Radiotracer Studies of Metal-Detergent Interaction by Means of a Dip Counter with an Evaporated Metal Film Window*

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The properties of metal-solution interfaces under equilibrium state have long been studied from various points of view,[1-5] studies which have offered useful information for the treatment of metals in water. However, for practical systems, the situations are fairly complicated, since several phenomena occur simultaneously and they are often not in equilibrium. Here, the factors affecting the equilibrium are not necessarily important for the kinetic properties of the interface. As for the kinetic nature of metallic interfaces, studies have also been

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reported by many authors of, for instance, the coulometric, chronopotentiometric or differential double-layer capacity measurement of surfaces.[6,7] However, the so-called reactive metals usually involve an irreversible process which renders difficult the analysis of the data obtained except for some special cases. Therefore, it may be desirable to trace directly the surface reaction itself, both chemically and electro-chemically, using radioisotopes.

The present paper will describe radiotracer studies upon the interfacial reaction between vacuum-evaporated metal films and an aqueous solution of sodium dodecyl sulfate (SDS). In the usual practice of the measurement of such a reaction or adsorption, solid samples are dipped in a solution containing a radioactive solute and the radioactivity measurements are made for the surface after withdrawing the solid. However, the counting rate due to a merely adhering solution inevitably obscures the counting rate due to the adsorption or chemical reaction, which is generally small compared with that due to the adhering liquid.[8,9] The rinsing of the solid surface often adopted[10] is, therefore, not desirable, since it ensures neither a complete removal of the adhering liquid nor a complete retention of the substance adsorbed. To avoid these difficulties, it is desirable to measure the counting rate directly in the state of immersion, as in the Aniansson's soft beta ray method[11,12] or as in Winkler's hard radiation method[13,14]. Here we adopted the Aniansson's method but somewhat modified it. The rate of the uptake of ^{35}S-labeled SDS from an aqueous solution by vacuum-deposited metals on a thin Tetoron window of the GM-tube was measured, and the surface nature of several metals was studied under the influence of air.

Experimental

Materials and Apparatus.—Radioactive and non-radioactive SDS were synthesized according to the usual method.[15] The radioisotope ^{35}S used in this experiment was obtained from CEA Saclay, France, in the form of a dilute aqueous solution of sulfuric acid. The solution was concentrated, the required amount of non-radioactive sulfuric acid was added, and the mixture was used for the sulfonation of dodecyl alcohol. In the course of the purification of SDS, non-radioactive sodium sulfate was added to remove radioactive sodium sulfate impurities of a high sepecific activity considered to be present and likely to cause an error in the measurement of the counting rate. The radioactive SDS thus prepared had the specific activity of 30 curies per mol. Copper, silver, gold, lead and iron, all of a commercially pure grade, were chosen as the sample metals. These metals were vacuum-deposited on a thin Tetoron film of the Mitsubishi Chemical Industries, Limited (polyethylene terephthalate, Diafoil Type S, No. 12, 1.3 mg./cm^2 thick) which had been previously degreased by ether. The apparatus used in this experiment is shown in Fig. 1, where G is the gas flow Geiger-Müller counting tube (Japan Radio Corporation, Aloka FC-16; effective aperture, 34 mm.) equipped with a tambour ring, T, for the exchange of the sample window film and, H, the housing to which the counting tube is fixed. The screw stage, LL′, adjusts the height of the adsorption cell, C, containing 8 cc. of a radioactive solution. The microscope, M, equipped with a calibrated scale measures the distance between the solution surface and the window of the GM tube.

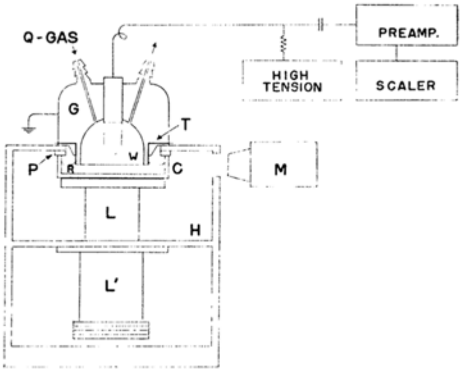

Fig. 1. Diagram of apparatus.

G	Gas flow GM-tube
W	Sample window
T	Tambour ring
C	Glass cell
R	Radioactive solution
M	Microscope
P	Rubber packing
H	Housing
LL′	Screw stage

Procedures.—The sample metal was deposited from vapor on the thin Tetoron film at the pressure of 10^{-6} mmHg under the specified conditions of electric current and evaporation time. The rates of deposition for copper, silver, gold, lead and iron samples were 3.83, 1.57, 4.67, 1.83 and 1.30 μg./cm^{2}sec. respectively. In each case, deposition was made for 30 sec., with the rejection of the initial portion by a magnetically-operated shutter in order

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to avoid the contamination of the film by metal oxide. To the opposite side of the window film, copper was deposited; this acted as a part of the cathode of counting tube. The thickness of the vacuum-deposited metal films was directly calculated from their weight, as measured in a special weighing tube in order to avoid errors caused by the electrostatic charge of the film. The measurement of the adsorption was made by directly immersing the window of the counting tube in a radioactive sample solution and by measuring the increase in the counting rate due to the accumulation of the solute on the metal film. This increase in the counting rate was multiplied by the calibration factor r which expresses the ratio of the actual amount of solute on the window to the counting rate resulting from it, which was determined by the separate measurement below. A known amount of radioactive solute was evenly placed in about 100 spots on an Acrylite disk of the same shape and area as those of GM-tube window. (The spots should be small enough to be free from self-absorption.) Then its activity was measured at varying distances, up to 3 mm., between the sample and the window. On the basis of this experiment, the counting rate at the distance zero was calculated by extrapolation. The amount of the sample, divided by this counting rate, gives the factor r in mol./ c. p. m. Since the factor r was determined for each sample film, solute and specific activity, the product of the observed counting rate and r gives the actual amount of solute as corrected for the decay of isotope and the absorption of radiation by the window. The correction for the dead time of 300 μ sec. of the GM tube was also made.

The counting rate due to the bulk of the solution was measured as follows. The surface count over the aqueous solution of surface-inactive but radioactive sodium sulfate of a known concentration was measured at varying distances in a manner similar to that used in the measurement of r. The value thus obtained was extrapolated to the counting rate at zero distance and was used for the evaluation of the counting due to the bulk of each SDS solution. It was also attempted to estimate the radiation from the bulk of the solution by measuring the surface counting rate of an alcoholic solution of radioactive SDS, which showed no surface tension change with concentration and may, therefore, be considered to be free from surface adsorption;[16] however, the measurement was not successful due to the evaporation, creeping and condensation of alcohol on the window of the counting tube.

Results and Discussion

Uptakes of Sodium Sulfate and Sodium Dodecyl Sulfate on the Tetoron Surface and Apparent Adsorption on the Aqueous Surface.—The counting rate before and after the dipping of the Tetoron film in an aqueous solution of sodium sulfate and a SDS solution were measured first as a function of the time; they are shown in Figs. 2 and 3 respectively. In each figure, the points show the total sum of the counting rate (left ordinate) due to the solute taken up by the Tetoron film and the solute in the bulk of the solution. The broken line indicates the counting rate due to the solute in the bulk of the solution. Therefore, the portion of the ordinate above the broken line in Figs. 2 and 3 represents the counting rate proportional to the excess amount of solute (right ordinate) on the Tetoron-solution interface. The points on the vertical axis in these figures indicate, for comparison, a counting rate referring to the counting rate of the aqueous surface. We can see in Fig. 2 that the apparent amount of the adsorption of sodium sulfate at the air-water interface is about the same as the adsorption on Tetoron except for the early period of the contact of Tetoron with water; this anomaly is probably due to the agitation of the surface by the immersion. In the case of SDS, the adsorption on the aqueous surface decreases when the air is replaced by Tetoron.

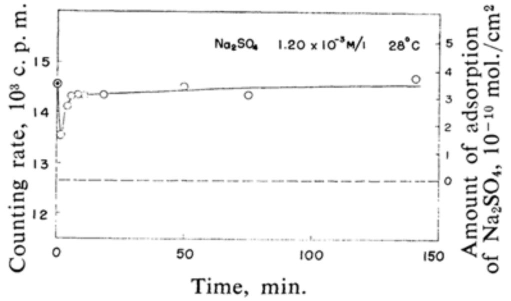

Fig. 2. Adsorption of sodium sulfate on Tetoron surface. Counting rate and amount of adsorption of sodium sulfate on aqueous surface (⊙), Tetoron surface (○), and bulk of the solution (— —).

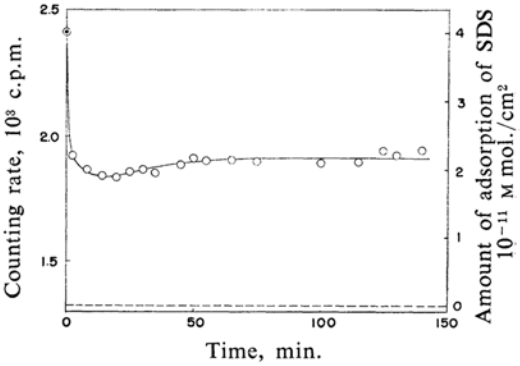

Fig. 3. Adsorption of sodium dodecyl sulfate on Tetoron surface.
Counting rate and amount of adsorption of sodium dodecyl sulfate on Tetoron surface (○), aqueous surface (⊙), and bulk of the solution (— —).

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Here it should be emphasized that, since we cannot expect any actual adsorption of sodium sulfate on the water surface, the excess counting rate mentioned above is evidently an apparent one exclusively due to the inevitable evaporation of water from the aqueous surface, although the experiment was conducted in a closed vessel. Detailed experiments on an aqueous surface, which will be reported on precisely in a following paper, also revealed that the mere exposure of the aqueous surface to an atmosphere with 40% humidity at 21°C without a special air current resulted in an apparent increase in the 3% surface concentration for a sodium sulfate solution.

Considering this, an evaporation effect may also be responsible to some extent for the apparent adsorption of SDS on an aqueous surface shown in Fig. 3. As will be mentioned in the following paper, this apparent adsorption gradually decreases as the space above the aqueous surface becomes saturated with water vapor. Therefore, it should at least be remarked that such an evaporation effect would introduce in some cases a serious error in the adsorption measurement on the aqueous surface. Throughout the main experiment which follows, we took special care to avoid evaporation, as is illustrated in Figs. 2 and 3, and to confirm the equilibrium count rate of the radiation from the bulk of the solution on he basis of its steady value.

Uptake of SDS on Various Metals.—The uptakes of SDS from its aqueous solution onto the surfaces of lead, copper, silver and gold are plotted against the time at pH from 6 to 9 in Fig. 4. From these curves it is possible to classify the metals employed as reactive or non-reactive, as has usually been done. With reactive metals like copper and lead, we can observe the dissolution of metals, as is seen from the change of pH shown in Fig. 4, and the growth of the surface film composed of the reaction product between the metal and SDS, as can be confirmed by the remarkable increase in the counting rate shown in the same figure. In this experiment, iron behaved as a non-reactive metal, like electrochemically-noble gold and silver, instead of as a usual reactive metal. This is probably due to the passivation of iron in the present experimental conditions of exposing its surface to an oxygen atmosphere.

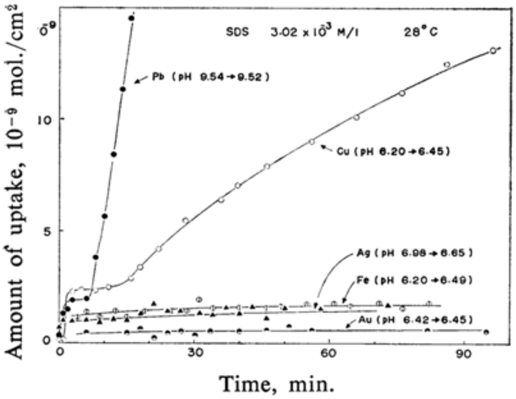

Fig. 4. Uptake of sodium dodecyl sulfate on various metals.

For non-reactive metals, a fluctuation in the counting rate exceeding the statistically probable errors of counting was observed for one and the same surface, whereas the fluctuation was very little for reactive-metal surfaces. It can be observed in Fig. 4 that the plateau appears in an early stage of the uptake curve for lead and copper at the pH listed for each case where the solution does not suffer from the change in pH in the course of SDS uptake, while in other pH regions such a plateau did not appear and the curves of uptake simply and gradually increased, though no diagrams are shown. Such a plateau and succeeding rapid increase in SDS uptake may reasonably be explained by taking account of two processes: rapid physical adsorption, resulting in a monolayer on the metal which is completed in a short time after the immersion of the metal in solution, and the slow formation of a surface film by a certain chemical reaction with the aid of oxygen, such as

$$O+Cu+2RSO_4H \rightarrow Cu(RSO_4)_2+H_2O$$

$$\text{or}\quad Cu+O+RSO_4H \rightarrow Cu(OH)SO_4R$$

both processes being independent of the change in pH. Here R indicates the C_{12} hydrocarbon chain.

The Estimation of the Surface Roughness.—The roughness factor, namely, the ratio of the actual area to the apparent area of the solid surface, can be obtained by calculating the

TABLE I. SURFACE ROUGHNESS OF VARIOUS METALS

Surface	pH	Uptake of dodecyl sulfate mol./cm² $\times 10^{-9}$	Weight of metal film mg./cm²	Roughness factor
Cu	5.60	1.68	0.290	3.64
	6.20	1.53	0.071	3.32
	6.55	1.76	0.102	3.82
	6.65	1.71	0.116	3.71
	7.40	1.86	0.127	4.04
	6.20	2.40	0.497	5.21
Pb	9.54	1.92	0.055	4.17
Fe	6.20	2.00	0.039	4.34
Ag	6.98	1.70	0.047	3.69
Au	6.42	0.90	0.140	1.74

actual area, assuming the completion of monolayers at the plateau region in Fig. 4 and an area of 36 Å² per molecule for SDS.[17] The results for copper, lead, silver, gold and iron are shown in Table I. Table I indicates that copper films of a similar weight show almost the same roughness, independent of the pH used for the measurement.

The Rate of Surface-film Growth.—It has already been mentioned that lead and copper reacted with SDS to form a surface film of metallic soap and that these reaction products increased with time beyond the initial plateau region. The rate of uptake is considerably larger for lead than for copper. In both cases, however, the rate tends to decrease gradually with time (Fig. 4). This is considered to be due to the presence of the surface film, which acts to retard further reaction because of the slow diffusion of ions through the film. We can reasonably assume the reaction of surface film formation to take place at the film solution interface[18,19] and consider that, during the film growth, the concentration of metallic ions at a film-solution interface is almost zero, while at a film-metal interface it is large and constant. Since the diffusion rate of metallic ions and, hence, the rate of film growth is proportional to its concentration gradient in the film, the rate of film growth is considered to be proportional to the reciprocal of the film thickness, m, as follows:

$$\frac{\mathrm{d}m}{\mathrm{d}t}=\frac{k}{m} \tag{1}$$

where k is the proportionality constant. The integration of Eq. 1 gives the following parabolic rate equation, where c is the integration constant:

$$\frac{1}{2}m^2=kt+c \tag{2}$$

Equation 2 was checked by using the data for copper and lead already shown in Fig. 4. Figure 5 shows the square of the amount of the uptake of dodecyl sulfate plotted against the time for both copper and lead. A linear relation for copper, can be seen 30 min. after the immersion and after 20 min., for lead, which proves the validity of Eq. 2 as a whole. Further, it may be presumed from Fig. 5 that a film of a tight structure grows on copper, whereas a loose film grows on lead.

The Effect of pH on the Rate of Uptake.—The effect of the initial pH on the uptake of dodecyl sulfate was measured at various pH values for both copper and lead surfaces. The measurement of the final pH of the solution after one hour's immersion of metals was also made. Figures 6 and 7 show the results for copper and lead respectively. The tail of the arrow in these figures shows the initial pH of the solution, while the head shows the final pH measured after one hour's immersion of the metal (abscissa) and the amount of the uptake of dodecyl sulfate (ordinate). The rate of the uptake of dodecyl sulfate shows a maximum at pH 7 and decreases towards both the acid and alkaline sides. The pH increases in the acid region and decreases in the alkaline

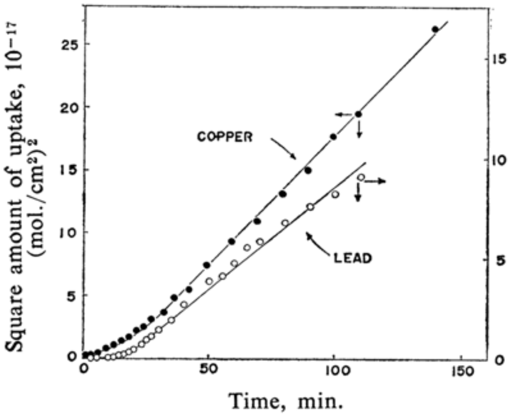

Fig. 5. Film growth on copper and lead in aqueous solution of SDS.

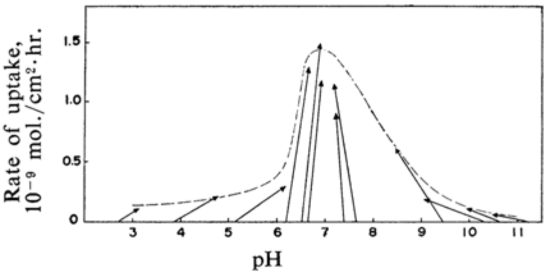

Fig. 6. Effect of pH on the rate of uptake of dodecyl sulfate on copper.

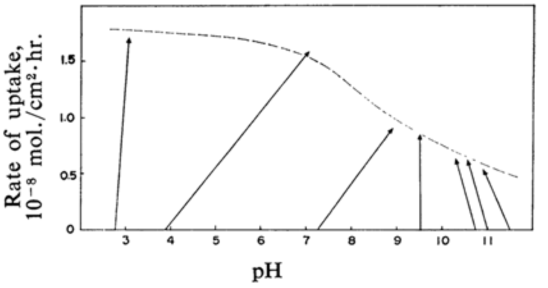

Fig. 7. Effect of pH on the rate of uptake of dodecyl sulfate on lead.

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region in the course of metal dipping, but it changes little at pH 7, where the rate of uptake is at a maximum. For the lead surface, the rate of uptake is larger in the acid region and it gradually decreases toward the alkaline region. The point of no change in pH appears at pH 9; this point, however, does not correspond to the maximum rate of uptake for copper. Though the exact mechanism of these pH effects is not clear at present, a tentative explanation may be made as follows. Two fundamental types of reactions,

$$\left.\begin{aligned}&RSO_4H \rightleftharpoons RSO_4^- + H^+\\&RSO_4^- + H_2O \rightarrow ROH + H^+ + SO_4^{2-}\end{aligned}\right\}\quad (A)$$

$$\left.\begin{aligned}&Cu + O + 2H^+ + 2RSO_4^- \rightleftharpoons\\&\qquad Cu(RSO_4)_2 + 2H_2O\\&Cu + O + H^+ + RSO_4^- \rightleftharpoons Cu(OH)SO_4R\\&Cu + O + 2H^+ \rightleftharpoons Cu^{2+} + H_2O\end{aligned}\right\}\quad (B)$$

can be considered to play roles in the change in pH during metal immersion. The hydrolysis reaction of A[20] is slow and H^+-producing, while reaction B is H^+-consuming. In the acid region reaction B may be dominant, while in the alkaline region reaction A may be considered to affect the pH; in an intermediate pH, the two reactions will be balanced and the pH of the solution is unchanged during the film growth, as has been mentioned above.

However, the matter is not as clear as far as the phenomena in the alkaline region are concerned, since the error introduced during the pH measurement by the inevitable absorption of carbon dioxide obscures the results obtained.

It is interesting to repeat that the characteristic appearance of a plateau in the uptake curves is only observable at the point of no change in pH, that is, pH 7 for copper and pH 9 for lead.

Summary

The accumulation of solute on metal surfaces has been studied using a radiotracer technique. A dip GM-counter with an end window covered with an evaporated metal film was immersed in an aqueous solution of ^{35}S-labeled sodium dodecyl sulfate, and the change in counting rate due to the accumulation of solute on the metal surface was traced with time for various metals and pH values of the solution. The accumulation curves obtained turned out to be composed of an initial plateau, representing the region of the physical adsorption of the detergent onto the the metal surface, and/or a rising portion of the accumulation curve, indicative of chemisorption. Assuming the closely packed adsorption of solute, the roughness factors of various metal surfaces have been calculated from these plateau characteristics. The rising portion of the curve corresponds to the formation of a thick metallic soap film. The rate of film growth is controlled by the migration of the detergent or metal ions through the film, and this rate decreases as the thickness of the surface film increases. This leads to the parabolic formula for the surface film growth, which is in good agreement with the experimental results. The effect of the pH of the solution on the rate of the uptake of dodecyl sulfate has also been measured for both copper and lead surfaces. For copper surfaces the rate of the uptake of a detergent shows a maximum at pH 7 and decreases in both acid and alkaline regions. For lead surfaces, the rate is large in the acid region and gradually decreases twoards the alkaline region.

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