

EFFECT OF BETA RADIATION ON MERCURY/PHOSPHORIC ACID SOLUTION INTERFACE IN THE PRESENCE OF THIOUREA

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The effect of beta radiation on mercury/0.2 N H_3PO_4 solution interface studied using capillary electrometer. Electrocapillary curves were obtained for different concentrations of thiourea, using both radioactive and nonradioactive H_3PO_4 as base electrolytes. It is found that there is enhanced adsorption from radioactive base electrolyte. Thermodynamic parameters like the charge on the metal surface (q^M) and the surface excess of organic compound adsorbed (Γ_{org}) have been evaluated for adsorption from both electrolytes. From the calculated adsorption data, it is clearly seen that adsorption of thiourea from radioactive and nonradioactive phosphoric acid obeys the same isotherm i.e. virial isotherm. This conclusion has been arrived at by analysing the adsorption from both electrolytes. From the calculated adsorption data, by a graphical method as well as by a recently developed computer programme. From the intercept values of isotherm plots, free energies of adsorption for different values of q^M have been evaluated. The above study clearly proves the fact that the introduction of a radioactive element in the base electrolyte affects only the extent of adsorption.

Key words: Beta radiation, mercury-phosphoric acid interface, electrocapillary curves

INTRODUCTION

In electrochemical research it has been a practice to employ radiotracer technique to examine electrode behaviour. It has been assumed that the adsorption and electrocapillary behaviour are the same, whether the medium is radioactive or not. But linear transfer energy of radiation gives rise to many short lived and long lived radiolytic products like H_2O_2 in aqueous solutions and can produce significant changes at the interface. It was found that the electrochemistry of a number of radioactively labelled compounds are appreciably different from their nonradioactive counterparts. This observation is based on experiments using capillary electrometer, polarography, tensammetry and other similar techniques. Recently Kapali and Joshi [2] studied the difference in the electrochemical behaviour of mercury/nonradioactive solution interface and mercury/radioactive solution interface in the presence of organic adsorbates like thiourea and benzotriazole. The results indicate that β activity of the radioactive sulphur atom of sulphuric acid could alter the mercury surface giving rise to appreciable changes in the adsorption behaviour of organic adsorbates. In the present work, adsorption of thiourea has been studied in the presence of radioactive phosphoric acid as the base electrolyte, in order to understand the influence of radioactivity on its adsorption at the mercury/solution interface.

EXPERIMENTAL

The design of the electrometer was the same as used earlier. The design of the cell used for capillary electrometer measurement was the same as used by Peries [4]. It consists of a main compartment, through which capillary electrometer can be inserted and the two side connections, one leading to the reference electrode compartment through the water seal stop joint and the other to the hydrogen inlet. Mercury used was of analar grade which was purified electrolytically and distilled in all glass pyrex Hulett still [6] under reduced pressure with an air stream. All solutions were prepared using conductivity water. Phosphoric acid and thiourea were of Glaxo products. Radioactive phosphoric acid solution was prepared from labelled phosphoric acid solution of energy 1.71 MeV (which was obtained from BARC, Bombay). A saturated calomel electrode (SCE) with a salt bridge was used as the reference electrode. All the measurements

were carried out in an air thermostat controlled at a temperature of 298 ± 0.2 K. Mercury in the capillary electrometer was polarised to various values of potential by means of a precision potentiometer.

RESULTS

Electrocapillary curves

Figure 1 gives the electrocapillary curves for 0.2 N phosphoric acid in the presence of different concentrations of thiourea. The reproducibility of the method is ± 0.2 dynes.cm⁻¹ around ecm and ± 0.8 dynes.cm⁻¹ on the extremes of the electrocapillary curve. Figures 2 and 3 give electrocapillary curves for 0.2 N radioactive phosphoric acid of two different activities (0.03395 and 0.0610 mci.ml⁻¹) in the presence of different concentrations of thiourea.

Charge on the metal surface, q^M

Charge on the metal surface (q^M) was evaluated by graphical differentiation and also by a computer programme from the electrocapillary curve. Graphical differentiation was performed at 50 mV intervals. Maximum error limits for q^M are 0.15 μ C.cm⁻² around ecm to 0.5 μ C.cm⁻² at extremes of the curve. Values of q^M obtained by the two methods are in agreement. Values of q^M obtained by graphical differentiation method are plotted as a function of E for non-radioactive and radioactive 0.2 N H_3PO_4 (activity 0.03395 mci.ml⁻¹) in the presence of different concentrations of thiourea and are shown in Figs. 4 and 5.

Surface excess of thiourea adsorbed (Γ_{org})

The surface excess of thiourea adsorbed is a function of the rate of change of interfacial tension (γ) with concentration or activity of thiourea at constant E and is obtained using the equation

$$[\partial \gamma / \partial \log C] E_{ref} = -\Gamma_{org} \quad (1)$$

Values of surface excess are evaluated by graphical differentiation of the curve, interfacial tension (γ) vs log C at constant E. Values of Γ_{org} obtained for various concentrations of thiourea as a function of q^M for both nonradioactive and radioactive H_3PO_4 are shown in Figs. 6 & 7.

DISCUSSION

Electrocapillary curves

Figure 1 indicates that thiourea is adsorbed on the positive side of the electrocapillary curve and adsorption is found to increase with increase in concentration of thiourea. Potential of electrocapillary maximum is found to shift to more negative values with increase in concentration of the adsorbate. There is no desorption of the adsorbate at the extreme positive charge. There is desorption of the organic molecule at the extremes of negative charge, because more polarisable water molecules easily displace organic molecules from the metal surface at extreme negative charges. The adsorption on the positive side is due to the interaction between positively charged metal surface and negatively charged sulphur atom.

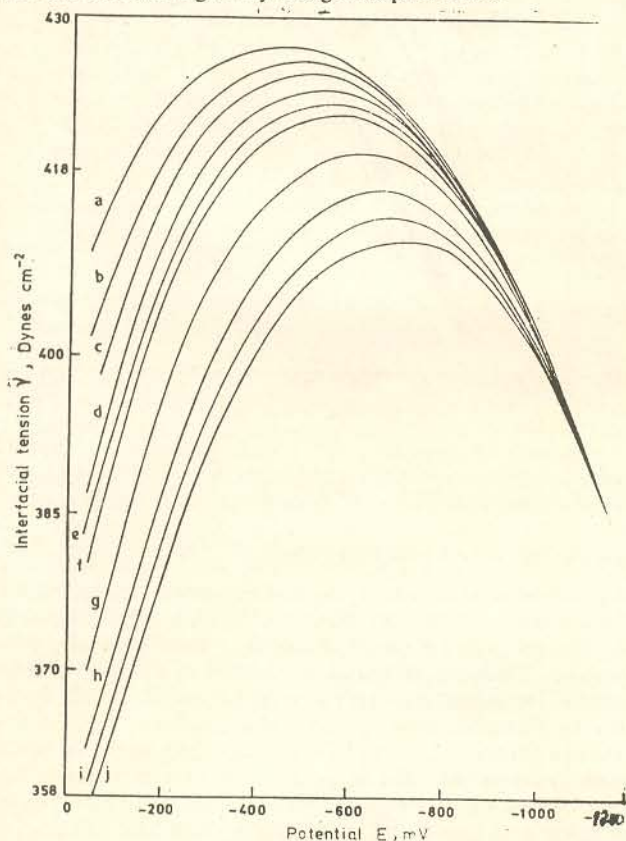


Fig. 1: Electrocapillary curves for different concentrations of thiourea in 0.2N H_3PO_4 . Concentration of thiourea, M: (a) 0 (b) 1×10^{-3} (c) 2.5×10^{-3} (d) 5×10^{-3} (e) 7.5×10^{-3} (f) 1.0×10^{-2} (g) 2.5×10^{-2} (h) 5×10^{-2} (i) 7.5×10^{-2} (j) 1.0×10^{-1}

Figures 2 and 3 show the electrocapillary curves for radioactive phosphoric acid of two different activities (0.03395 and 0.0616 $mc\cdot ml^{-1}$ respectively) in the presence of different concentrations of the organic molecule where it is found to adsorb on the positively charged metal surface and desorb on the extremes of negatively charged surface. It is also found that the adsorption is found to be more in the case of radioactive phosphoric acid as the base electrolyte. Moreover, adsorption is found to increase with increase in the activity of the base electrolyte. The enhanced adsorption on the positively charged metal surface may be due to the fact that negatively charged beta particles increase the negative charge on the sulphur atom thereby leading to more adsorption. Adsorption of thiourea can be compared with the adsorption of anions having strong adsorption on the positively charged metal surface. The orientation of the thiourea molecule has been found to be perpendicular to the metal surface with the sulphur atom next to the metal. The adsorption of thiourea

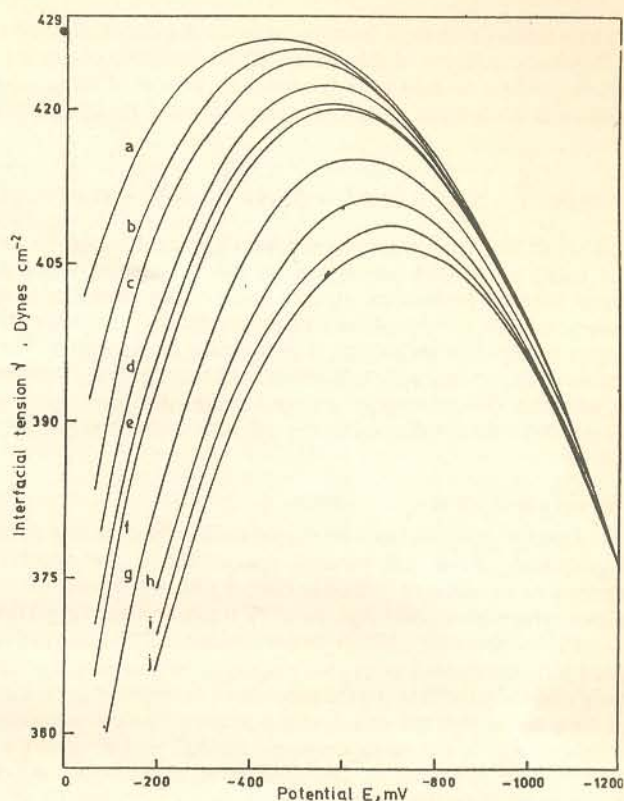


Fig. 2: Electrocapillary curves for different concentrations of thiourea in radioactive $0.2N H_3PO_4$ (0.03395 $mc\cdot ml^{-1}$) (Concentrations of thiourea — same as Fig. 1)

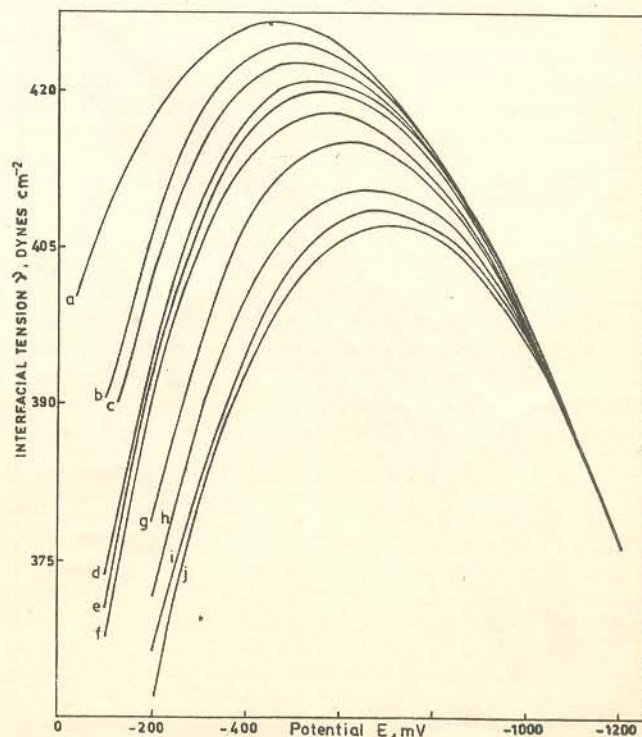
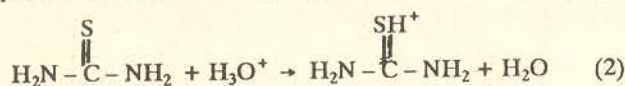


Fig. 3: Electrocapillary curves for different concentrations of thiourea in radioactive $0.2N H_3PO_4$ (0.0616 $mc\cdot ml^{-1}$) (Concentration of thiourea — same as Fig. 1)

is operated through covalent bonding between mercury and sulphur [7,8]. In an acid solution of thioamides, there are some protonated species in addition to molecular species. Protonation of thioamides takes place at the sulphur atom giving rise to protonated species [9].



In acids of low concentration, the amount of protonated species will be small and so the adsorption on the negative side due to positively charged protonated species will be less. At extreme of negative potentials, these protonated species will be replaced by water molecules of higher polarisability. The increase in adsorption from radioactive solution may also be due to strengthening of the chemical bond between the positively charged metal and the thiourea molecules because of the influence of negatively charged beta particles.

Charge (q^M) vs E curve

Values of charge (q^M) obtained from graphical differentiation of the electrocapillary curve, are plotted against the E for different concentrations of thiourea, added to both 0.2 N nonradioactive and radioactive phosphoric acid (Figs. 4 and 5). It is found from Fig. 4 that the curves obtained with different concentrations of thiourea are far removed from the curve for the base electrolyte at positive potentials and they come almost close to the base curve at negative potentials. This clearly shows that the adsorption is more at positive potentials and considerably less at negative potentials. q^M and E curves for different concentrations of thiourea from radioactive 0.2 N phosphoric acid ($0.03395 \text{ mci.ml}^{-1}$) show almost the same trend as the curves for adsorption from nonradioactive phosphoric acid. It is seen that the adsorption is uniformly high throughout, on the positively charged mercury surface.

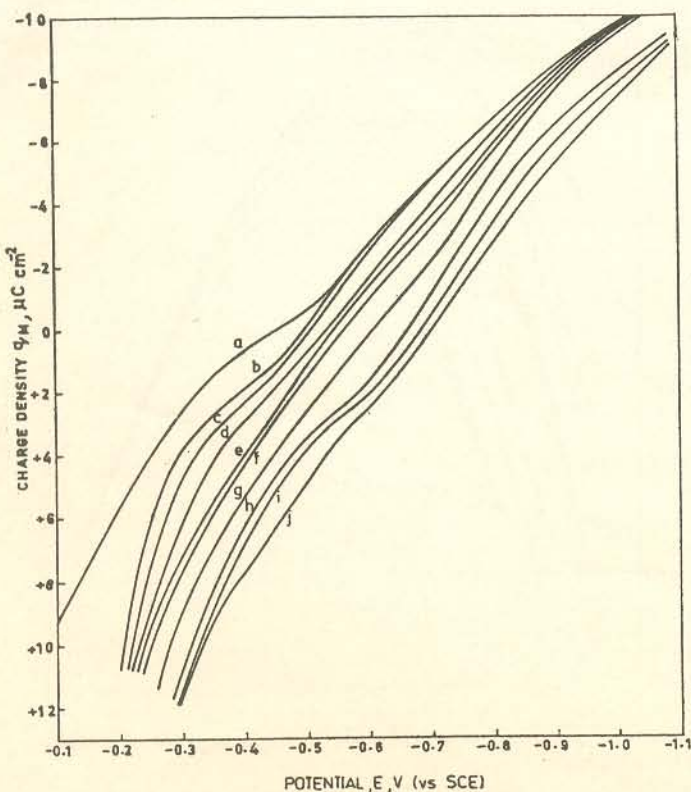


Fig. 4: Variation of charge density, q^M ($\mu\text{C.cm}^{-2}$) with potential (E) for the adsorption of different concentrations of thiourea on mercury in H_3PO_4 (0.2 N) (Concentrations of thiourea — same as Fig. 1)

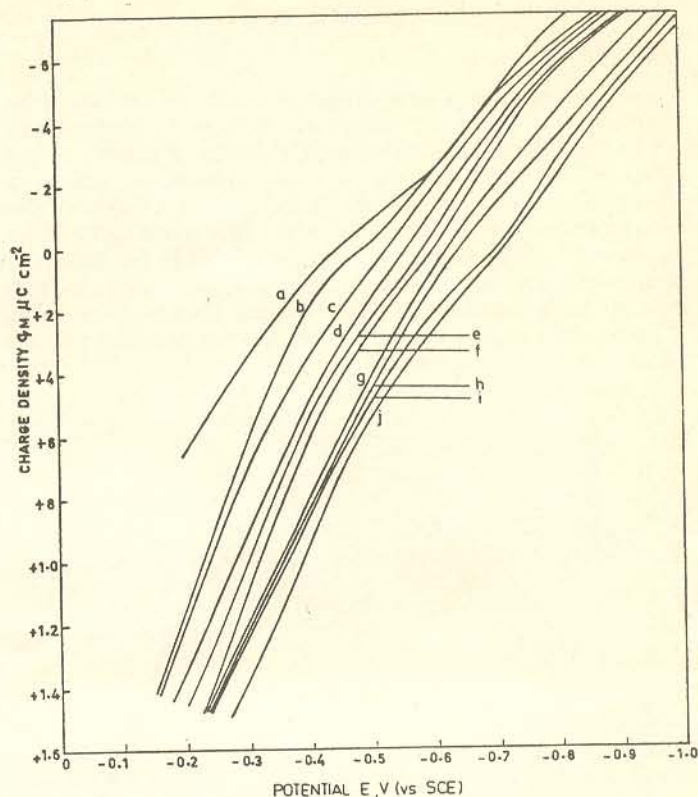


Fig. 5: Variation of charge density q^M ($\mu\text{C.cm}^{-2}$) with potential (E) for the adsorption of different concentration of thiourea on mercury in radioactive 0.2 N phosphoric acid ($0.03395 \text{ mci.ml}^{-1}$) (concentrations of thiourea — same as Fig. 1).

Surface excess versus potential curve

Surface excess as a function of potential for various concentrations of thiourea adsorbed from nonradioactive H_3PO_4 is given in Fig. 6. It is seen that the adsorption of thiourea is maximum at positive potentials. Thiourea is found to desorb at extreme negative potentials. The same trend has been reported earlier [10–12]. Surface excess vs potential curve for the adsorption of thiourea from radioactive phosphoric acid ($0.03395 \text{ mci.ml}^{-1}$) shows the same trend as in the previous case. But as can be seen from the curve in Fig. 7 surface excess values obtained for adsorption from radioactive phosphoric acid are found to be higher than that obtained for nonradioactive phosphoric acid. So radioactivity favours the strengthening of chemical bond between the metal and sulphur atom of thiourea.

Surface coverage (θ) vs charge (q^M)

The coverage has been evaluated using the relation $\Gamma/\Gamma_m = \theta$ where Γ_m is the maximum value of surface excess obtained from (i) initial slope of C/Γ vs C curve at $q^M = 0$ and (ii) from the molecular area obtained from the molecular model of thiourea (supplied by Catalin Products Ltd., England). Value of the surface excess maximum (Γ_m) is found to be equal to $11.12 \times 10^{-10} \text{ molecules.cm}^{-2}$. Coverage (θ) vs q^M curves for adsorption of thiourea from nonradioactive and radioactive base electrolytes show the same trend as the surface excess vs potential curve.

Assignment of isotherms

Isotherms for the adsorption of thiourea have been tested both by the graphical method and by computer analysis in basic language [2]. This computer programme is used to assign the Langmuir, Frumkin, Virial and logarithmic Temkin's isotherms for the input of surface coverage (θ) and concentration C at constant charge (q^M). The

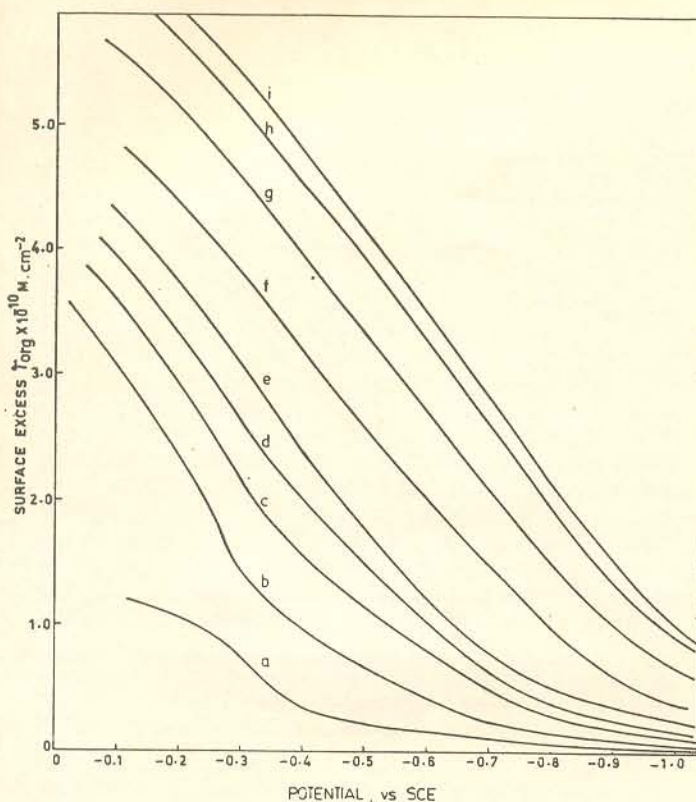


Fig. 6: Variation of surface excess with potential for the adsorption of different concentrations of thiourea on mercury in 0.2 N H₃PO₄. Concentration of thiourea, M: (a) 1×10^{-3} (b) 2.5×10^{-3} (c) 5×10^{-3} (d) 7.5×10^{-3} (e) 1×10^{-2} (f) 2.5×10^{-2} (g) 5×10^{-2} (h) 7.5×10^{-2} (i) 1×10^{-1}

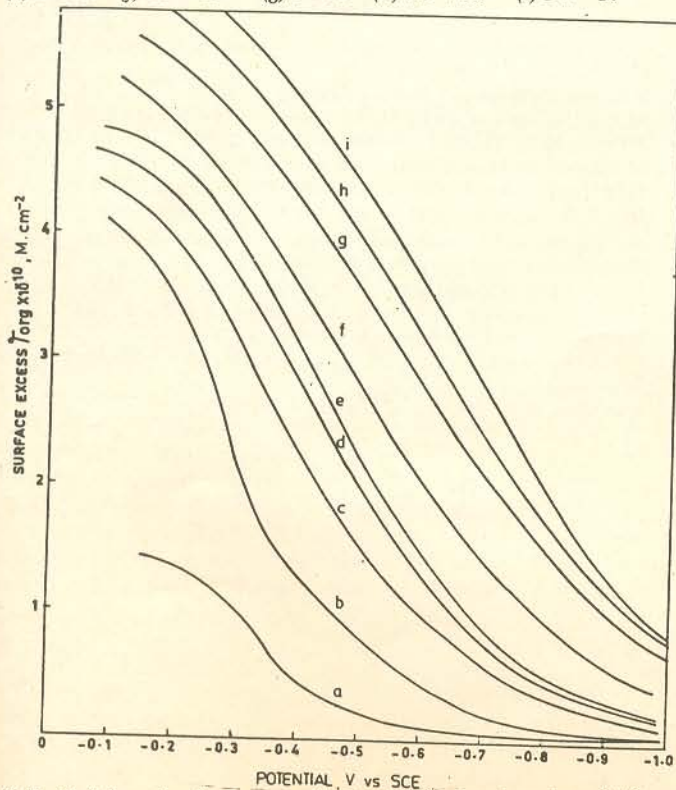


Fig. 7: Variation of surface excess with potential for the adsorption of different concentrations of thiourea on mercury in radioactive 0.2 N phosphoric acid (0.03395 mci.ml⁻¹) (Concentration of thiourea — same as Fig. 6)

correlation coefficients are shown in Table I. 99% correlation as indicated by a correlation coefficient of 0.99 had been fixed as the cut-off value for the selection of the isotherm. Although 99% correlation is obtained for Langmuir's isotherm, it is not assigned because the slopes obtained for the assignment are far different from unity. The correlation coefficients obtained from Temkin's and Frumkin's isotherms are less than 0.98 at extreme negative charges and these isotherms cannot be chosen as the best fit.

TABLE-I: Assignment of isotherm for the adsorption of thiourea from nonradioactive 0.2 N H₃PO₄

Charge density q^M ($\mu\text{C}.\text{cm}^{-2}$)	Correlation coefficient			
	Langmuir	Temkin	Frumkin	Virial
+ 8	0.9984	0.9974	0.9839	0.9978
+ 6	0.9984	0.9988	0.9923	0.9962
+ 4	0.9966	0.9967	0.9902	0.9984
+ 2	0.9984	0.9989	0.9636	0.9975
0	0.9968	0.9978	0.9522	0.9994
- 2	0.9975	0.9909	0.9007	0.9968
- 4	0.9981	0.9857	0.9795	0.9978
- 6	0.9991	0.9799	0.9798	0.9982
- 8	0.9962	0.9789	0.9461	0.9969

The adsorption data are plotted graphically for assigning various isotherms, but the Virial isotherm has been found to give the best agreement (Fig. 8). A family of parallel straight lines are obtained when values of $\log C/\Gamma$ are plotted against Γ for various values of q^M . So this fact clearly shows that Virial isotherm is the best choice for explaining the adsorption characteristics. This is in agreement with the fact observed by Parsons [13] who studied the adsorption of thiourea at Hg/0.1 N NaF solution interface.

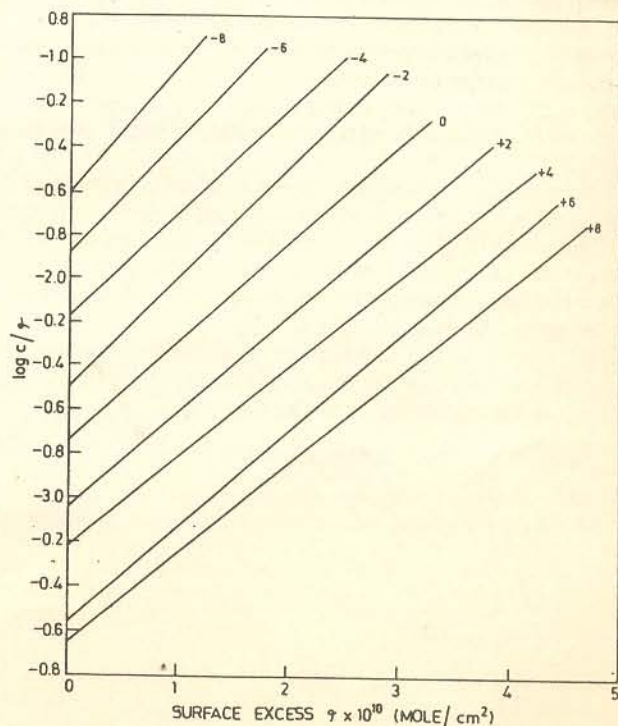


Fig. 8: Plot of $\log C/\Gamma$ vs surface excess (Γ) for the adsorption of thiourea at different values of charge q^M ($\mu\text{C}.\text{cm}^{-2}$) at the interface

The assignment of isotherms for the adsorption of thiourea from radioactive 0.2 N phosphoric acid had been carried out using the computer programme alone. Values of correlation coefficients for

different isotherms are given in Table II. It is seen from the values that Langmuir's isotherm gives 99% correlation indicated by a correlation coefficient of 0.99 for all the charges. But the values of slope obtained for all charges are different from unity. So Langmuir's isotherm cannot be assigned for the adsorption of thiourea from labelled phosphoric acid. So the next possible and best choice was Virial isotherm which gives a correlation coefficient of more than .96% for most of the charges. Other two isotherms give considerably lesser values of correlation coefficient and their choice has to be ruled out.

TABLE-II: Assignment of isotherm for the adsorption of thiourea from 0.2 N labelled H_3PO_4 ($0.03395 \text{ mcl.ml}^{-1}$)

Charge density q^M ($\mu\text{C.cm}^{-2}$)	Correlation coefficient			
	Langmuir	Temkin	Frumkin	Virial
+ 8	0.9971	0.8691	0.908	0.9248
+ 6	0.9953	0.8820	0.943	0.9543
+ 4	0.9963	0.8895	0.995	0.4634
+ 2	0.9974	0.8955	0.958	0.9658
0	0.9988	0.8908	0.8924	0.9993
- 2	0.9957	0.8974	0.8834	0.8999
- 4	0.9941	0.8940	0.898	0.9773
- 6	0.9940	0.8884	0.8921	0.9923
- 8	0.9968	0.9839	0.9496	0.9539

Free energy of adsorption vs q^M

The free energy of adsorption of thiourea at the mercury surface charged to various charge densities ranging from $(-) 8 \mu\text{C.cm}^{-2}$ to $(+) 8 \mu\text{C.cm}^{-2}$ are evaluated from the values of intercepts taken from $\log C/\Gamma$ vs Γ graphs and plotted against q^M (Fig.9). It is seen from this curve that the free energy of adsorption at $q^M = 0$ is equal to 22.55 K cal.mole $^{-1}$ which agrees well with the value obtained by Parsons [13]. The curve clearly shows that the adsorption and therefore $-\Delta G$ is more at positive charges which gradually decreases with decrease in positive charge or increase of negative charge. The strong adsorption at the positively charged metal surface can be due to the formation of a covalent bond between the metal and sulphur atom of thiourea.

Free energies of adsorption for the adsorption of thiourea from labelled phosphoric acid have been evaluated from the intercepts for different values of q^M and are plotted in Fig. 9A comparison of free energies of adsorption from nonradioactive base electrolyte and radioactive base electrolyte clearly shows some difference between the two sets of values at different q^M . This observation clearly shows that the introduction of radioactivity in the base electrolyte will not have significant effect on the adsorption characteristic of thiourea on mercury except enhancing the adsorption.

CONCLUSION

The beta activity of the base electrolyte enhances the extent of adsorption on the anodic side of ecm for thiourea. The increase in

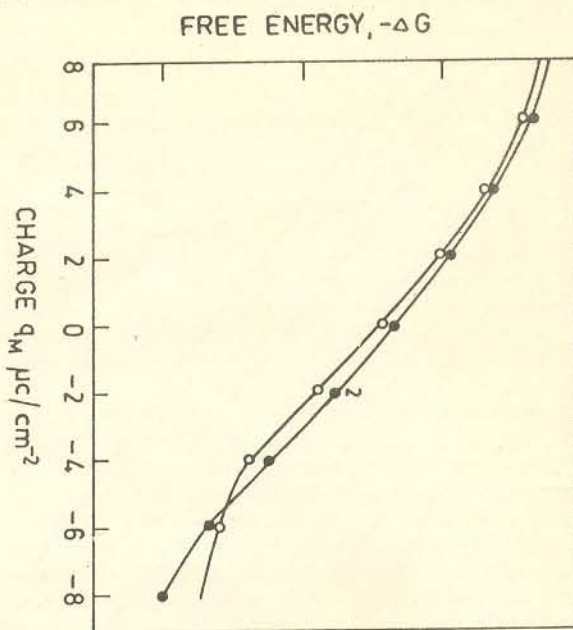


Fig.9 Variation of free energy of adsorption ($-\Delta G$ K cal. mole $^{-1}$) as a function of charge at the interface.

- (1) thiourea in nonradioactive phosphoric acid
- (2) thiourea in radioactive phosphoric acid.

adsorption may be attributed to the increase in nonelectrostatic (chemical) free energy of adsorption, thereby increasing the adsorption of thiourea on mercury.

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