

## INFLUENCE OF RADIOACTIVE SPECIES IN THE STUDY OF AQUEOUS ELECTROCHEMICAL SYSTEMS

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It has been found that radioactively labelled substances used as tracers in studies of the action of corrosion inhibitors in aqueous systems can produce effects different from those of the corresponding non-radioactive substances. Such effects have been found in systems containing calcium-45 and sulphur-35. A similar effect has also been detected in solutions containing radioactively labelled chromate. In order to confirm that radioactively labelled substances can alter the normal electrochemical behaviour of substances, experiments have been carried out in respect of corrosion inhibition, polarisation, electrocapillary, polarographic and voltammetric behaviour in systems containing radioactive calcium and radioactive sulphur. The observations supporting the different behaviour of radioactively labelled substances are reported in this paper.

**Keywords :** Radioactive Species; Aqueous Electrochemical Systems; Calcium-45; Sulphur-35; Radiolysis

### INTRODUCTION

IN electrochemical research, it has been the practice to employ the radiotracer technique to examine the electrode behaviour or to follow the course of electrode reactions in the implicit belief that radioactive species and their non-radioactive counterparts do not differ in their chemical behaviour. It has been assumed that the thermodynamics and kinetics of electrode processes are identical with respect to a given chemical species, whether it is radioactive or not. The possibility that radiation emanating from a radioactively labelled substance can itself alter the course of the electrode reaction has been overlooked. The interaction of nuclear radiation with the aqueous phase gives rise to many short and long lived radiolytic products. For example, the production of hydrogen peroxide in a radioactive aqueous solution is a well-established fact (Byalobzheskii, 1970). On the other hand, the interaction of the nuclear radiation with metals in aqueous electrolytes may lead to changes in the nature of the surface or surface films or in the basic structure of the metallic phase. These influences of the radiation may bring about changes in the behaviour of electrochemical systems in which radioactive isotopes have been incorporated for purposes of studying the nature and course of reactions in such systems.

From this point of view a series of studies has been undertaken in the Central Electrochemical Research Institute, Karaikudi. A review of the observations made in these studies is given.

## EXPERIMENTS AND RESULTS

*Calcium Citrate Combination* (Subramanian & Kapali, 1971)

In a programme of work taken up to explore the possibility of using aluminium as a galvanic anode in sodium hydroxide solution, it was found that most of the metal was wasted by local cell corrosion and the anode utilisation efficiency was only of the order of 2 per cent. In order to suppress the wastage of aluminium by local cell action, several inhibitors were tried and finally it was found that a combination of calcium and citrate ions was very effective in suppressing local cell corrosion without affecting the galvanic performance of aluminium. In order to understand the mechanism of action of this combination, experiments were carried out with Calcium-45 and it was found that in solutions containing only Calcium-45, there was an uptake of activity, whereas in the solutions containing Calcium-45 and citrate there was no uptake of activity, though it was this combination that was very effective in suppressing local cell corrosion. Quite unexpectedly, it was also found that in the presence of Calcium-45 there was acceleration of corrosion of aluminium in sodium hydroxide solution (Table I). It was this observation that led to the study of the other systems.

TABLE I

*Effect of radioactive Ca<sup>2+</sup> on the inhibition of corrosion of aluminium in, 0.2M NaOH by Ca<sup>2+</sup> and citrate ions*

System	Percentage inhibition in the presence of non-radioactive Ca <sup>2+</sup>				Percentage inhibition in the presence of radioactive Ca <sup>2+</sup>			
	1 hr.	2 hrs.	4 hrs.	6 hrs.	1 hr.	2 hrs.	4 hrs.	6 hrs.
0.2M NaOH + 0.135% NaCl + 0.1% CaO	25.3	26.1	27.4	25.2	-42.4	-6.6	-26.2	-22.54
0.2M NaOH + 0.135% NaCl + 0.1% CaO + 5% Na citrate	67.0	71.0	61.0	56.0	-26.2	-133.1	-101.2	-53.2

*Calcium Hexametaphosphate Combination* (Subramaniyan *et al.*, 1978a)

The second system that was taken up for study was the use of sodium hexametaphosphate with calcium as a corrosion inhibitor for steel in 0.01 per cent NaCl at pH values, 9.0, 7.5 and 5.5. In these solutions, corrosion inhibition efficiency obtained in the presence of non-radioactive calcium and radioactive calcium is brought out in Table II. It can be seen from this table that the inhibition of corrosion of steel is quite high at pH 7.5 and 9.0, but is only 14 per cent at pH 5.5. But in the presence of radioactive calcium the inhibition efficiency even at pH 7.5 and

9.0 is considerably brought down and in the presence of radioactive calcium alone corrosion is accelerated. In accordance with this trend the values of inhibition efficiency at pH 5.5 are all negative.

TABLE II

*Effect of radioactive calcium on the inhibition of steel by calcium and sodium hexametaphosphate*

Duration of test = 1 month

Temperature =  $30 \pm 2$  °C

Circular specimen of 2cm<sup>2</sup> area

Composition of the solution	Inhibition efficiency at various pH values in (%)		
	pH = 5.5	pH = 7.5	pH = 9.0
1. 0.01 per cent NaCl + non-radioactive calcium oxide (20 ppm) + sodium hexametaphosphate (100 ppm)	14	98	89
2. 0.01 per cent NaCl + radioactive calcium + non-radioactive calcium oxide (20 ppm) + sodium hexametaphosphate (100 ppm)	-21	37	67
3. 0.01 per cent NaCl + radioactive calcium + sodium hexametaphosphate (100 ppm)	-45	8	37
4. 0.01 per cent NaCl + radioactive calcium	-106	-42	-20

An illustration of the polarisation of steel and the uptake of activity by steel in solution containing radioactive calcium and sodium hexametaphosphate at pH 7.5 is given in Figs. 1 and 2. It is to be noted that at this pH value of the solution, the polarisation of steel in the base solution is very much pronounced. Among the other solutions anodic polarisation is more in the solution containing only Ca-45 (Fig. 1) than that containing non-radioactive calcium upto a certain potential, beyond which there is depolarisation. The uptake of activity increases with increasing potential and at the more positive potentials, it is more in the solution containing only Calcium-45 and manifests humps. But the combinations of radioactive calcium with the other constituents are less polarising than Calcium-45 alone or even the base solution (Fig. 2) and the uptake increases smoothly with the potential. This would indicate that radioactive calcium inspite of being a cation gets adsorbed on steel at the positive potentials. The specimens were corroded at potentials above -0.4V and red corrosion product was sticking to the specimens.

In view of the above mentioned observations, electrocapillary measurements were carried out with calcium chloride solutions to which radioactive calcium was added. The effects produced is shown in Fig. 3. In 1.0M calcium chloride solution (Fig. 3), it is seen that the electrocapillary curve is lifted above that of the base solution on the positive side of the electrocapillary maximum (e.c.m) in the presence

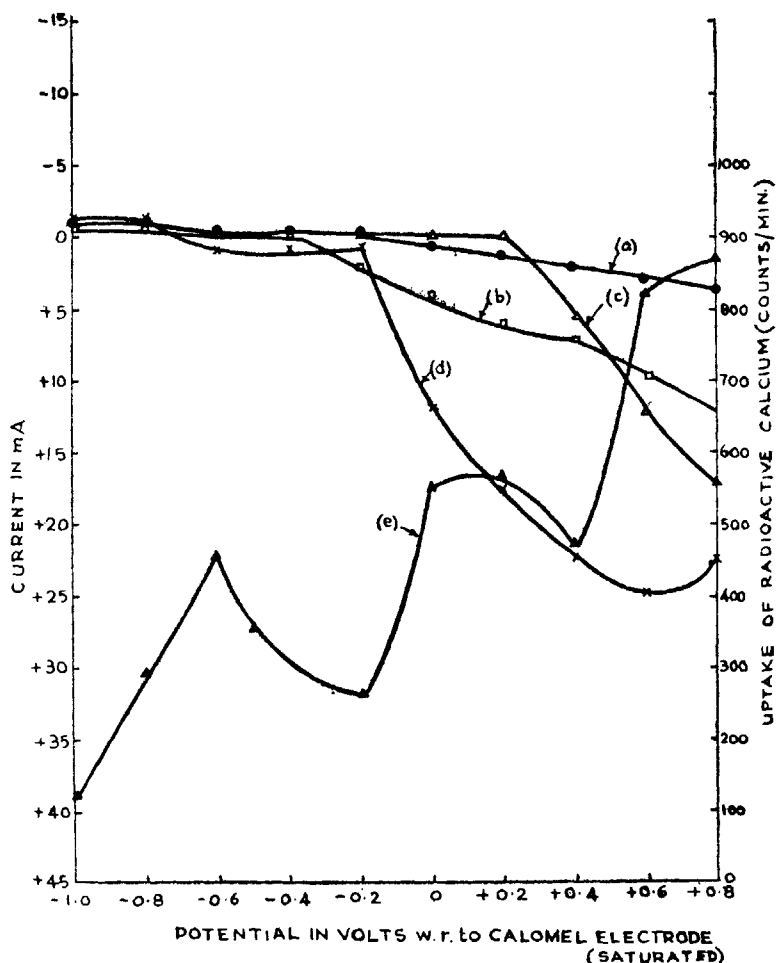


FIG. 1. Potentiostatic polarisation of and uptake of calcium-45 by mild steel in various solutions at pH 7.5.

- (a) —●—●— 100ppm sodium chloride solution.  
 (b) —□—□— 100ppm sodium chloride solution containing 20ppm inactive calcium.  
 (c) —×—×— 100ppm sodium chloride solution containing 100ppm sodium hexameta-phosphate.  
 (d) —△—△— 100ppm sodium chloride solution containing active calcium.  
 (e) —▲—▲— Uptake of calcium-45 by mild steel in 100ppm sodium chloride solution containing active calcium.

of calcium-45 ions. It is also seen that the extent of lifting of the curve increases with the content of calcium-45 in the solution. It has been observed that in 0.1M NaCl solution even 0.5ml of the radioactive calcium solution is able to bring about the same extent of lifting on the positive side of the e.c.m. as 2.0ml in 1.0M solution. In 0.01M calcium chloride solution the similar extent of lifting of the curve with reference to the base solution is almost twice that obtained with 1.0M and 0.1M

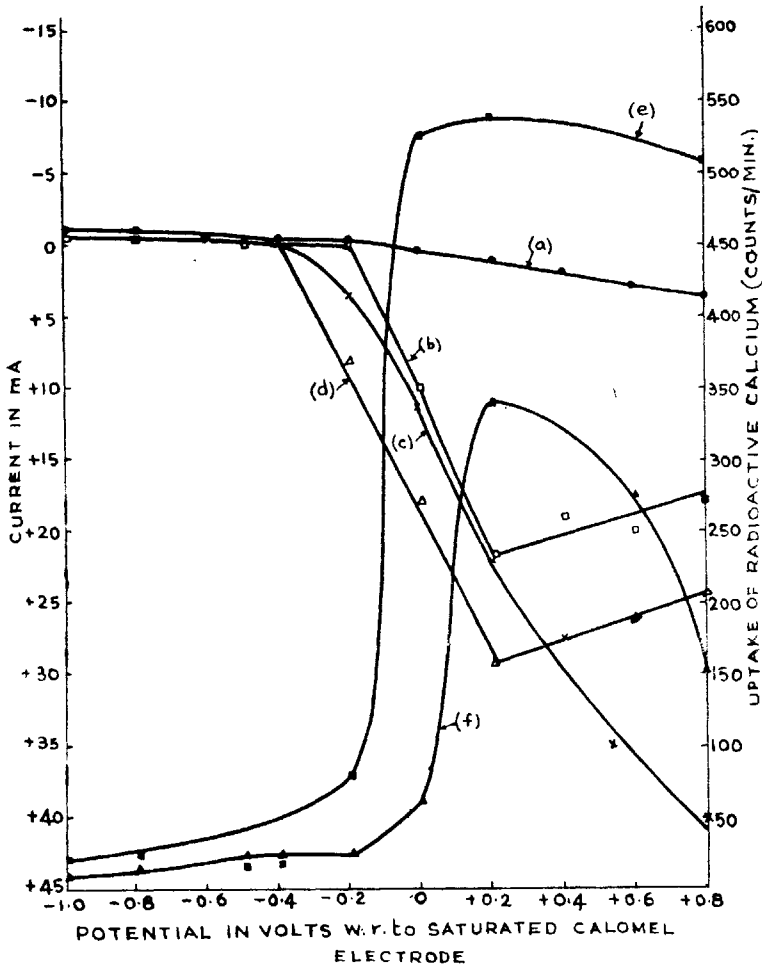


FIG. 2. Potentiostatic polarisation of and uptake of calcium-45 by mild steel in various solutions at pH 7.5.

- (a) —●—●— 100ppm sodium chloride solution.
- (b) —□—□— 100ppm sodium chloride solution containing 20ppm inactive calcium and active calcium.
- (c) —×—×— 100ppm sodium chloride solution containing 20ppm inactive calcium and 100ppm sodium hexametaphosphate.
- (d) —△—△— 100ppm sodium chloride solution containing 20ppm inactive calcium, active calcium and 100ppm sodium hexametaphosphate.
- (e) —■—■— Uptake of calcium-45 by mild steel in 100ppm sodium chloride solution containing 20ppm inactive calcium, active calcium.
- (f) —▲—▲— Uptake of calcium-45 by mild steel in 100ppm sodium chloride solution containing 20ppm inactive calcium, active calcium and 100ppm sodium hexametaphosphate.

calcium chloride solution for the same addition of radioactive calcium. These instances of enhanced lifting may be attributed to the higher ratio of calcium-45 to non-radioactive calcium in the diluted solutions.

It is seen that the corrosion of steel in sodium chloride solution is accelerated and also that the inhibitive action of the combination of calcium and sodium

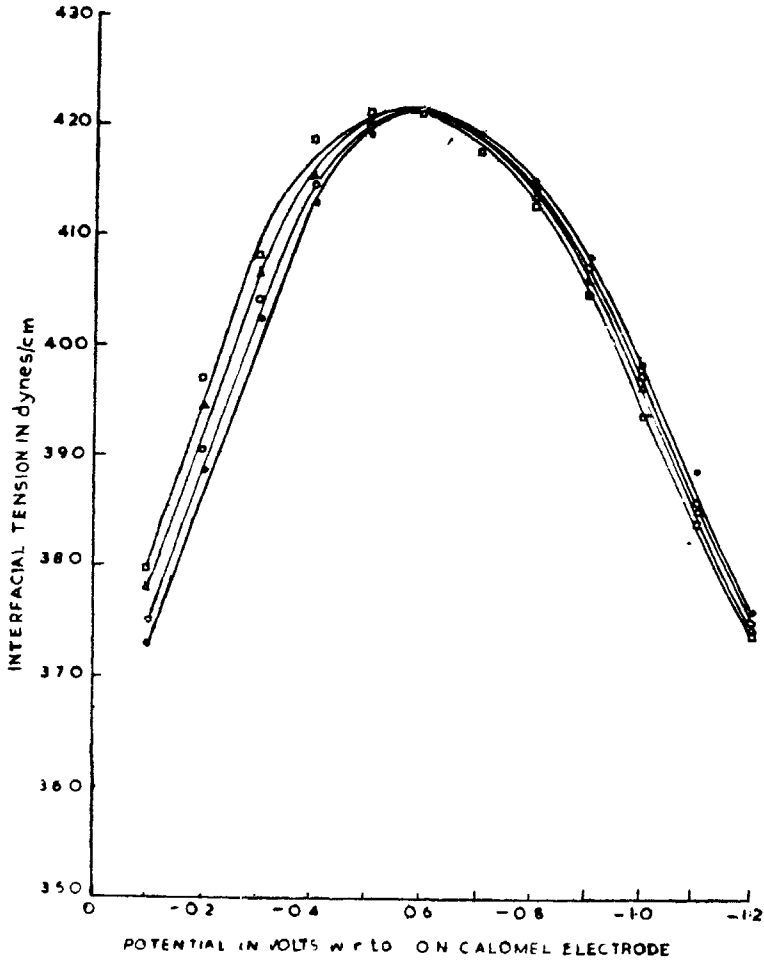


FIG. 3. Electrocapillary curves for 1.0M  $\text{CaCl}_2$  solution in the presence of various concentration of radioactive calcium chloride.

- (a) —●—●— 1.0M  $\text{CaCl}_2$  solution alone.
- (b) —○—○— 1.0M  $\text{CaCl}_2$  solution containing 1.0ml active calcium as calcium chloride.
- (c) —△—△— 1.0M  $\text{CaCl}_2$  solution containing 0.5ml of active calcium as calcium chloride.
- (d) —□—□— 1.0M  $\text{CaCl}_2$  solution containing 2.0ml of active calcium as calcium chloride.

hexametaphosphate is substantially brought down in the presence of calcium-45. This may be broadly attributed to two factors viz., the production of hydrogen peroxide by radiolysis and the influence of radiation on the electrode process. It has been verified in the course of the study that hydrogen peroxide is produced in the solutions containing calcium-45. It is known that various products like hydrogen peroxide and short-lived OH radical are formed by radiolysis (Allen, 1961) and that corrosion of steel is accelerated by hydrogen peroxide which acts as a cathodic depolariser. However, the polarisation diagrams show that in all the solutions the cathodic polarisation is very strong as evidenced by the fact that negligible current flows even at the high negative values of the applied potential. Obviously under the influence of an externally applied field, the conditions around the electrode are such as to bring out only the effects of the factors favourable for polarisation.

It has been further noted that radiation from calcium-45 also affects the electrode surface. The uptake of activity of steel at the positive potentials shows that calcium-45 behaves like a bundle of negative charges or virtually as anions. At the same time it is also observed that compared to the striking cathodic polarisation in the presence of calcium-45 in all cases, the anodic polarisation is very much less. This behaviour is in consonance with the electrocapillary behaviour of calcium-45. The lifting of the electrocapillary curves on the positive side of the e.c.m. in the presence of calcium-45 can also be interpreted in a similar way, that is, the calcium-45 ions being a source of negatively charged beta particles may act as a bundle of negative charges and get attracted by the positively charged mercury phase. Having come to the point of the closest approach, the beta particles emanating from them may neutralise the positive charge on the mercury surface and bring about the lifting of the curves. Another contributing factor in the lifting of the curve can be the purifying action of hydrogen peroxide produced by radiolysis of water on the solution itself. It has been verified that the electrocapillary curve for non-radioactive calcium chloride solution is lifted by the addition of hydrogen peroxide but the effect is marginal.

#### *Dibutyl Sulphide in Sulphuric Acid (Subramanian et al., 1978b)*

In this system the influence of sulphur-35 labelled di-n-butyl sulphide on the corrosion and polarisation of steel and its electrocapillary behaviour in 1.0N sulphuric acid have been investigated. In Table III, the corrosion inhibitive effects of radioactive dibutyl sulphide (d.b.s.\*) and non-radioactive dibutyl sulphide (d.b.s.) have been brought out. It can be seen that d.b.s. is very effective particularly at the high concentrations, in inhibiting the corrosion of steel in sulphuric acid. On the other hand in the presence of d.b.s.\* the inhibition efficiency is substantially reduced and in some cases, corrosion is even accelerated with the progress of time. Since this may be due to hydrogen peroxide produced in the solution by radiolysis, experiments were carried out with solutions containing d.b.s. and hydrogen peroxide. In this case also the inhibition of corrosion is significantly brought down thereby proving that radiolytically produced hydrogen peroxide is responsible for the lowering of inhibition or even for the acceleration of corrosion by d.b.s.\* It has been verified that the solution saturated with d.b.s.\* contains hydrogen peroxide.

TABLE III

*Influence of dibutyl sulphide (d.b.s.) on the corrosion of mild steel in 1N H<sub>2</sub>SO<sub>4</sub>*

Concentration of d.b.s. in moles/litre	Sl. No.	Inhibition efficiency (%)					
		Radioactive d.b.s. solution at				Non-radioactive d.b.s.	
		3rd	5th	7th	10th	only with 55ppm of H <sub>2</sub> O <sub>2</sub>	
$1.33 \times 10^{-4}$ *	1	96	72	12	50	91	35
$0.6665 \times 10^{-4}$	2	55	6	11	—	87	—
$0.3325 \times 10^{-4}$	3	97	-14	18	—	85	—
$0.16625 \times 10^{-4}$	4	60	-22	15	—	60	—
$0.083125 \times 10^{-4}$	5	29	-51	12	—	12	—

\*Solubility of d.b.s. in 1N H<sub>2</sub>SO<sub>4</sub> at 30 °C =  $1.33 \times 10^{-4}$  moles/litre  
(After Subramanyan, 1971)

The polarisation behaviour of steel in 1N sulphuric acid solution and in the solutions containing various other constituents are shown in Fig. 4. The polarisation experiments were carried out in the seventh month from the date of despatch of d.b.s.\* It is seen that the maximum anodic polarisation is manifested by the solution containing d.b.s.\* The solution containing only non-radioactive d.b.s. is next in its effect on anodic polarisation followed by the one containing d.b.s. + hydrogen peroxide and lastly by the base solution. This brings out the fact that some influence other than the production of hydrogen peroxide is responsible for the anodic polarisation of d.b.s.\* On the cathodic side the labelled d.b.s.\* and the combination of d.b.s. + hydrogen peroxide are less polarising than d.b.s. alone, which is in accordance with the corrosion data.

Studies on the uptake of activity by steel at various potentials from a solution saturated with d.b.s.\* indicates that there is significant uptake of activity by the steel specimen at the negative potentials and it comes down with increase potential in the positive direction. The greater uptake of activity and the larger polarisation at the negative potentials as compared to that at the positive potentials may be attributed to the adsorption of sulphoxide derived from d.b.s. by reaction with hydrogen peroxide produced *in situ* by radiolysis. This explanation is supported by the fact that in the case of the combination of d.b.s. and hydrogen peroxide the cathodic polarisation behaviour is similar to that of d.b.s.\* The adsorption of sulphoxide at a negatively charged metal surface is possible because the sulphur atom in the sulphoxide is said to carry a net positive charge.

It is interesting at this juncture to refer to the anodic polarisation of platinum in solutions similar to those used with steel (Subramanyan *et al.*, 1979). In this case d.b.s.\* is found to be the least polarising unlike with steel. This divergence in the



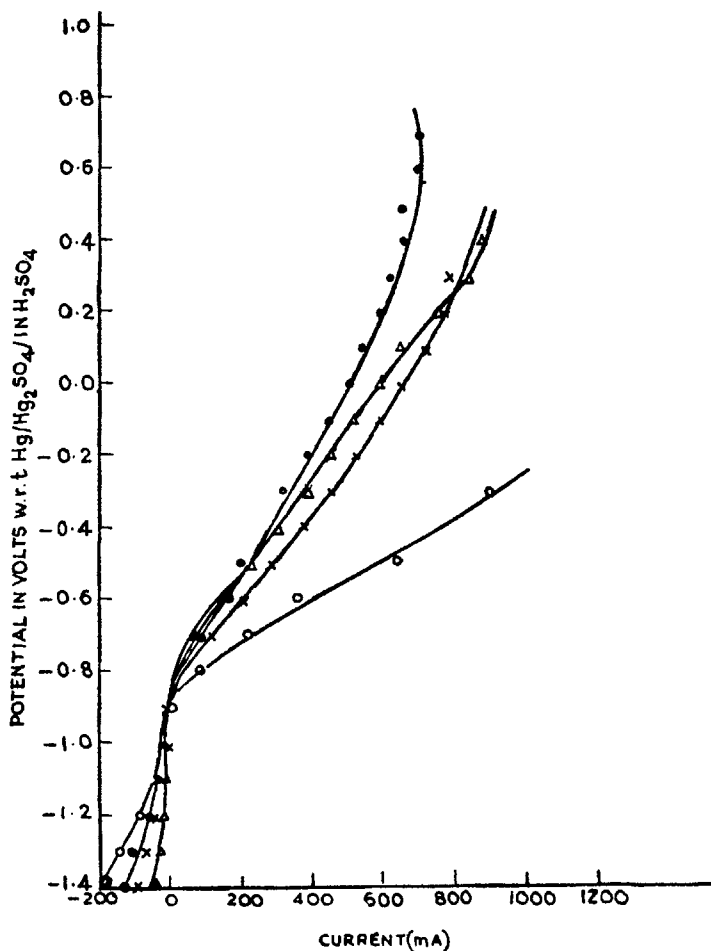


FIG. 4. Potentiostatic polarisation of mild steel in various solutions.

- (a) —○—○— 1N sulphuric acid solution.  
 (b) —△—△— 1N sulphuric acid saturated with non-radioactive n-dibutyl sulphide.  
 (c) —●—●— 1N sulphuric acid saturated with radioactive n-dibutyl sulphide (7th month from the date of despatch).  
 (d) —×—×— 1N sulphuric acid saturated with non-radioactive dibutyl sulphide + hydrogen peroxide (55ppm).

effect of d.b.s.\* can be understood as follows : In a system like steel in sulphuric acid, d.b.s.\* adsorbed on the metal and being a source of negatively charged beta-particles hinders the similarly charged sulphate ions from approaching the electrode and hence manifests an apparent polarising influence on the system, though inherently, it has a depolarising effect as in the case of platinum in sulphuric acid, which is a non-corroding system.

The electrocapillary behaviour of d.b.s. and d.b.s.\* have been studied to understand the difference in effect between them on electrocapillary curves. It has been observed that d.b.s. is absorbed over a range of potentials on either side of the e.c.m. However, the slight suppression of the curves on the positive side and the shifting of the e.c.m. in the negative direction indicate anodic adsorption of d.b.s. Thus, there seems to be both molecular adsorption and adsorption through the sulphur atom of d.b.s.

With d.b.s.\* (Fig. 5) the extent of adsorption is significantly lowered on the positive side of the e.c.m. and there is a clear lifting of the curve on the negative side. The electrocapillary curves obtained with 1N sulphuric acid containing only hydrogen peroxide or a combination of d.b.s. and hydrogen peroxide also show lifting of the curve on the negative side of the e.c.m. It is thus established that in the case of d.b.s.\* it is the hydrogen peroxide that is mainly responsible for its effects, different from that d.b.s. The general adsorption around the e.c.m. as obtained with d.b.s. is also not seen in the case of d.b.s.\*

#### *Polarographic and Voltammetric Behaviour of d.b.s.\* (Subramanyan et al., 1979)*

In view of the observations reported above, it was of interest to examine the polarographic and voltammetric behaviour of d.b.s.\* Since the special effects of radioactive substances in aqueous systems would be attributed to hydrogen peroxide, experiments were also carried out as before with the systems containing d.b.s. and hydrogen peroxide for comparison. The amount of hydrogen peroxide added was that corresponding to the corrosion of mild steel for 30 days in 0.01 per cent sodium chloride solution at room temperature ( $28 \pm 2$  °C). The experiments were carried out in 1N sulphuric acid and in 1N potassium sulphate.

In the range from  $-300$  to  $-1300$ mV, the polarograms for d.b.s. and for d.b.s.\* in 1N sulphuric acid are not similar in shape to that of the base solution and the curves are exalted to different extents (Subramanyan *et al.*, 1979). The exaltation is more in the case of d.b.s.\* than in d.b.s. This would lead one to conclude that d.b.s.\* solution contains a greater amount of the reducible species than the base solution or the d.b.s. solution. The solution containing hydrogen peroxide or d.b.s. and hydrogen peroxide give still higher currents as expected.

In the higher range of potentials also viz., from  $-1300$  to  $-1700$ mV (Fig. 6), it is seen that there is a clearcut distinction between the behaviour of d.b.s.\* and d.b.s. The current voltage curve for d.b.s.\* is a little higher than that for the base solution. It is worth noting that in the base solution it was not possible to get reproducible diffusion current readings beyond  $-1.5$ V because of hydrogen evolution whereas in d.b.s.\* solution it was possible to go up to  $-1.7$ V. It may also be noted that pronounced reduction sets in at a much less negative potential in the case of d.b.s. than in d.b.s.\* The following explanations are given for these observations :—

1. The reduction of hydrogen and that of hydrogen peroxide that are likely to occur in this range of potentials are obstructed by d.b.s.\* But since even in the solutions containing only hydrogen peroxide, the curve is almost similar to that of

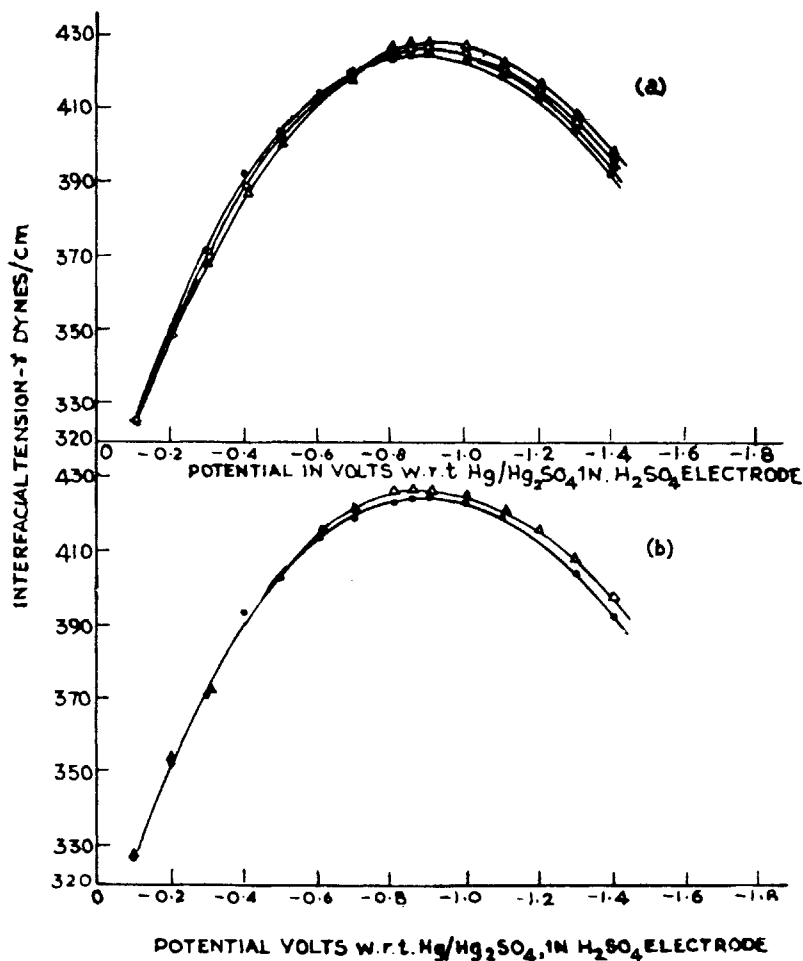


FIG. 5. Electrocapillary curves for 1N sulphuric acid solution in the presence of various concentrations of radioactive dibutyl sulphide (8th month from the date of despatch).

- (a) —●—●— 1N sulphuric acid alone.
- ×—×— 1N sulphuric acid one fourth saturated with radioactive dibutyl sulphide.
- 1N sulphuric acid half saturated with radioactive dibutyl sulphide.
- △—△— 1N sulphuric acid fully saturated with radioactive dibutyl sulphide.
- (b) —●—●— 1N sulphuric acid alone.
- △—△— 1N sulphuric acid + hydrogen peroxide (55ppm).

d.b.s.\*, it may be inferred that d.b.s.\* increases the hydrogen over-voltage and hinders hydrogen reduction.

2. D.b.s. favours or catalyses the reduction of hydrogen ions whereas in the presence of hydrogen peroxide or d.b.s.\* this is hindered.

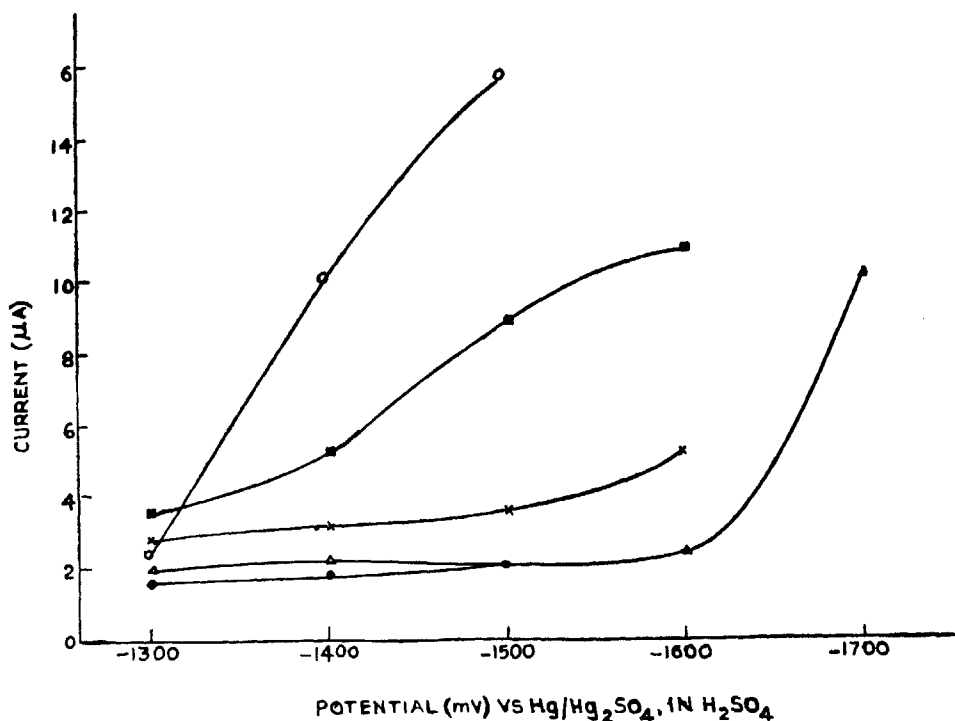


FIG. 6. Polarographic behaviour of labelled dibutyl sulphide (S-35) in 1N sulphuric acid (–1300 mV to –1500mV).

- (a) —●—●— 1N sulphuric acid.  
 (b) —Δ—Δ— 1N sulphuric acid saturated with d.b.s.\*.  
 (c) —×—×— 1N sulphuric acid + hydrogen peroxide (1.1mg/40ml).  
 (d) —□—□— 1N sulphuric acid saturated with d.b.s. + hydrogen peroxide (1.1mg/40ml).  
 (e) —○—○— 1N sulphuric acid saturated with d.b.s.

3. D.b.s.\* itself being a source of negatively charged particles is not able to approach the dropping mercury electrode at these negative potentials for favouring the reduction of hydrogen like d.b.s. .

4. The possibility of extending the polarograms even upto –1700mV in the case of d.b.s.\* points to the fact that though it may come in the way of hydrogen evolution reaction, additional species which are reducible only at the higher negative potentials are produced. Finally, with regard to the exact value of the half-wave-potential for the reduction of d.b.s.\* in 1N sulphuric acid, it can only be said that it may occur at a far negative value which is not reached in the acid medium.

In order to overcome the difficulty mentioned above the same polarographic experiments were carried out in 1N sulphuric acid neutralised with KOH (Subramanyan *et al.*, 1979). From the above experiments it is seen that the reduction wave in the range from –300mV to –1500mV in the presence of d.b.s.\* lies higher

than that of d.b.s. as observed in the acid solution. However, the reduction wave for d.b.s. is very much different from that for the base solution or for the base solution and hydrogen peroxide. It may also be noted that the reduction wave with d.b.s. and hydrogen peroxide is higher than that of d.b.s. alone. This may be a case of exaltation of the wave for d.b.s. by hydrogen peroxide which holds good in the case of d.b.s.\* also. From Fig. 7 which brings out the polarographic behaviour at higher negative potentials, some interesting observations can be made. In the range from  $-1600$

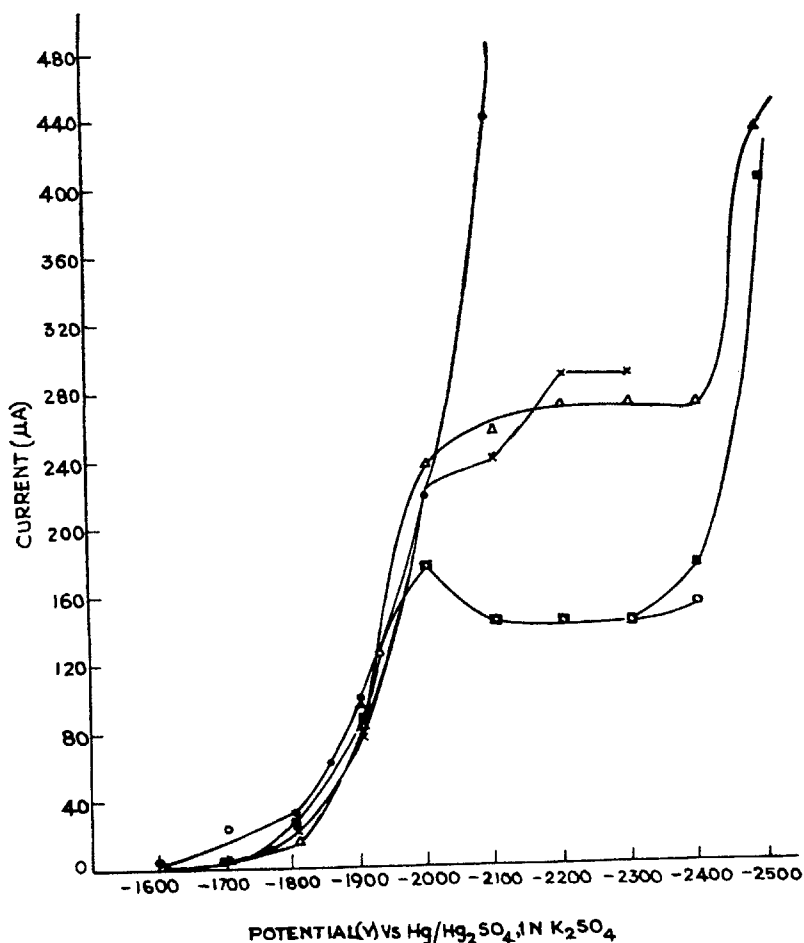


FIG. 7. Polarographic behaviour of labelled dibutyl sulphide (S-35) in 1N potassium sulphate ( $-1600\text{mV}$  to  $-2500\text{mV}$ ).

- (a) —●—●— 1N potassium sulphate.
- (b) —△—△— 1N potassium sulphate saturated with d.b.s.\*.
- (c) —×—×— 1N potassium sulphate + hydrogen peroxide (1.1mg/40ml).
- (d) —■—■— 1N potassium sulphate saturated with d.b.s. + hydrogen peroxide (1.1mg/40ml).
- (e) —○—○— 1N potassium sulphate saturated with d.b.s.

to  $-2000\text{mV}$  where the discharge of potassium ions and/or hydrogen ions may take place the curves follow the same pattern. But at  $-2100\text{mV}$ , the wave for the base solution rises to high diffusion current values whereas in the case of other solutions plateaus characteristic of limiting currents are obtained. In the potential range between  $-2100\text{mV}$  and  $-2400\text{mV}$ , d.b.s. with or without hydrogen peroxide and also d.b.s.\* seem to come in the way of reduction of hydrogen ions and/or of the potassium ions, and beyond  $-2400\text{mV}$ , the normal cathodic process such as the discharge of potassium ions takes place. It has to be noted that the limiting diffusion current got in the case of d.b.s.\* is almost double that obtained with d.b.s. proving thereby that d.b.s.\* is electrochemically different from d.b.s. There is no difference in the behaviour between d.b.s. and its combination with hydrogen peroxide. The higher limiting current obtained in the case of d.b.s.\* can be attributed to some effect of the beta radiation such as electrons ejected from mercury (Barker 1966) or hydrated electrons (Mathesan, 1965).

Voltammetric experiments were carried out in 1N potassium sulphate solution with 99.9 per cent pure platinum wire electrode, having a cross sectional area of  $0.021\text{cm}^2$ . The electrode was polished by rubbing lightly over Whatman filter paper No. 41 and then given a dip treatment in a mixture of hydrochloric acid and nitric acid for one minute. The electrode was removed, washed repeatedly with distilled water and quickly inserted into the cell. The observations made in two ranges of potentials were considered. Fig. 8 brings out the behaviour of the different solutions in the potential range from  $-0.3\text{V}$  to  $+1.0\text{V}$ . It is in this region that the peculiar behaviour of d.b.s.\* is strikingly brought out. It can be seen that the current values obtained with d.b.s.\* in the potential range from  $-0.3\text{V}$  to  $+0.5\text{V}$  are higher than in the other solutions and the increase is pronounced upto about  $+0.2\text{V}$ . This can be attributed to the effect of the nuclear radiation of the labelled atom which may produce additional charge carriers like hydrated electrons. The general voltammetric behaviour of d.b.s.\* is different from that of d.b.s. or its combination with hydrogen peroxide or hydrogen peroxide alone over the whole range of potential.

At potentials more positive than  $+1.3\text{V}$  (Fig. 9) the current values are of a higher magnitude and rise progressively with increase in potential. It is likely that oxygen evolution is the most predominant reaction in this region, since the slopes of the curves for the various systems are almost equal. However, it is seen that compared to the base solution, the other systems permit only lesser currents to flow at the corresponding potentials. This would indicate that some amount of polarisation is brought about in these systems probably due to the formation of an oxide film and/or adsorption of some of the oxidised species like sulphoxide and sulphone produced in the system. It is to be noted that in this region the solution containing d.b.s.\* causes more polarisation than d.b.s. or the other solutions containing hydrogen peroxide, contrary to the expectation that, with the extra charge carriers produced by radioactivity, d.b.s.\* would be less polarising. This fact may be explained in the following way: Apart from the initial oxide films formed on platinum, the products of oxidation of d.b.s. and the products generated by radiation might have transformed the electrode surface by adsorption and brought about polarisation compared to the base solution.

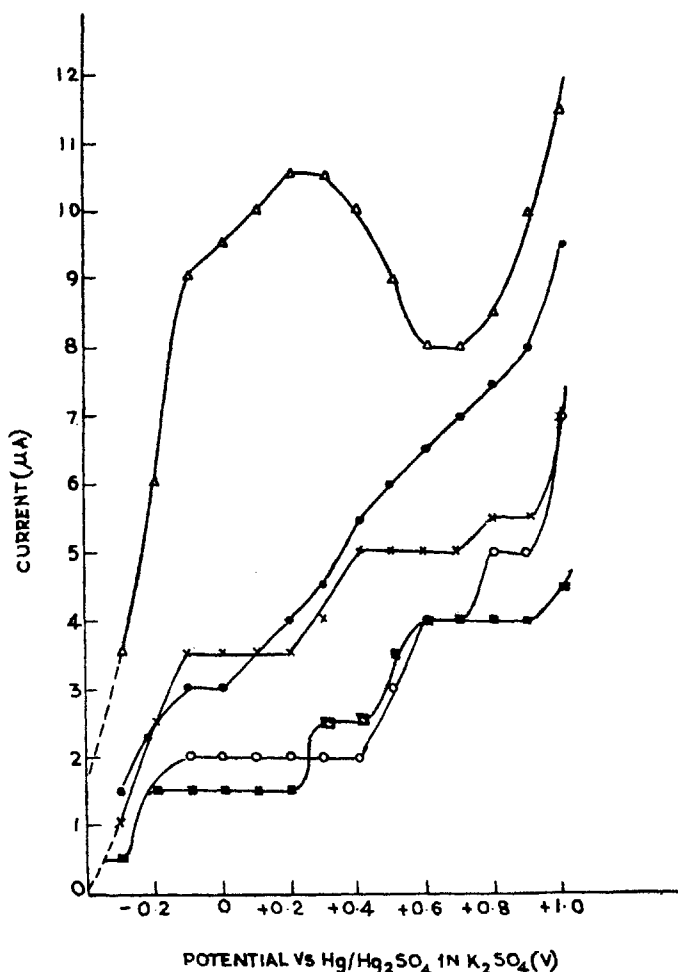


FIG. 8. Effect of labelled dibutyl sulphide on the potentiostatic polarisation of platinum electrode in 1N potassium sulphate ( $-0.3\text{V}$  to  $+1.0\text{V}$ ).

- (a) —●—●— 1N potassium sulphate.  
 (b) —△—△— 1N potassium sulphate saturated with d.b.s.\*  
 (c) —×—×— 1N potassium sulphate + hydrogen peroxide (1.1mg/40ml).  
 (d) —■—■— 1N potassium sulphate saturated with d.b.s. + hydrogen peroxide (1.1mg/40ml).  
 (e) —○—○— 1N potassium sulphate saturated with d.b.s.

#### Radioactive Chromate Solution (Subramanyan *et al.*, 1980)

In order to find out whether the radiation from a gamma emitter also may produce effects other than that of the non-radioactive analogue, a few exploratory experiments were carried out with steel in 0.01 per cent sodium chloride solution to which non-radioactive chromate and chromium-51 labelled chromate had been added. The polarisation behaviour of steel in these solutions is shown in Fig. 10. From

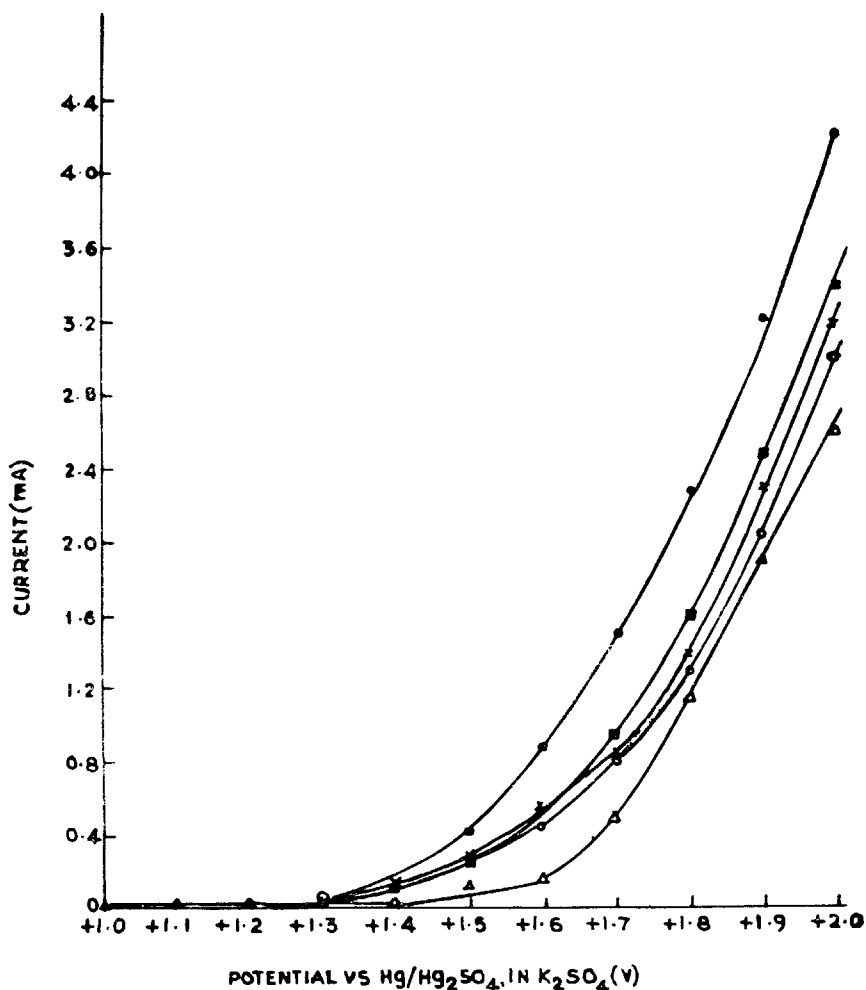


FIG. 9. Effect of labelled dibutyl sulphide on the potentiostatic polarisation of platinum electrode in 1N potassium sulphate (+1.1V to +2.0V).

- (a) —●—●— 1N potassium sulphate.  
 (b) —△—△— 1N potassium sulphate saturated with d.b.s.\*.  
 (c) —×—×— 1N potassium sulphate + hydrogen peroxide (1.1mg/40ml).  
 (d) —□—□— 1N potassium sulphate saturated with d.b.s. + hydrogen peroxide (1.1mg/40ml).  
 (e) —○—○— 1N potassium sulphate saturated with d.b.s.

this, it can be seen that there is a clear difference between the non-radioactive chromate and radioactive chromate solutions. Non-radioactive chromate causes significant cathodic polarisation whereas in the presence of radioactive chromate the polarisation is less than even in the base solution, particularly at the high current density values. In other words, there is a depolarisation of the electrode in the presence of radioactive chromate. This can again be attributed to the depolarising action of hydrogen



peroxide produced by radiolysis. Apart from this, Fig. 10 clearly shows that the anodic polarisation also is less in the case of the solution containing radioactive chromate than in the base solution or in the solution containing radioactive chromate along with non-radioactive chromate. This observation would suggest that the dissolution of the metal is facilitated by activation of the metal surface by gamma radiation.

### CONCLUSIONS

1. The normal inhibitive action of established corrosion inhibitors is seriously affected if they contain a radioactive element.

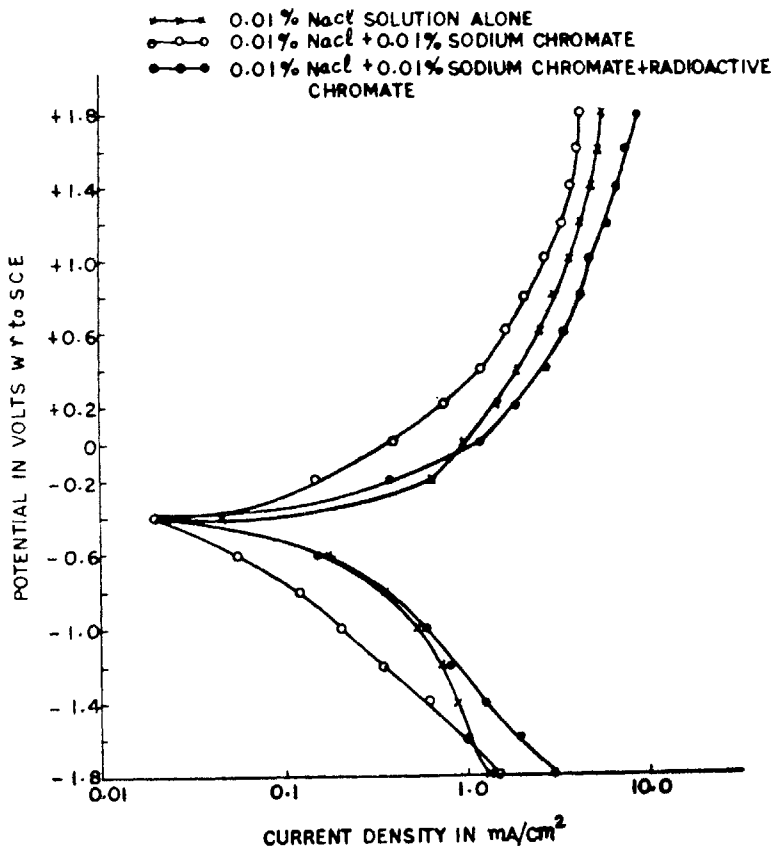


FIG. 10. Effect of radioactive chromate on the potentiostatic polarisation of mild steel in various solutions.

- (a) —x—x— 0.01 per cent sodium chloride solution.  
 (b) —o—o— 0.01 per cent sodium chloride solution + 0.01 per cent non-radioactive sodium chromate.  
 (c) —●—●— 0.01 per cent sodium chloride + 0.01 per cent non-radioactive chromate + labelled chromate.

2. The reduction in the effectiveness of corrosion inhibitors in the presence of radioactive elements can be attributed to the presence of hydrogen peroxide produced by radiolysis and also to the activation of the metal surface by the nuclear radiation.

3. In aqueous metal/solution systems, the polarisation behaviour of metals is affected by the presence of radioactive substances in different ways depending upon the nature of the systems.

4. The electrocapillary features of radioactively labelled substances are different from those of the corresponding non-radioactive substances.

5. The polarographic and the voltammetric behaviour of sulphur-35 labelled dibutyl sulphide is quite different from that of non-radioactive dibutyl sulphide in both acidic and neutral media.

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#### Discussion

- G. A. TEDORADZE (*Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow*) : Are you sure, that your samples of radioactive Calcium didn't contain the organic impurities ? You had to analyse them.
- N. SUBRAMANYAN : Though we did not analyse the radioactive calcium for impurities, we believe that it would not have organic impurities. Even assuming that it had some organic impurities they should have suppressed the electrocapillary curves and not lifted them above the curve for the base solution.
- A. V. VANNIKOV (*Institute of Electrochemistry, Academy of Sciences of USSR, Moscow*) : 1. What stationary concentrations of products of radiolysis exist in your experiments ? 2. Do you have the same results, if the radiolysis is caused by external radiation ?

- N. SUBRAMANYAN : 1. In our experiments, we found that there was 27.5 parts per million of hydrogen peroxide. We did not make any attempt to find out the other products of radiolysis and assumed that they are short-lived species and would have no effects on the systems studied.
2. We have not done experiments so far using external radiation. We are having plans to carry out studies with radiation.
- L. I. KRISHTALIK (*Institute Electrochemistry, Academy of Sciences of USSR, Moscow*) : V. E. Kazarinov has shown that the drastic discrepancy between electrochemical and radio tracer data on the methanol adsorption on Pt was due to the influence of selfradiolysis products in methanol and they disappear after due purification. In your experiments is some similar effect excluded ? Were the samples of Ca\* and d.b.s.\* purified from the products of their decay and radiolysis ? Was some attempt made to diminish the H<sub>2</sub>O<sub>2</sub> content by, say deaeration of solutions or addition of peroxide decomposition catalysts ?
- N. SUBRAMANYAN : In our experiments, we did not purify the Calcium-45 and Sulphur-35 solutions because we felt that there was no point in removing H<sub>2</sub>O<sub>2</sub> or O<sub>2</sub>, since they will be continuously produced in the systems by radiolysis. Even if all the impurities were removed, the effect of the radiation on the electrode cannot be ignored. The objective of our experiments was to bring out the influence of both the radiative and the products radiolysis on the corrosion and electrochemical behaviour of metals.