Adsorption Characteristics of ^{60}Co-ions towards Polystyrene Treated with Sulfuric Acid Relative to Radioactive Decontamination

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The surface treatment of plastics has drawn the attention of many investigators since it has much to do with such practical problems as anti-electrification, adhesion, radioactive decontamination, etc. It is also a problem of theoretical interest from the viewpoint of the relation of the adsorption to the nature of the surface concerned(1). Concerning these problems, it is of basic importance to know the amount of solute adsorbed on a solid surface, about which much literature is available(2). In such studies, however, the total uptakes of a solute have often been roughly treated as the adsorption and no due distinction has been drawn between the adsorption and adhesion(3), especially concerning practical problems, in spite of the fact that such a distinction is rather important in the practice, for instance, of decontamination. Further, as for the adsorption which is measured as a surface excess, several types have been distinguished according to their natures(4), but in practice they have also often been treated without distinction. In order to contribute to the study of such problems we have studied the details of the adsorption of cobalt ions on a polystyrene surface, and also the effect of sulfuric acid treatment on the adsorption.

Experimental

The samples of plastics used in these experiments were polystyrene ("Styron-666-General Purpose" of Asahi-Dow Ltd.) cut in $0.2\times2\times2$ cm. plates. The sulfuric acid used was of a commercial pure grade. An aqueous solution of cobaltous chloride (8×10^{-7} mol./l.) tagged with ^{60}Co-ions was used for the adsorption experiment. The specific activity under the experimental geometry was 6.7×10^{-14} g./cm^2 c.p.m. The sample plates cleaned with a soap solution were immersed under various conditions of dipping time and temperature into sulfuric acid, withdrawn, rinsed with distilled water, and dried in a desiccator. The samples thus treated were weighed and floated on the surface of 4 cc. of an aqueous solution of radioactive cobaltous chloride. After 30 minutes' contact, which was considered to be sufficient for equilibration, they were then taken out of the radioactive solution, weighed to measure the amounts of liquids which adhered to the samples, and dried using an infrared lamp. The radioactivities of the samples were then mesured with a GM-Counter (Ten Model SA-10, 100 Scaler), equipped with a GM-tube with a 2.95 mg./cm^2 mica window (Ten GM 131). The amount of adsorption was determined as the difference between the total radioactivity taken up by the plastics samples and that radioactivity due to the solution adhering to the polystyrene sample, under

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1) M. Muramatsu and T. Sasaki, *Radioisotopes*, **7**, 36, 42 (1958) (in Japanese); T. Sasaki, M. Muramatsu, H. Hotta and Y. Wadachi, ibid., 7, 47 (1958) (in Japanese); P. C. Tompkins et at., *Ind. Eng. Chem.*, **42**, 1475 (1950).

2) J. H. Schulman et al., *Kolloid-Z.*, **146**, 77 (1956).

3) C. V. King and B. Levy, *J. Phys. Chem.*, **59**, 910 (1955).

4) C. H. Giles et al., *J. Chem. Soc.*, **1960**, 3973.

the assumption that the concentration of ^{60}Co-ions is the same for both the adhering solution and the bulk of the solution. The specific activity of cobalt ions necessary for this calculation was measured at the same time under the same geometry as for the standard sample, which was prepared by evaporating a known amount of a radioactive sample solution put in 20 spots on a polystyrene sample. For the measurement of the radioactivity, only β-ray counting was used, the difference between the counting rates taken with and without a γ-ray filter. The samples of plastics were further dipped into 50 cc. of various rinsing liquids and were taken out of them after a desired immersion time. The remaining radioactivities on the plastics surface were then measured, and from the values obtained, the amount of the desorption of ^{60}Co-ions from the samples was determined. For each successive dipping, the rinsing liquid was renewed.

Results

Figure 1 shows the changes in the uptake of ^{60}Co-ions with the immersion time of polystyrene in sulfuric acid at 40°C. The desorption of cobalt ions using various rinsing liquids was measured; these results are shown in Figs. 2 and 3. The polystyrene samples appearing in Fig. 3 had been immersed in a sulfuric acid solution for 30 sec. at 85 to 88°C; those in Fig. 2 had not been so treated. The amounts of ^{60}Co-ions remaining on the plate taken as a vertical axis, were expressed as percentages of the original amount of ^{60}Co-ions adsorbed, as was stated in the preceding section. The values above 100 per cent came from the adhering portion of the liquid which was used for the cobalt ion adsorption. Here we can notice that, although the cobalt ions adsorbed initially on an untreated surface (Fig. 2) are much fewer than those on a treated surface (Fig. 3), the former as a whole is rather harder to remove by rinsing than the latter, regardless of the nature of the rinsing liquid; i. e., the steady portion of the curves of Fig. 2 attained after prolonged rinsing is higher (2.95×10^{-11} g./cm^2) than would be presumed from the small initial amount of cobalt ion uptake. This may come from the irreversible portion of the adsorption of cobalt ions due to the impurities in the original sample; the impurities may possibly be removed or altered to the center of reversible adsorption during the sulfuric acid treatment.

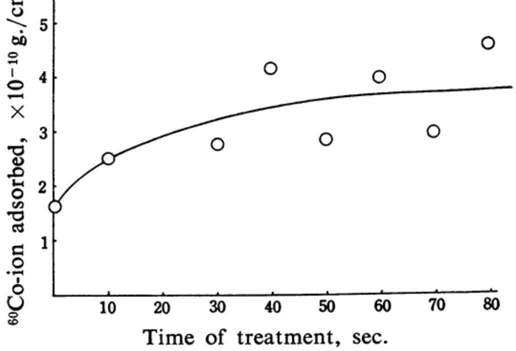

Fig. 1. Change of adsorption of ^{60}Co-ion on polystyrene with time of immersion into sulfuric acid.

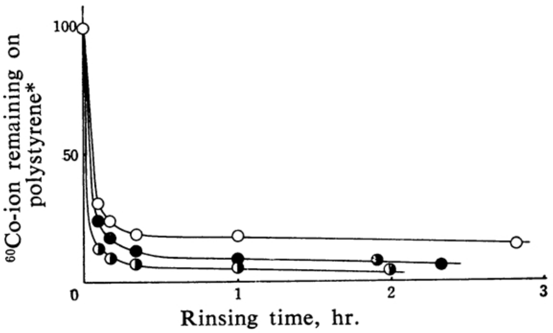

Fig. 2. Desorption of ^{60}Co-ion from polystyrene not treated with sulfuric acid.
Initial activity being 2500 c.p.m.; rinsing liquid used being 0.1 mol. aqueous cobalt chloride (○), distilled water (●) and aqueous 1 % EDTA solution all at pH 7.8 (◑).
* Relative counting rate of ^{60}Co-ion

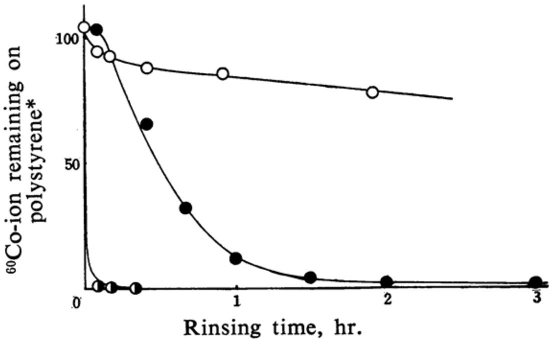

Fig. 3. Removal of ^{60}Co-ion-contamination from polystyrene treated with sulfuric acid.
Initial radioactivity; 15000～5000 c.p.m. (^{60}Co; $4.1\sim1.4\times10^{-9}$ g.) rinsing liquids; absolute ethanol (○); distilled water (●); 0.1 mol. aqueous cobaltous chloride solution (◑).
* Relative counting rate of ^{60}Co-ion

It can be seen in Fig. 3 that, in the case of treated polystyrene, the initial amount of adsorption is much larger than that of an untreated surface and that the desorption curves change markedly with the nature of the rinsing liquids. Thus, the rinsing with distilled water gradually decreases the adsorbed cobalt ions, while almost all of the cobalt ions are removed instantly by rinsing with a non-radioactive 0.1 mol. aqueous cobaltous chloride solution; this reduces the residual amount of cobalt ion adsorption to less than 3.08×10^{-12} g./cm^2. On the basis of this desorption behavior, shown in Figs. 2 and 3, it may be concluded that the major part of the adsorption of cobalt ions by the treated (sulfonated) polystyrene is the ion-exchange adsorption. This conclusion is further confirmed by the fact that the rate of desorption by the anhydrous ethyl alcohol is smaller than that by distilled water. Here we employed ethyl alcohol because it is a nonionizing solvent, thus offering no ions for ion-exchange with the adsorbed ion, and yet it shows a larger solubility for cobaltous chloride than does distilled water. The desorption curves are also shown in Fig. 3.

In this situation, we should like to draw further attention to the problem of radioactive contamination and decontamination. Concerning these problems, Jackson and Garard made a similar experiment(5) for plastics surfaces using nuclear fission products as contaminants. The amount of adsorbed fission products they obtained, as well as the final amount of activity after rinsing the contaminated sample with 5 per cent ammonium citrate, is higher than those of our results for the sulfonated (ion-exchanging) polystyrene surface. In our case, the sulfonation of polystyrene was mainly restricted to its surface, and it was shown that, in such a case, adsorbed cobalt ions are rather readily desorbed; even a simple water (a weakly ionizing liquid) rinsing is fairly effective, as is shown in Fig. 3.

In the case of radioactive decontamination, it is the easy and widespread practice to use water, a detergent solution or an acid solution as the rinsing liquid or decontaminant. Quite often, howeve, these treatments leave some persistent contamination behind, though a large portion of contamination is readily removed. This residual contamination, though small in amount, may often be quite undesirable. Our present findings on the adsorption and desorption of ^{60}Co-ion by polystyrene have some bearing on this problem. It may be said that, if the sample of polystyrene is properly treated with sulfuric acid, such residual contamination will be reduced practically to zero even by a simple rinsing with water, though the surface is rendered rather susceptible to contamination. However, the problem still remains to find the optimum conditions, giving minimum susceptibility, for such a surface treatment.

In conclusion, we should like to emphasize that, judging from the results of the present experiment on the adsorption characteristics of cobalt ions on a polystyrene sample, the information concerning the properties of solid surfaces and the nature of the adsorption of a solute on them can properly be obtained from such experiments as sulfuric acid treatment and from the measurement of desorption curves for treated and untreated surfaces using various rinsing liquids.

Summary

The adsorption of cobalt ions by polystyrene treated with sulfuric acid was measured using the radiotracer technique. We also studied the type of adsorption of the cobalt ions by polystyrene, with or without sulfuric acid treatment, by observing the rate of desorption by the use of several rinsing liquids. It was confirmed that, although cobalt ion adsorption on an untreated surface is much less than that on a treated surface, the former is rather harder to remove by rinsing than the latter, regardless of the nature of the rinsing liquid.

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5) E. W. Jackson and L. Garard, *Nature*, 171, 442 (1953).