Very Slow Exchange of Sulfur Atom between Sulfate and Dodecyl Sulfate Ions

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Introduction

Radioactive sodium dodecyl sulfate (SDS) has been used for studying various surface-chemical processes such as adsorption at solution surfaces⁽¹⁾, incorporation into fabric cotton⁽²⁾, and self-diffusion in aqueous media⁽³⁾, using solutions of SDS alone or SDS accompanying various salts such as sodium or potassium sulfate which is currently used as a builder in detergency. In many cases of these experiments, SDS is labeled with ³⁵S under the assumption that the S-containing group in the molecule remains unchanged throughout the processes. To verify the assumption, one has to confirm the slowness to the hydrolysis reaction,

in comparison with the surface-chemical processes involved in SDS-water system. We thus measured the radioactivity of ³⁵SO₄²⁻ formed by the reaction (1), for which ca. 40 years and 180 days, for instance, were found as half life for the solutions of pH 4 and 1, respectively, and of initial concentration of 1×10^{-3} mol/l⁽⁴⁾.

If, however, the system contains inorganic sulfate(s) added to SDS-water system, one must take an additional account of the exchange reaction,

otherwise, confusion may take place with the radioactivity of SDS-³⁵S as an expression of

the process involved.

Present paper deals with the exchange reaction (2) in relation to the hydrolysis(1), as well as to the similar exchange reactions between sulfate and sulfonates. It has been reported that the sulfur atom of inorganic sulfate does not exchange appreciably with that of various organic sulfonates such as benzene sulfonate and its derivatives⁽⁵⁾.

Experimental

Sodium sulfate labeled with ³⁵S (specific activity, 5–6 Ci/mol) and non-radioactive SDS were mixed to form aqueous solutions of concentration ranging $(1-4) \times 10^{-3}$ mol/l for each component. The acidity was kept to ca. pH 1 for all solutions, as acidic medium was found to enhance the reaction (1)⁽⁴⁾. The exchange mixture was kept standing in a thermostat at 40–60°C. After a given time, an aliquot of 0.5ml of the mixture was taken out to make 100ml of precipitation mixture which contained additional 6×10^{-5} mol of non-radioactive SDS as a carrier. Immediately, 3×10^{-5} mol of barium chloride of as high concentration as possible was added to the precipitation mixture. Barium dodecyl sulfate (BDS) thus formed was filtered, washed and mounted for counting radioactivity by Aloka FC-IE 2 π windowless gas flow counter.

Sodium sulfate used was purified by repeated recrystallizations. SDS was synthesized by

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the reaction of dodecanol with sulfonic acid and purified thoroughly to give no depressions in surface tension-concentration curve.

3. Results and Discussions

It is always a problem how to separate an exchange species from the precipitation mixture with least contamination. In the present experiments, the separated BDS was accompanied more or less by sulfate whose specific activity was much higher than that of BDS. Fig. 1 gives the radioactivity of BDS as a function of pH of the precipitation mixture at exchange time to be zero, *viz.*, when the precipitation procedures followed in the wake of formation of the exchange mixture. It can be seen in Fig. 1 that the co-precipitation of sulfate with BDS is minimized at around pH 11, where radioactivity of 20-60 cpm was always found in BDS sample obtained. We have thus taken this pH value for acidity of precipitation mixture.

Fig. 1 Effect of pH of precipitation mixture upon radioactivity of inorganic sulfate accompanying BDS.

Precipitation mixture contains 5×10^{-7} mol of sodium sulfate and 5×10^{-7} mol (original) plus 6×10^{-5} mol (carrier) of SDS. Exchange time, 0 hr; Temperature, 60°C .

It was found that the radioactivity of BDS was not increased with elapsing the time of exchange reaction. This was indeed the case with any combination of concentrations of SDS and sulfate, so far tested, and at any temperature up to 60°C . Typical example is shown in Fig. 2 in which the count rate is plotted against the elapsed time. As is usuals

of this sort of experiment, the count rate gives a fluctuation due to the irregular co-precipitation. It should be recognized, however, that the fluctuation is almost within the inevitable scattering of 20-60 cpm given in Fig. 1. It must also be mentioned that the hydrolytic reaction (1) using SDS- ^{35}S of same specific activity has resulted in an increment of 10^4 - 10^5 cpm at the elapsed time of 14 days under the similar experimental conditions⁴⁾. Therefore, exchange rate of the reaction (2), if any, should be of the order of magnitude of at least 10^5 - 10^6 years in its half life. Such a slowness of the reaction (2) seems to permit us to use a system containing SDS- ^{35}S and SO_4^{2-} without care about the ambiguity as to the radioactivity measured thereof.

Fig. 2 Effect of elapsed time upon radioactivity of BDS.

Exchange mixture, 1.0×10^{-3} mol/l for each of SDS and sodium sulfate; pH 1.13; Temperature, 40°C .

It has been a problem whether $\text{C}_{12}\text{H}_{25}-\text{O}\cdot\text{SO}_3^-$ or $\text{C}_{12}\text{H}_{25}\cdot\text{O}-\text{SO}_3^-$ bond rupture is involved in the hydrolytic reaction (1)⁴⁾. It seems that the present results suggest the likelihood of the latter possibility rather than the former which should lead to easier exchangeability with sulfate ion. This suggestion is in accord with the conclusion that the hydrolytic reaction of carboxylate ester involves the rupture of $\text{R}\cdot\text{O}-\text{CO}\cdot\text{R}^{6)}$.

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