

## ELECTRIFIED INTERFACE WITH RADIOACTIVE BASE ELECTROLYTES

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The investigation aims at a detailed examination of the electrified interface at Hg/aqueous  $\text{H}_2\text{SO}_4$  solution interface. The electrocapillary curves of the radioactive base electrolyte are found to be appreciably different from those of the corresponding nonradioactive electrolyte. The effect of  $\text{H}_2\text{O}_2$  on the electrocapillary curves is to lift the electrocapillary curves of nonradioactive base electrolyte. The relative positive charge on mercury on the anodic side of the electrocapillary curve is reduced by the  $\beta$ - radiation emanating from  $(\text{SO}_4)^{2-}$  of the base electrolyte and at the same time the relative negative charge on mercury on the cathodic side is increased. This indicates that the electrostatic interaction of  $\beta$ -radiation with mercury is more than the effect due to  $\text{H}_2\text{O}_2$  that is produced in situ. This study indirectly indicates that the charge density of the metal is a more fundamental electrical variable than the electrode potential.

Key words: Electrocapillary curve, radioactive, charge density

## INTRODUCTION

Electrochemistry of a number of radioactively labelled compounds has been found to be appreciably different from that of the corresponding nonradioactive counterparts [1-12]. This aspect has been systematically studied [12] and it has been observed that the radioactivity or radiation appreciably changes the thermodynamics of electrode processes. Detailed investigations of the electrified interface at mercury/aqueous  $\text{H}_2\text{SO}_4$  solution have been compared with the mercury/aqueous  $\text{H}_2\text{SO}_4$  solution [12, 13] system. All the studies have been made using capillary electrometer [14, 15].

## EXPERIMENTAL

## Solutions

Radioactive  $\text{H}_2\text{SO}_4$  was procured from BARC and made up with the corresponding aqueous  $\text{H}_2\text{SO}_4$  solution to the required concentrations. Recrystallised analytical grade  $\text{Na}_2\text{SO}_4$  and KCl were used. The requisite solutions were prepared with conductivity water. Analytical grade  $\text{H}_2\text{SO}_4$  was used for the preparation of various dilutions in conductivity water. The solutions were used after suitable pre- electrolysis.

## Mercury

Analytical grade mercury was cleaned as usual and then distilled 3 times under vacuum [12, 13].

## Temperature control

The temperature was maintained at  $303 \pm 0.2\text{K}$ . Air thermostat described elsewhere [12, 13] was used.

The capillary electrometer used in this investigation had been described elsewhere [14,15]. The reference electrode was Hg/Hg $_2$ SO $_4$  -  $\text{H}_2\text{SO}_4$ . The concentration of  $\text{H}_2\text{SO}_4$  used in the reference electrode was the same as that of the test electrolyte solution used in the cell. Calibration of the set up was carried out using 1N KCl or 1N  $\text{Na}_2\text{SO}_4$  and the  $\gamma$ -values obtained were found to be exactly the same as those of the established standard results [15]. Experiments were repeated atleast 3 times.

Results were highly reproducible within the error limits discussed elsewhere[12, 13].

The  $\gamma$ -values obtained experimentally were plotted against potential values. The  $\gamma$ -E curves were differentiated both graphically and by the computerised procedure to get the corresponding  $q^M$  values. The resulting  $q^M$  values were plotted against E values.

## RESULTS AND DISCUSSION

Calibration of capillary electrometer with 1N KCl and  $\text{Na}_2\text{SO}_4$  solutions

Interfacial tension values for 1N KCl and 1N  $\text{Na}_2\text{SO}_4$  solutions were plotted as a function of the potential measured with reference to 1N calomel electrode and Hg/Hg $_2$ SO $_4$  - 1N  $\text{Na}_2\text{SO}_4$  solution electrode respectively. A comparison with Peries data shows that the values determined with the capillary electrometer are well within the error limits.

## Ionic adsorption

Effect of specific activities of 0.8N  $\text{H}_2\text{SO}_4$  solution on the electrocapillary curves

Electrocapillary curves for 0.8N  $\text{H}_2\text{SO}_4$  aqueous solution with different specific activities are given in Fig. 1. Electrocapillary curves of the system Hg/0.8N  $\text{H}_2\text{SO}_4$  solution containing varied amounts of  $\text{H}_2\text{O}_2$  are given in Fig. 2.

The values of  $q^M$  (obtained by graphical differentiation of  $\gamma$ -vs ln E curves) are given as a function of E for the system (i) Hg/0.8N  $\text{H}_2\text{SO}_4$  solution and (ii) Hg/0.8N  $\text{H}_2\text{SO}_4$  solution in Fig. 3.

Difference in the electrocapillary (ec) behaviour of non-radioactive and radioactive  $\text{H}_2\text{SO}_4$  solution

In the presence of radioactive 0.8N  $\text{H}_2\text{SO}_4$  solution, the ec curve is found to be characteristically different from that of non-radioactive 0.8N  $\text{H}_2\text{SO}_4$  solution. The effect of  $\beta$ - radioactivity or radiation is as follows: Interaction of  $\beta$ -radiation emanated by  $\text{H}_2\text{SO}_4$  with



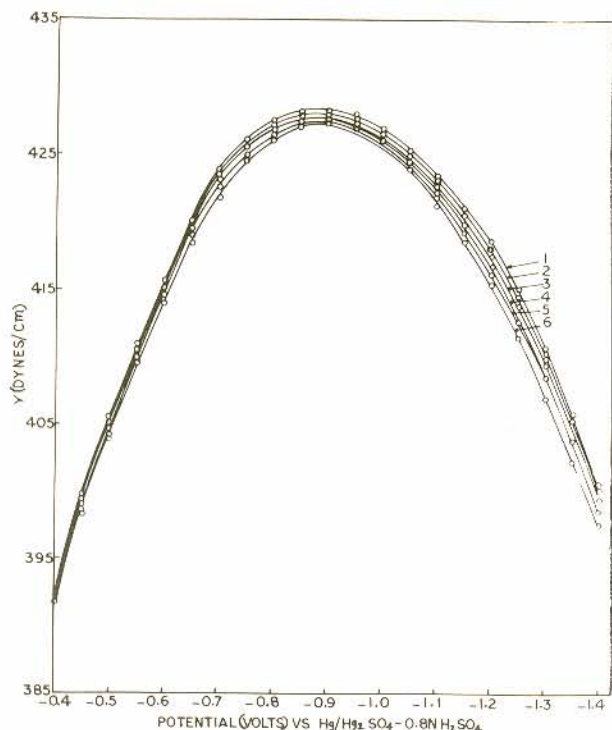


Fig. 1: Effect of  $\beta$ -radiation on the electrocapillary behaviour of Hg/0.8N  $H_2SO_4$  system

(1) 0.8N  $H_2SO_4$  (2) 0.8N  $H_2SO_4$  (Radioactivity 0.000125 mci/ml (3) 0.8N  $H_2SO_4$  (Radioactivity 0.00015 mci/ml) (4) 0.8N  $H_2SO_4$  (radioactivity 0.00025 mci/ml) (5) 0.8N  $H_2SO_4$  (radioactivity 0.00075 mci/ml) (6) 0.8N  $H_2SO_4$  (radioactivity 0.001 mci/ml)

water gives rise to  $H_2O_2$  as a permanent product of radiolysis. The effect of  $H_2O_2$  on the electrocapillary curve of 0.8N  $H_2SO_4$  has been the lifting of the base curve and this lifting is found to increase with increase of concentration of  $H_2O_2$ . But on the other hand, the effect of  $\beta$ -radioactivity is the suppression of the base curves of 0.8N  $H_2SO_4$  solution. Further, this suppression is found to increase with increase of  $\beta$ -radioactivity (increase of specific activity of the radioactive solution) in 0.8N  $H_2SO_4$  solution.  $E_{ecm}$

values of the Hg/ $H_2SO_4$  system are not affected by  $\beta$ -radioactivity. The electrocapillary curves are suppressed one below the other as the radioactivity increases and the  $E_{ecm}$  is only slightly affected. All these observations go to prove that  $\beta$ -radioactivity emanated

by the  $SO_4^{2-}$  ions impart appreciable negative charge to the Hg surface thereby reducing the positive charge on the anodic branch and increases the negative charge on the cathodic branch of the ec curve. This change in relative charges of mercury on the anodic and the cathodic branches gives rise to new charge conditions which are responsible for the appreciable differences in the electrocapillary

behaviour of  $H_2SO_4$  from that of  $H_2SO_4$ . The fact that  $E_{ecm}$  values are not affected by  $\beta$ -radioactivity, indicates beyond doubt that the interaction of  $\beta$ -radioactivity with the charge on the metal is almost purely electrostatic in nature. It can also be said that the individual effect of  $\beta$ -radiation has been dominating over the effect of  $H_2O_2$  on the nature of electrocapillary curve in radioactive

solution viz. 0.8N  $H_2SO_4$  whose specific activity is of the order 0.0010 mci.ml $^{-1}$ . Effect of the presence of still higher specific activities of base electrolyte needs further study. The  $q^M$  vs E curves for the different systems:

Hg/0.8N  $H_2SO_4$  and Hg/0.8N  $H_2SO_4$  systems clearly confirm

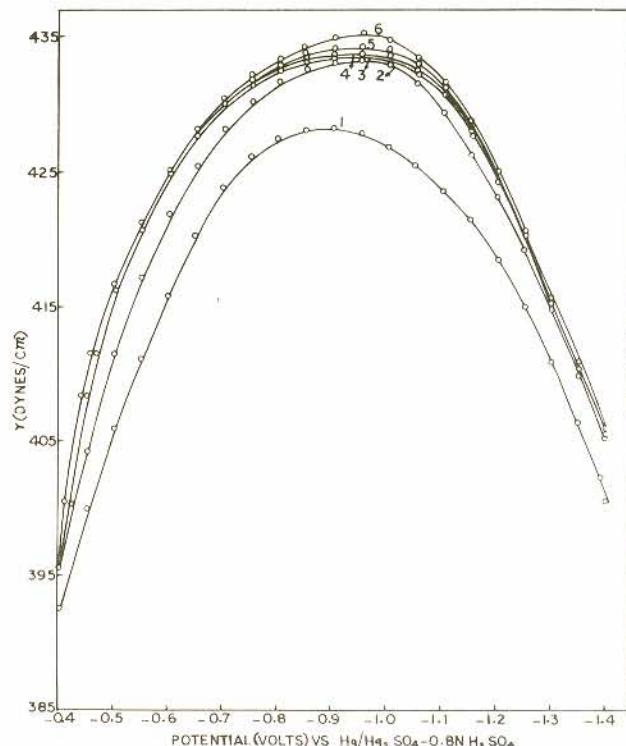


Fig. 2: Effect of  $H_2O_2$  on the electrocapillary behaviour of Hg/0.8N  $H_2SO_4$  system

(1) 0.8N  $H_2SO_4$  (2) 0.8N  $H_2SO_4$  + 0.01 ppm  $H_2O_2$  (3) 0.8N  $H_2SO_4$  + 0.1 ppm  $H_2O_2$  (4) 0.8N  $H_2SO_4$  + 1.0 ppm  $H_2O_2$  (5) 0.8N  $H_2SO_4$  + 5.0 ppm  $H_2O_2$  (6) 0.8N  $H_2SO_4$  + 10.0 ppm  $H_2O_2$

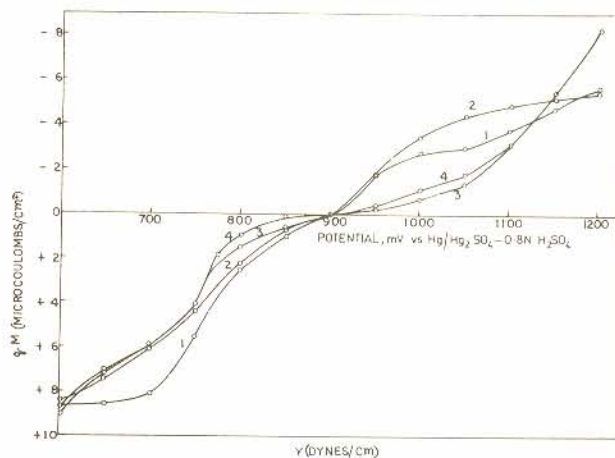


Fig. 3:  $q$  vs  $E$  curves for different systems

(1) 0.8N  $H_2SO_4$  (303) Nonradioactive  
(2) 0.8N  $H_2SO_4$  (303) Radioactive  
(3) 0.8N  $H_2SO_4$  (311) Nonradioactive  
(4) 0.8N  $H_2SO_4$  (311) Radioactive

the explanations given above with regard to the interaction of  $\beta$ -radioactivity with the  $q^M$  of the Hg surface (Fig. 3).

**Capillary thermodynamics at Hg/radioactive electrolyte and Hg/0.8N  $H_2SO_4$  and at Hg/0.8N  $H_2SO_4$  +  $H_2O_2$  system**

The Lippmann's capillary equation for the above systems has been arrived at using the method [16, 17] invoking Gibbs's adsorption equation. For the sake of brevity, the final equations relating the charge densities and different surface excesses of species involved at metal/solution interface are given as follows:



Systems Hg/0.8N H<sub>2</sub>SO<sub>4</sub>

$$-d\gamma = q^M dE + H^+ d\mu_{H_2SO_4} + H_2O \cdot d\mu_{H_2O} \quad (1)$$

where the different terms have their usual significance.

System Hg/0.8N H<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O<sub>2</sub>

$$-d\gamma = +q^M dE - +H_2O_2 \cdot d\mu_{H_2O_2} + H^+ d\mu_{H_2SO_4} + H_2O \cdot d\mu_{H_2O} \quad \dots (2)$$

Since H<sub>2</sub>O<sub>2</sub> is introduced in the 0.8N H<sub>2</sub>SO<sub>4</sub> solution, new surface excess and chemical potential terms become the necessary consequences.

In the case of addition of H<sub>2</sub>O<sub>2</sub> to the systems Hg/0.8N H<sub>2</sub>SO<sub>4</sub> solution, the electrocapillary base curve is lifted systematically with the increase of the addition of H<sub>2</sub>O<sub>2</sub>. On the other hand, thiourea or any other organic compound suppresses the ec curves of the same systems continuously as its addition is increased. This indicates that the organic substance and the H<sub>2</sub>O<sub>2</sub> are both capillary active, but their effects on the interfacial tension are opposite. Generally the  $\sqrt{\sigma\gamma}$  is known to be a positive quantity and hence  $\sqrt{H_2O_2}$  should be opposite i.e. negative in nature [18].

System Hg/0.8N H<sub>2</sub>SO<sub>4</sub> solution

The new change conditions that are created at the Hg/0.8N H<sub>2</sub>SO<sub>4</sub> solution interface leads to the actual suppression of the ec curve of the nonradioactive base electrolyte when it is replaced by the corresponding  $\beta$ -radioactive base electrolytes.

The net effect is (inspite of H<sub>2</sub>O<sub>2</sub> being produced in situ in the case of radioactive base electrolyte) to change by electrostatic interaction the charge condition prevalent at Hg/electrolyte interface which can be understood from the thermodynamics point of view by representing the actual capillary thermodynamics of the two systems.

$$-dr = (q^M + Q^M) dE + \sqrt{H^+} \cdot d\mu_{H_2SO_4} + \sqrt{H_2O_2} d\mu_{H_2O_2} \quad (3)$$

$q^M$  is the change in the charge condition on the metal due to its interaction with  $\beta$ -radiation. This may give rise to some appreciable changes in the electrosorption characteristics of organic adsorbates. Moreover, the study is found to indirectly indicate that  $q^M$  is a more reliable or fundamental electrical variable than the potential for both ionic and organic adsorption especially in the presence of  $\beta$ -radiation emanating from the base electrolyte since the  $q^M$  can be changed simply by varying the  $\beta$ -radioactivity of the base electrolyte solution without changing the value of potential applied.

## CONCLUSION

$\beta$ -radiation emanating from 0.8N H<sub>2</sub>SO<sub>4</sub> aqueous solution reduces the relative positive charge on the anodic branch and increases the negative charge of the cathodic branch of the electrocapillary curve leading to a new charge condition at Hg/0.8N H<sub>2</sub>SO<sub>4</sub> solution interface.

Increase of  $\beta$ -radioactivity of the base electrolyte of fixed chemical concentration i.e. 0.8N H<sub>2</sub>SO<sub>4</sub> increases systematically the suppression of the anodic and cathodic branches of the electrocapillary curve without, however, affecting the value of  $E_{ecm}$  indicating that the effect due to  $\beta$ -radiation on the  $q^M$  of Hg is purely electrostatic in nature.

Capillary thermodynamics of the new situations that are met with at the electrified interface in the system Hg/0.8N H<sub>2</sub>SO<sub>4</sub> is clearly represented by the capillary equation based on Devanathan and Parson's approach.

This study indirectly indicates that  $q^M$  is a more reliable electrical variable than the potential for electrosorption at metal/electrolyte solution interface.

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