proceed simultaneously. A complete description of the reaction rate appears to be a formidable task. Certainly this complex and interesting system deserves further study.

The authors wish to acknowledge many helpful discussions regarding this problem with Dr. F. R. Duke.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Solubilization of Dodecylammonium Thiosulfate in Dodecylammonium Bromide Solutions at 50°[1]

BY I. M. KOLTHOFF AND W. F. JOHNSON

A new type of solubilization is described which consists of the solubilization of an insoluble salt of a detergent in solutions of freely soluble salts of the detergent. A study of the solubility of slightly soluble dodecylammonium thiosulfate in solutions of dodecylammonium bromide showed that below the critical concentration the dodecylammonium bromide behaves as a normal strong univalent electrolyte in suppressing the solubility of the thiosulfate. Above the critical concentration the solubility of the thiosulfate salt was found to increase linearly with the concentration of the bromide salt. This solubilization is explained by an exchange between bromide and thiosulfate ions on the micelles, resulting in a decreased concentration of free thiosulfate ions in the solution. The solubility product of dodecylammonium thiosulfate was found to be 3.8×10^{-9} at 50°.

Solubilization of organic compounds in aqueous micellized solutions of detergents is considered to occur for apolar substances in the "sandwich" layer between the two parts of the micelle and for polar substances between the parallel paraffin chains.

A new type of solubilization is considered in this paper. Confining ourselves to a cationic detergent the solubilization described below is that of a slightly soluble salt of the detergent in a solution of a freely soluble salt of the detergent. According to the mass action law effect the solubility of a slightly soluble salt of a cation detergent decreases in a solution of a freely soluble salt of the cation detergent until the critical concentration of the latter is attained. When the concentration becomes greater than the critical concentration micelles are formed, anions being the counter ions of the micelle. These anions adsorbed on the micelle can exchange with other anions in the bulk of the solution. Denoting by DA the slightly soluble salt of the detergent and by DB the freely soluble salt we have above the critical concentration,

$$(\mathrm{Mic}^{n+})\left|\, n\mathrm{B}^- + y\mathrm{A}^- \rightleftarrows (\mathrm{Mic}^{n+})\right|\begin{matrix}(n-x)\mathrm{B}^- \\ \text{and} \\ x\mathrm{A}^-\end{matrix} + x\mathrm{B}^- + (y-x)\mathrm{A}^-$$

By this exchange A^- ions are withdrawn from solution, and the apparent solubility will increase above the critical concentration. Dependent on the equilibrium in the above reaction the solubility of DA may become much greater in DB solution than in water.

What has been said for cationic detergents also holds for anionic detergents. It is to be expected that for the reason given above that a slightly soluble fatty acid soap will be solubilized by a freely soluble soap, which not necessarily has to be derived from the same fatty acid.

In the present study we have determined the solubility of the slightly soluble salt, dodecylammonium thiosulfate, in solutions of the free soluble cationic detergent, dodecylammonium bromide.

Dodecylammonium thiosulfate is only slightly soluble in water at 50°, but is soluble to a much greater extent in solutions of dodecylammonium bromide. This investigation of the solubilization of dodecylammonium thiosulfate was made primarily as a preliminary to a study of the reaction between thiosulfate ion and dodecyl bromide in solutions of dodecylammonium bromide.

Experimental

Dodecylammonium thiosulfate was prepared by adding dropwise a one molar solution of sodium thiosulfate and dodecylammonium chloride (in 50% ethanol–water solution) to approximately 1.5 liters of conductivity water maintained at about 70°. The solution was kept well stirred during the precipitation. As nearly as possible the dodecylammonium chloride solution was added at twice the rate at which the sodium thiosulfate solution was added to prevent an excess of either reagent accumulating during the precipitation. The solid dodecylammonium thiosulfate floated to the surface and was skimmed off with a watch glass. The product was transferred to a büchner filter funnel and washed several times with water, sucked dry and dried in a vacuum desiccator over anhydrous magnesium perchlorate at room temperature.

Dodecylammonium bromide was prepared by passing 99.2% pure tank hydrogen bromide into a benzene solution of dodecylamine. The dodecylamine used was a sample obtained from Armour and Company. The amine was fractionally distilled through a 20-inch column. The salt was recrystallized twice from benzene and twice from absolute ethanol and dried in a vacuum desiccator.

Analysis of the solutions was accomplished by titration with standard iodine solution, using the rotating platinum micro-electrode to detect the end-point amperometrically. In order to test the effect of micellized dodecylammonium bromide on the titration, the following experiments were carried out. To approximately 90 ml. of 0.1 *N* dodecylammonium bromide solution contained in a 100-ml. volumetric flask immersed in a 50.0 ± 0.1° thermostat, 10.00 ml. of 0.1002 *M* sodium thiosulfate solution was added. The flask was removed from the thermostat and shaken to dissolve the precipitate of dodecylammonium thiosulfate which had formed. The flask was returned to the thermostat and allowed to stand for 15 minutes before the solution was made to volume. The solution was again shaken prior to the removal of 10.00-ml. samples for titration. The ten-ml. sample was added to 20 ml. of absolute alcohol and titrated with 0.01000 *N* iodine solution. Similar experiments were carried out in which the concentrations of sodium thiosulfate and iodine were one-tenth of those given above.

For the titration of the 0.01002 *N* sodium thiosulfate solutions the average error and average deviation of a single determination from the mean were both 0.2%. With 0.001002 *M* sodium thiosulfate solution the average error of

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a single determination was 0.4% and the average deviation of a single determination 0.2%.

The galvanometer employed had a sensitivity of 0.003 μa. per millimeter scale deflection and was equipped with an Ayrton shunt so that at various dilutions of sodium thiosulfate titrated, different sensitivities could be employed. All titrations were made with the platinum electrode at a potential of +0.1 volt with respect to the saturated calomel electrode to avoid interference from oxygen reduction. The end-points were sharp; the addition of 0.01 milliliter of 0.01 *N* iodine solution gave a galvanometer deflection of 10 millimeters.

To check the decomposition of thiosulfate in the presence of dodecylammonium bromide a solution was prepared which was 0.01002 *M* in sodium thiosulfate and 0.100 *M* in dodecylammonium bromide. Samples of solution were removed and titrated 15 minutes, 18 hours and 94 hours after preparation. The solution was maintained at 50.0 ± 0.1° during this time. The samples taken at 18 hours showed no change in titer; the samples removed at 94 hours showed an increase in titer of 0.7%. Measurements of the solubility of dodecylammonium thiosulfate in dodecylammonium bromide solutions completed in 94 hours then are virtually not subject to error because of decomposition of thiosulfate.

Dodecylammonium thiosulfate was found to be soluble in a 75 to 25 volume mixture of isopropyl alcohol and water which was 1.0 *M* in potassium bromide. Six samples of the salt in this solvent (approximately 0.1 *M*) were titrated with 0.1000 *N* iodine solution. The average deviation from the mean of these determinations was 0.4%. The average value of the titer gave 99.2% of the theoretical thiosulfate content of the salt.

A stock solution of 0.100 *M* dodecylammonium bromide was prepared from which other solutions were obtained by dilution. For solubility measurements approx. 100 ml. of solution was put into a 4-oz. prescription bottle, excess solid dodecylammonium thiosulfate added and the bottle sealed with a cap having a clean Koroseal liner. The bottles were agitated end-over-end at 50.0 ± 0.1° for 20 hours. The bottles were allowed to stand quietly at 50° for three days. Samples were removed with a pipet having a tightly packed glass wool filter on the tip. The period of standing was required to allow the excess solid to agglomerate sufficiently to obtain clear samples. The solubility of dodecylammonium thiosulfate was determined by titrating 10.00-ml. samples of solution with standard iodine solution by the method described previously.

The solubility of dodecylammonium thiosulfate at 50° as a function of the dodecylammonium bromide concentration is given in Table I.

TABLE I

SOLUBILITY OF DODECYLAMMONIUM THIOSULFATE IN SOLUTIONS OF DODECYLAMMONIUM BROMIDE AT 50°

Concn. dodecylammonium bromide (mole/liter)	Concn. dodecylammonium thiosulfate (mole/liter)
0.000 (water)	8.36×10^{-4}
.002	3.56×10^{-4}
.004	1.92×10^{-4}
.006	1.34×10^{-4}
.010	3.25×10^{-5}
.012	3.76×10^{-5}
.014	7.2×10^{-6}
.020	4.3×10^{-3}
.040	4.97×10^{-3}
.060	9.04×10^{-3}
.080	1.27×10^{-2}
.100	1.64×10^{-2}

The data of Table I are plotted in Fig. 1. It is seen from either that, as the concentration of dodecylammonium bromide is increased, the solubility of dodecylammonium thiosulfate at first decreases and then increases. The initial decrease of solubility is expected on the basis of the mass action law. The increase in solubility is attributed to incorporation of dodecylammonium thiosulfate in the micelle of dodecylammonium bromide, *i.e.*, solubilization through exchange of thiosulfate with bromide ions. The intercept of the straight line obtained at the four highest dodecylammonium bromide concentrations on the zero dodecylammonium thiosulfate concentration axis is 0.013 *M*. This corresponds to the critical concentration of dodecylammonium bromide at 30° which is about the same as at 50°.

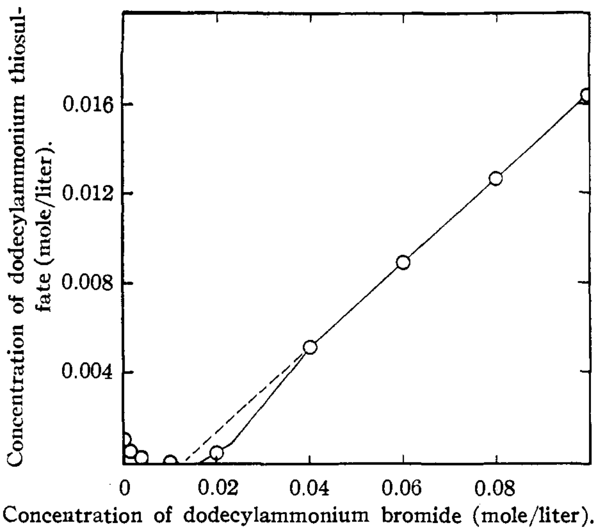

Fig. 1.—Solubility of dodecylammonium thiosulfate in solutions of dodecylammonium bromide at 50°.

The ratio of solubilized dodecylammonium thiosulfate to micellized dodecylammonium bromide (total concentration minus critical concentration) is constant in the range of dodecylammonium bromide concentrations between 0.04 and 0.10 *M* from the slope of the linear part of the curve in Fig. 1; a value of 0.19 is calculated for this ratio.

The solubility product of dodecylammonium thiosulfate may be calculated from the values in Table I for concentrations of dodecylammonium bromide less than the critical concentration. This has been done and the values obtained are given in Table II. These values were obtained at an ionic strength below 0.012. No correction was made for the activity coefficient.

TABLE II

SOLUBILITY PRODUCT OF DODECYLAMMONIUM THIOSULFATE AT 50°. CALCULATED FROM SOLUBILITY IN DODECYLAMMONIUM BROMIDE SOLUTIONS

Concn. of dodecylammonium bromide *M*	Solubility product
Water	3.6×10^{-9}
0.002	2.6×10^{-9}
.004	3.7×10^{-9}
.008	4.8×10^{-9}
.010	3.3×10^{-9}
.012	5.2×10^{-9}
Average	3.8×10^{-9}

No trend is observed in the values of the solubility product, given in Table II, as the concentration of dodecylammonium bromide increases up to the critical concentration. This may be taken as an indication that below the critical concentration the dodecylammonium bromide behaves as a normal strong uni-univalent electrolyte.

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