hexanoate.

Introduction

In two previous papers (*1*, *2*) we have presented the hydrotropic effect of low-equivalent-weight organic salts, "protosurfactants". In this paper we compare the hydrotropic effect of three protosurfactants with two low-equivalent-weight surfactants.

The three protosurfactants are sodium 2,5-diisopropylbenzenesulfonate, sodium 3,5-diisopropylsalicylate, each of which has six alkyl carbons on the benzene ring, and sodium cyclohexanoate, which also has six alkyl carbons. The two alkyl-substituted aromatic sulfonate and hydroxybenzoate may form small aggregates (*3*), but there is no evidence of micellar formation. Sodium cyclohexanoate, which has a compact arrangement of the six alkyl carbons, also does not form micelles (*4*). The two surfactants chosen to study are sodium *n*-hexanoate with six alkyl carbons and sodium *n*-octanoate with eight alkyl carbons. Although there appears to be no definite cmc (critical micellar concentration) value for sodium *n*-hexanoate, it is reported to form small aggregates at lower concentration (*5*-*7*), which increase to the micellar range as the concentration increases (above 1.2 M) (*6*), and become quite large at high concentration (*6*, *7*). Sodium *n*-octanoate forms moderate-size micelles at lower concentration (the cmc of octanoate at 25 °C is reported to be 0.39 mol/(kg of H_2O)) (*8*) and the micelle number is said to increase approximately linearly with concentration relative to the cmc (*9*).

The primary goal of this study is to compare the hydrotropic effect (or solubilization of hydrocarbons in water) of these organic salts (protosurfactant and surfactant) with an equivalent number of alkyl carbons but different structural arrangement. The solubilities of toluene and *n*-octane in aqueous solutions of either sodium *n*-hexanoate or sodium *n*-octanoate were found to be much lower than in aqueous solutions of sodium 2,5-diisopropylbenzenesulfonate and sodium 3,5-diisopropylsalicylate at corresponding aqueous concentrations.

Experimental Section

Materials. The source of toluene, sodium 2,5-diisopropylbenzenesulfonate, and sodium 3,5-diisopropylsalicylate used in this study can be found in ref *1* and *2*. Sodium *n*-hexanoate (Tokyo Kasei/TCI), sodium *n*-octanoate (BDH Lab), and *n*-octane (Aldrich) were used as received without further purification. Cyclohexanecarboxylic acid (Fluka AG) was converted to the sodium salt by titration to pH 7 with 10% NaOH. After the titration the solutions were filtered and washed several times with $CHCl_3$ to remove excess acid and the salt was crystallized after volume reduction. The crude product was recrystallized 2 more times from water. Analysis of this salt was done by Galbraith Laboratories, Inc., Knoxville, TN, and the results are as follows. Anal. Calcd: C, 55.97; H, 7.39. Found: C, 55.94; H, 7.41.

The aqueous organic salt solutions were prepared with distilled water, and concentrations are expressed in terms of molality, *m* (mol/(kg of H_2O)).

Methods. The hydrocarbon-saturated aqueous solutions were prepared as follows: In a 6-mL Hypo-vials (Pierce), 1 mL of hydrocarbon was added to 2 mL of distilled water or aqueous salt solutions; then the vials were sealed with neoprene septa (Pierce) and aluminum seals. The vials were shaken vigorously for ca. 10 min and put upside down into a test tube which was set inside a 25 ± 1 °C water bath for equilibration for at least 4 days. In between, the vials were shaken gently several times in order to get rid of any tiny hydrocarbon drops from the

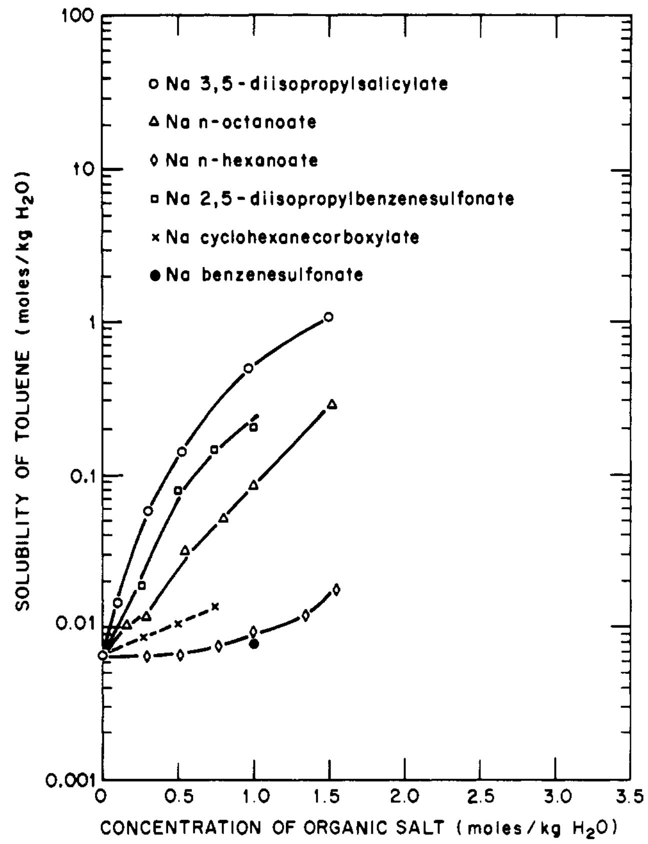

Figure 1. Solubility of toluene in aqueous organic salt solutions at 25 °C.

aqueous phase. The aqueous sample was withdrawn through the septa and injected directly into the gas chromatograph.

Gas Chromatography. Solubilities of toluene and *n*-octane in water and aqueous organic salt solutions were determined at least in duplicate by a Perkin-Elmer Sigma 3 gas chromatograph with either hot wire or flame ionization detector. The column (6 ft × $^1/_8$ in. o.d. stainless steel) was packed with 60/80 mesh Tenex GC. Column temperature was programmed from 100 (4-min hold) to 225 °C with an increase of 10 °C/min. Inlet and detector were set at 250 °C; helium carrier gas was used with inlet pressure at 75 psig. The instrument was calibrated with standard solutions of hydrocarbon in 2-propanol. Accuracies of gas-chromatographic analyses were about ±5%.

Results and Discussion

The solubilities of toluene and *n*-octane in aqueous protosurfactant and surfactant solutions at 25 °C are given in Table I. The protosurfactants are sodium cyclohexanoate, sodium 2,5-diisopropylbenzenesulfonate, and sodium 3,5-diisopropylsalicylate and the surfactants are sodium *n*-hexanoate and sodium *n*-octanoate.

Table I. Solubilities of Toluene and *n*-Octane in Aqueous Organic Salt Solutions at 25 °C

[organic salt], mol/(kg of H_2O)	solubility, mol of hydrocarbon/(kg of H_2O): toluene	solubility, mol of hydrocarbon/(kg of H_2O): *n*-octane
Sodium Cyclohexanoate		
0.26	0.0090	
0.50	0.0109	
0.72	0.0128	
Sodium 2,5-Diisopropylbenzenesulfonate		
0.27	0.019	
0.50	0.080	
0.74	0.15	
1.0	0.21[a]	
Sodium 3,5-Diisopropylsalicylate		
0.11	0.0145	
0.28	0.058	
0.53	0.14	
0.97	0.50	
1.50	1.065	
0.0		0.00018
0.27		0.0053
0.53		0.025
0.72		0.055
1.0		0.116
1.24		0.186
Sodium *n*-Hexanoate		
0.28	0.0066	
0.51	0.0066	
0.77	0.0076	
0.98	0.0096	
1.34	0.012	
1.54	0.018	
Sodium *n*-Octanoate		
0.17	0.0105	
0.30	0.0116	
0.55	0.032	
0.80	0.051	
1.0	0.076	
1.52	0.29	
0.25		0.00022
0.50		0.00056
0.70		0.0015
0.75		0.0020
1.06		0.0375
1.55		0.049

[a] From ref 1.

Figure 1 compares the solubilities of toluene in aqueous protosurfactant and surfactant solutions as a function of molality at 25 °C. The aqueous salt solution concentration is in the range of 0.1–1.5 mol of salt/(kg of H_2O). The solubility of toluene in water without the presence of organic salt at 25 °C, which we determined before to be 0.008 mol of toluene/(kg of H_2O) (*1*), was rechecked and found to be in the same range, i.e., 0.0065 mol of toluene/(kg of H_2O). The value is in agreement with the literature, which lists 0.006 at room temperature (*10*), and 0.0054 (*11*) -0.007 (*12*) mol/(kg of H_2O) at 25 °C. It can be seen from Figure 1 that in aqueous surfactant solutions the solubility of toluene increases with the increasing number of alkyl carbons, which is similar to the protosurfactant systems (*1*, *2*). With two extra alkyl carbons on the alkyl chain of octanoate, the solubility of toluene, say in 0.75 *m* aqueous *n*-octanoate solution, is ca. 6 times higher than in *n*-hexanoate solution. The solubility of toluene in aqueous organic salt solutions also increases with the increase of aqueous concentration. However, at low concentrations of *n*-hexanoate, the increase is slight. The solubility does not increase until the aqueous hexanoate concentration exceeds 0.5 *m*, but the overall increase is small in comparison to the solubility in the other four organic salt solutions. The pattern is similar to the solubility vs. molality curve of toluene in aqueous sodium benzenesulfonate which we reported before (*1*), although the temperatures are different. Sodium *n*-hexanoate has an approximately equal hydrotropic effect as sodium benzenesulfonate, which is demonstrated as the solubility of toluene in 1 *m* benzenesulfonate at 25 °C (*1*) (see Figure 1). The compact structure of sodium cyclohexanoate apparently helps to dissolve more toluene in water than is the case with *n*-hexanoate. The solubilities of toluene in aqueous *n*-octanoate solutions for some reason are scattered at low concentrations, and the solubility increases rapidly as the concentration increases. The most pronounced increase in solubility is with sodium 3,5-diisopropylsalicylate solutions. At 0.75 *m* aqueous concentration,

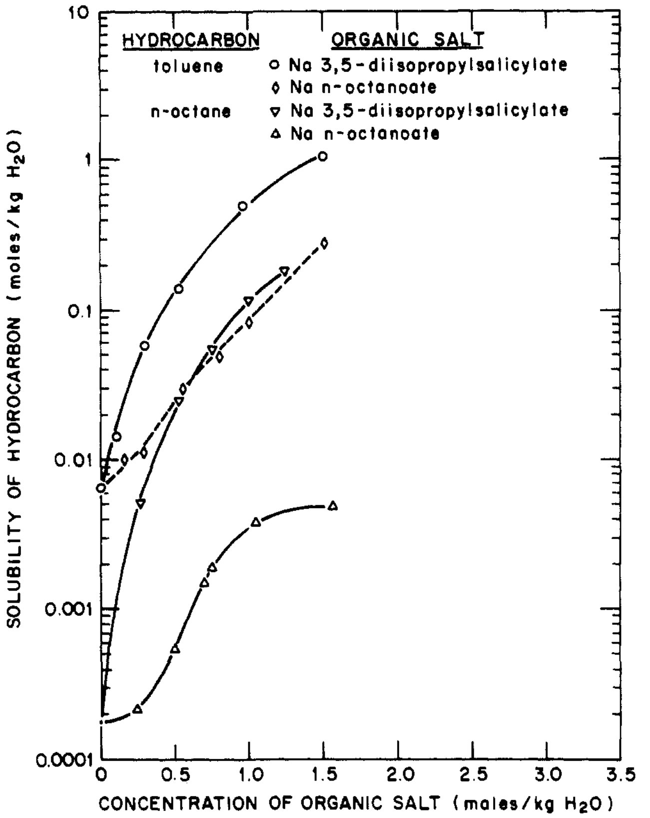

Figure 2. Solubility of *n*-octane in aqueous organic salt solutions at 25 °C and comparison of solubilities of toluene and *n*-octane in aqueous organic salt solutions.

the solubility of toluene in the diisopropylsalicylate solution is about 39 times higher than in *n*-hexanoate, 21 times higher than in cyclohexanoate, and 6 times higher than in octanoate solution. The solubility is also higher than in diisopropylbenzenesulfonate solution at corresponding concentration, and this is consistent with the trends of solubility of toluene in these two protosurfactant solutions at 55 °C (*2*).

Figure 2 presents the solubility of *n*-octane in aqueous sodium 3,5-diisopropylsalicylate and sodium *n*-octanoate solutions vs. molality of organic salt at 25 °C. From several repetitious determinations, the solubility of *n*-octane in water without organic salt is concluded to be 0.000 18 mol/(kg of H_2O) at 25 °C. The literature values we can find are 0.000 06 at 20 °C (*10*) and 0.000 12 mol/(kg of H_2O) at 16 °C (*13*). The solubility of *n*-octane in water increases rapidly with increase of organic salt concentration. The solubility in octanoate solutions first increases very rapidly up to 1 *m*, and then more slowly. The relatively strong solubilizing power of diisopropylsalicylate is again confirmed. The solubility of *n*-octane in diisopropylsalicylate solution is much higher than in octanoate solution at corresponding concentrations. At 1.0 *m* of aqueous salt concentration, the solubility of *n*-octane in diisopropylsalicylate is more than 32 times higher than in octanoate solution.

In Figure 2 we also compare the solubilities of toluene and *n*-octane as a function of molality of aqueous sodium 3,5-diisopropylsalicylate and sodium octanoate solutions. The solubility of toluene is much higher than that of *n*-octane in either water or aqueous organic salt solutions at corresponding concentrations. This is in agreement with the well-known fact that aromatic hydrocarbons, especially those low-molecular-weight members such as benzene, toluene, etc., are much more soluble in water than aliphatic hydrocarbons at closing or equivalent number of carbons (*14*). The shapes of the curves of solubility (as a function of molality) of toluene and *n*-octane in diisopropylsalicylate are very similar and almost parallel to each other, but are different in aqueous octanoate solutions.

The results indicate that the trends of the hydrotropic effect of hydrocarbon/water-containing systems in the presence of protosurfactants (hydrotropic salts) are similar to those in the presence of surfactants. That is, the solubilities of hydrocarbons in water in the presence of these organic salts increases with the increasing number of alkyl carbons (S_{AC}) of the hydrophobic portions of these compounds and with the salt concentration. However, it appears that protosurfactants increase the solubility much more effectively than the micelle-forming surfactants at corresponding number of alkyl carbons. This suggests that attribution of the increase of mutual solubility of hydrocarbon and water in the presence of amphiphilic compounds (both protosurfactants and surfactants) to surfactant formation of micelles may not be altogether correct. In fact, we have reported (*2*) earlier (a) that protosurfactants can increase solubilities of hydrocarbons in water by very large factors, even when alkyl substituents are much shorter than usually considered necessary for micelle formation, and (b) not only that the hydrotropic effect is affected by the alkyl groups, but that other substituents are important—the charged groups, SO_3Na and COONa to a modest extent, and the un-ionized *o*-hydroxy group to a particularly large extent. The structural arrangement of these substituents, which include both ionized and nonionized groups, should not be ignored either. Not only does the structural arrangement of these organic salts affect the hydrotropic effect, but it is also a decisive factor in micelle formation (*15*). It would be very interesting to compare the hydrotropic effect of aromatic amphiphilic compounds (protosurfactants and surfactants) substituted with equivalent number of alkyl carbons, but with these alkyl carbons distributed either on one side chain (straight or branched) or on several short side chains. This might elucidate the hydrotropic properties of these amphiphilic compounds.

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Registry No. Toluene, 108-88-3; octane, 111-65-9; sodium cyclohexanecarboxylate, 136-01-6; sodium 2,5-diisopropylbenzenesulfonate, 15763-80-1; sodium 3,5-diisopropylsalicylate, 79427-97-7; sodium *n*-hexanoate, 10051-44-2; sodium *n*-octanoate, 1984-06-1.

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