

Tracer studies of adsorption of Sr^{++} on copper

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Abstract. Adsorption of Sr^{++} ions on copper metal surfaces has been studied by the tracer technique. The strontium nitrate solutions of different concentrations were labelled with ^{90}Sr and the copper coupons of electrolytic quality were kept immersed in these solutions for different intervals of time. The activity of both the faces of the coupons were measured with a GM counter after washing and drying the coupons. Results have been obtained on the amount of adsorption as a function of time, concentration of strontium nitrate solution and temperature. The data have been found to be in accordance with the Freundlich adsorption isotherm equation. Interpretation of the data in the light of the findings of other authors in similar systems has been made.

Keywords. Adsorption; strontium on copper; tracer technique.

1. Introduction

Radioactive tracer technique has been applied for the study of adsorption of cations and anions on different metal surfaces with considerable interest during the last several decades (Palaicios and Baptista 1952; Hensley *et al* 1948, 1949; Camarcat *et al* 1949; Schweitzer and Wilhelm 1953; Haissinsky and Laflamme 1958; Simnad 1953; Arnikaar and Mehta 1960, 1961, 1969; Arnikaar *et al* 1972). Arnikaar and Mehta (1960, 1961, 1969) have studied the adsorption of cations like Sr^{++} and Ca^{++} and the anions like I^- , SO_4^{--} , PO_4^{--} in the concentration range 10^{-1}M to 10^{-5}M and 10^{-3}M to 10^{-12}M respectively. It was considered worthwhile to investigate the adsorption of Sr^{++} on metallic copper surface by the tracer technique for ^{90}Sr could be used as a tracer in this study. In the present work, the effect of concentration of Sr^{++} , temperature and time of immersion on the amount of adsorption have been investigated.

2. Experimental

Circular coupons of 2.2 cm and 2.0 cm in dia and having thicknesses of 0.008 cm and 0.011 cm respectively were taken from the copper sheet of electrolytic quality. These coupons were mechanically and chemically polished according to the procedure given by Siejka and Campbell (1958).

Labelling of $\text{Sr}(\text{NO}_3)_2$ with ^{90}Sr was done by adding 10 ml of dilute strontium—90 solution to each of the solutions of $\text{Sr}(\text{NO}_3)_2$ (of different known concentrations) before making the volume up to the mark.

The copper coupons prepared as above were clamped to a formica strip, which was fixed in a polythene bottle containing 40 ml of the tagged $\text{Sr}(\text{NO}_3)_2$ solution. The bottle was kept in a thermostat. The coupons were taken out from the bottle at different intervals of time. They were washed in three baths containing distilled water, then with a fresh lot of distilled water from a wash bottle and finally dried by using a heating lamp.

Radioactivity of these coupons was measured by using an end window GM counter. The coupons were placed in a planchett placed on a stand inside a lead castle. Constant geometry of the coupons was maintained during all the activity measurements. For each interval of time two coupons were taken and the activity of both the faces of each of the two coupons was measured. The mean of the four readings obtained for the two coupons was taken for each interval of time. Correction for background was made for all the activity measurements.

3. Results

Amount of Sr^{++} ions adsorbed on the copper metallic surface varies against time and after some time a saturation value is obtained (figures 1 and 2). There is some decrease in the activity after the saturation value is reached due to desorption, the amount of desorption being greater in the case of a solution of higher concentration. The amount of Sr^{++} ions adsorbed is proportional to the activity of the surface and this also depends on the concentration of the solution in which the copper coupon is immersed and as the concentration decreases, the amount adsorbed decreases (figure 3).

^{90}Sr (half life 28 years) decays to ^{90}Y , which is also radioactive with a half life of 64.2 hr. However, as the decay constant of ^{90}Y is very large compared to that of

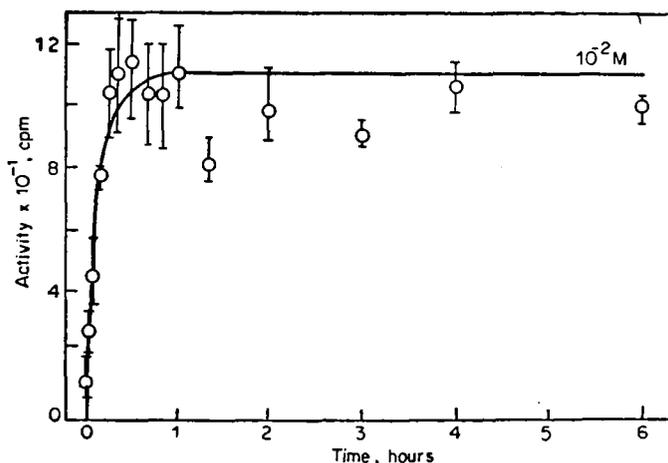


Figure 1. Plot of activity of Sr^{++} ions on copper surface (dia 2.0 cm) as a function of time (short time intervals) at 25°C.

^{90}Sr , Muramatsu (1973) has shown that the decaying daughter is equilibrated with the growing one, and the total radioactivity represents the number of mother atoms as if they were emitting a radioactivity measurable with the detection coefficient equal to the sum of the same for both the mother and the daughter.

The Freundlich adsorption isotherm equation is $x/m = k C^{1/n}$, where x is the amount in grams of the substance adsorbed by m grams of the adsorbing material, C is the equilibrium concentration of the solution, k and n are constants. Taking logarithm on both sides we get,

$$\log x/m = 1/n \log C + \log k.$$

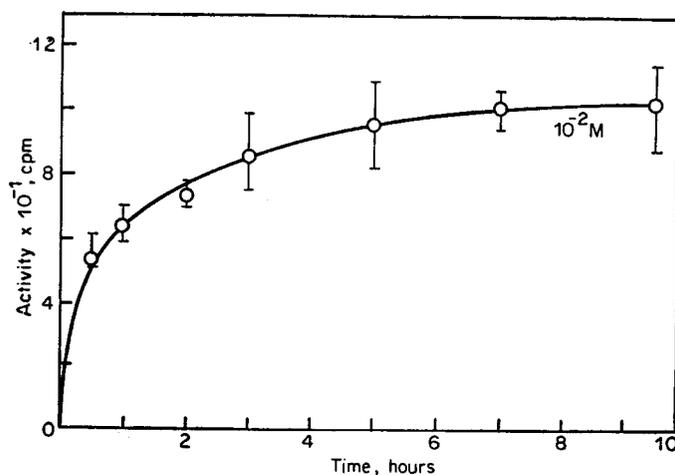


Figure 2. Plot of activity of Sr^{++} ions on copper surface (dia 2.0 cm) as a function of time (long time intervals) at $25^{\circ}C$.

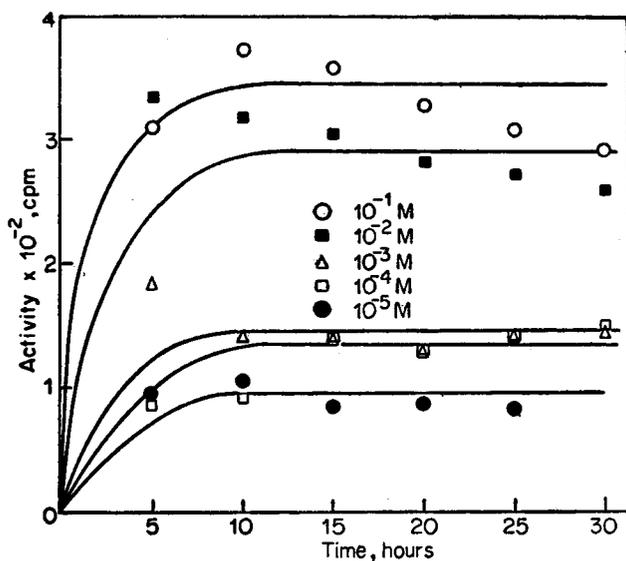


Figure 3. Plot of activity of Sr^{++} ions on copper surface (dia 2.2 cm) at various concentrations of $Sr(NO_3)_2$ solution as a function of time at $25^{\circ}C$.

On plotting $\log x/m$ as a function of $\log C$, a straight line should be obtained and the slope of the straight line gives the value of $1/n$. Since the activity is proportional to the amount of Sr^{++} ions adsorbed and the mass of the adsorbent copper remains constant, \log of activity can be plotted as a function of \log of concentration and this plot would give a straight line as the constant factor can always be separated from the variables x and C in a log-log plot and will not change the value of the slope. A plot of \log of activity as a function of \log of concentration gives a straight line (figure 4) within the limits of the experimental error. Thus from our results, the slope of the straight line was found to be 0.15.

The activity count obtained on the coupons at 25°C and 40°C under the same conditions of concentration and surface conditions shows a decrease in the amount of adsorption with increase of temperature (table 1).

4. Discussion

In their study of the adsorption of ^{60}Co , ^{90}Sr and ^{144}Ce on aluminium, Siejka and Campbell (1958) have observed that adsorption equilibrium was reached in about 30 min. In our work also, it is observed that there is no induction period (figure 1) and our results are in complete agreement with those of Siejka and Campbell (1958).

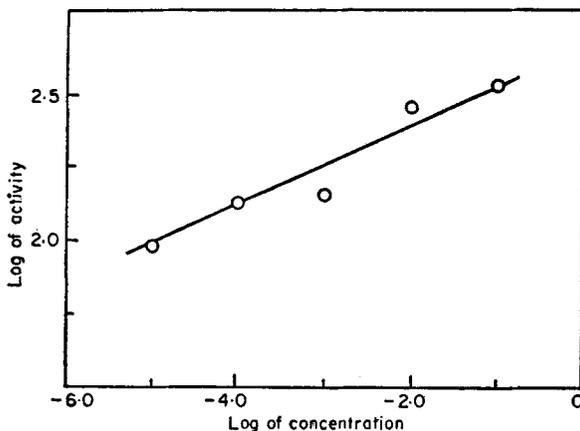


Figure 4. Plot of logarithm of saturation values of activity on copper (dia 2.2 cm) at 25°C as a function of logarithm of concentration of $\text{Sr}(\text{NO}_3)_2$.

Table 1. Adsorption of Sr^{++} on copper coupons (dia 2.2 cm) after 5 hr immersion for different concentrations of $\text{Sr}(\text{NO}_3)_2$ at 25°C and 40°C.

Concentration of Sr^* (NO_3) ₂ , M	True activity CPM (25°C)	True activity CPM (40°C)
10^{-1}	310	251
10^{-2}	337	211
10^{-3}	182	162
10^{-4}	88	83
10^{-5}	95	107

All the curves are continuous and concave towards the time axis similar to those obtained by Arnikaar *et al* (1972) in the adsorption of Ca^{++} and Sr^{++} ions on the aluminium surface. It is only in the case of solutions of higher concentration ($10^{-1}M$ to $10^{-2}M$) that a greater deviation from the equilibrium value is obtained which may be the result of a higher rate of desorption in these cases.

In the present work, the steady state values fall with decrease of concentration. There is some change in this value between the concentrations 10^{-1} and $10^{-2}M$. But there is a sudden fall in its value at 10^{-3} to $10^{-5}M$ (figure 3). Arnikaar *et al* (1972) have also observed that the steady state values for the adsorption of Sr^{++} ions on aluminium decrease only slightly in the concentration range 10^{-1} to $10^{-3}M$ but there was a sudden fall in these values at concentrations below $10^{-4}M$. A strongly heterogeneous surface could be the reason for this type of behaviour, which is not surprising as the coupons had been chemically polished before the adsorption.

Our data obey the Freundlich equation with the value of $1/n = 0.15$. Arnikaar and Mehta (1969) have found that in the adsorption of I^{-} ions on Au and Pt, the value of $1/n$ is unity at low concentrations and less than unity for higher concentrations. Since in our study, the lowest concentration taken is only $10^{-5}M$, which is much higher than the tracer concentrations (of the order of $10^{-12}M$) used by others, our data did not give the value for $1/n$ equal to unity. At tracer concentrations the number of sites covered may be a very small fraction of the total and hence the full span of heterogeneous sites is not covered. Under such conditions the adsorbent presents a far more uniform surface than that at higher concentrations.

In most of the adsorption studies a decrease in the amount of the substance adsorbed with an increase of temperature has been reported. In the present work also, there is some decrease in the activity of the coupons as the temperature is increased from $25^{\circ}C$ (table 1) as is expected in any exothermic process.

In moving the coupons from the solution, washing and drying, minimum time was spent to reduce any errors due to the possible adsorption of ^{90}Y , the daughter product of ^{90}Sr .

No period of induction was observed in this work and the process of adsorption was rather quick reaching the saturation in about 30 min, whereas Hackerman and Stephens (1954) have observed a much longer period of 16 hr for the approach of saturation in the adsorption of SO_4^{2-} on iron. It may be concluded that the adsorption of Sr^{++} on the copper surface as observed in the concentration range $10^{-1}M$ to $10^{-5}M$ is a physical one. In order to decide this point unequivocally, more data at different temperatures and with different pH of $Sr(NO_3)_2$ solution will have to be obtained and the heat of adsorption calculated.

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