

The adsorption of thiosemicarbazide at the mercury/phosphoric acid solution interface

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Adsorption of thiosemicarbazide on the mercury electrode from 0.2N phosphoric acid has been studied using a capillary electrometer. Electrocapillary curves have been obtained in the presence of different concentrations of the adsorbate. Thermodynamic parameters like charge on the metal surface (q_M) and surface excess of organic molecules adsorbed (Γ_{org}) have been calculated. From the adsorption data, it is clearly seen that the adsorption of this compound obeys Temkin's adsorption isotherm. The variation of free energy of adsorption with charge on the metal surface has been explained.

The adsorption of thiourea, a versatile compound, because of its favourable influence on corrosion inhibition, electroplating and electrocatalysis, has been well studied on different metals and from different base electrolytes¹⁻⁷. But very few studies have been carried out on the adsorption of thiosemicarbazide, which has an extra amino group in addition to the thiourea residue. Ateya⁸ studied the adsorption of this compound on iron to examine its influence as a corrosion inhibitor. The adsorption of this compound at the mercury/0.05M sodium sulphate solution interface has also been reported⁹. Recently, the adsorption of thiosemicarbazide on cathodically polarised copper has been studied to find out the type of isotherm which best explains the experimental data¹⁰. In the present study the adsorption of thiosemicarbazide at the mercury/0.2N phosphoric acid solution interface has been studied using a capillary electrometer.

Experimental

The design of the capillary electrometer and the experimental cell have been reported elsewhere¹¹. Mercury used was of AR grade; it was further purified electrolytically and distilled in all-glass set-up under reduced pressure. All the solutions were prepared using conductivity water. Phosphoric acid (BDH) and thiosemicarbazide (extrapure SISCO, India)

were used as such. All the measurements were carried out in an air thermostat ($25 \pm 0.2^\circ\text{C}$). The mercury in the capillary was polarised to various values of potential, applied with reference to saturated calomel electrode, via a salt bridge by means of a precision potentiometer (ECIL, Hyderabad). All the potentials were measured using a digital multimeter (HIL 2161).

Results

Electrocapillary curves for different concentrations of thiosemicarbazide are shown in Fig.1.

Values of charge on the metal surface were obtained by the graphical differentiation of electrocapillary curves for different concentrations of the adsorbate, and were plotted against potential ($-E$) as shown in Fig.2.

Values of surface excess were obtained by the graphical differentiation of the interfacial tension vs concentration curve at constant potential. Variation of surface excess with potential for different concentrations of the compound is shown in Fig.3.

Discussion

Electrocapillary curve

It is seen from Fig. 1 that thiosemicarbazide adsorbs on both the sides of the electrocapillary curve, but the extent of adsorption is found to be more than that for thiourea. The increase in the extent of adsorption may be due to its larger molecular area, and also due to the availability of extra nitrogen atoms which can interact with the positively charged metal surface. The adsorption on the positively charged metal surface may be due to the formation of a covalent bond between the sulphur atom of the organic molecule and the positively charged mercury surface¹²⁻¹⁴. It may also be due to the interaction of the -NH group of the molecule with positively charged metal surface¹⁵. The adsorption on the negatively charged mercury surface may be due to the interaction between the negatively charged metal surface and positively charged protonated species formed in the acidic solution^{16,17}.

Charge vs potential curve

These curves show almost the same characteristics as observed for the adsorption of thiourea on mercury. There is no intersection of charge vs potential curves at any point, as seen in the case of thiourea.

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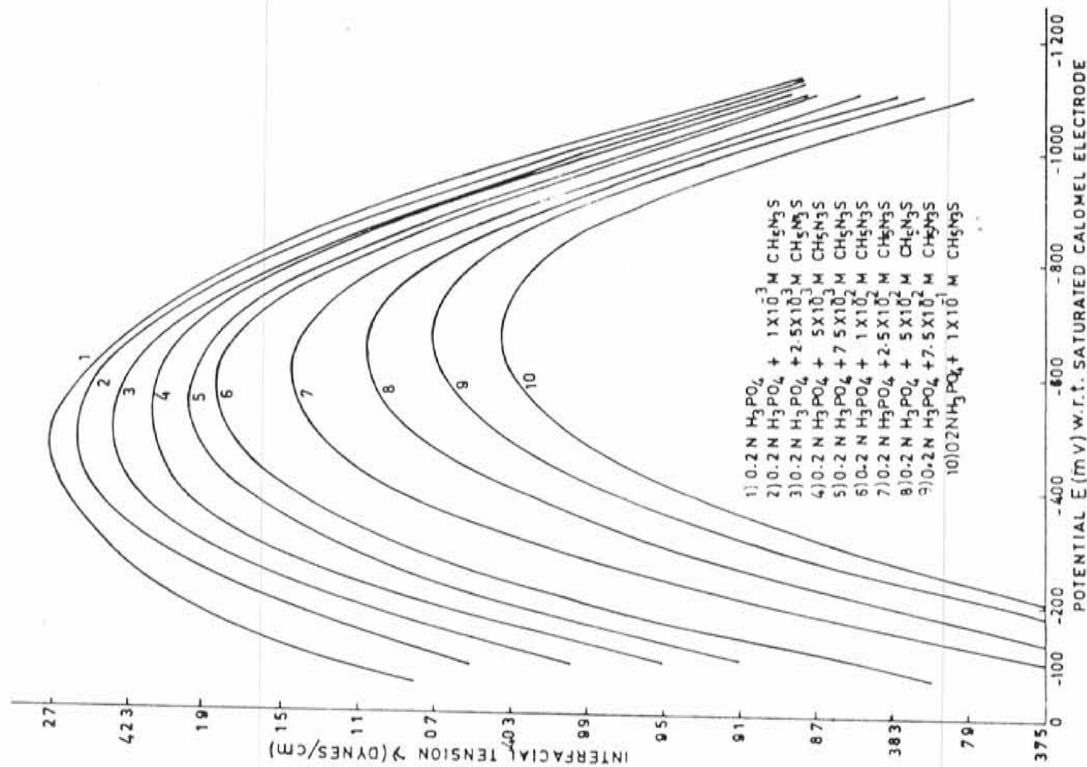


Fig. 1—Electrocapillary curves of thiosemicarbazide in 0.2M H₃PO₄

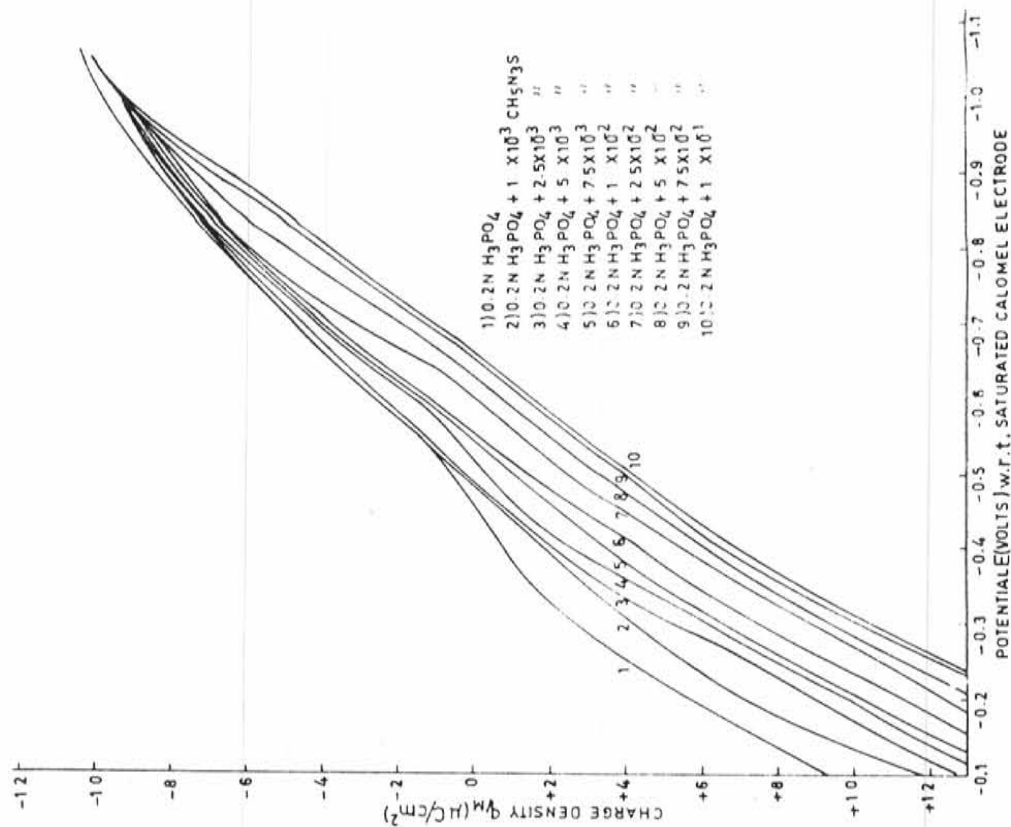


Fig. 2—Variation of charge density q_M (μC/cm²) with potential (-E) for the adsorption of thiosemicarbazide on mercury

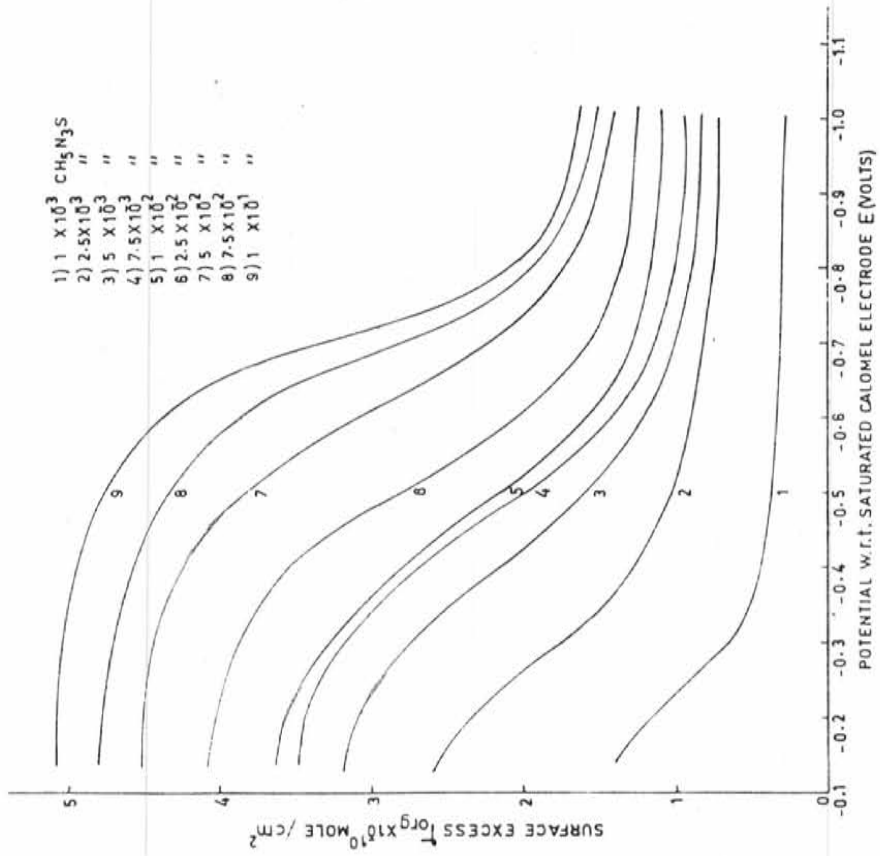
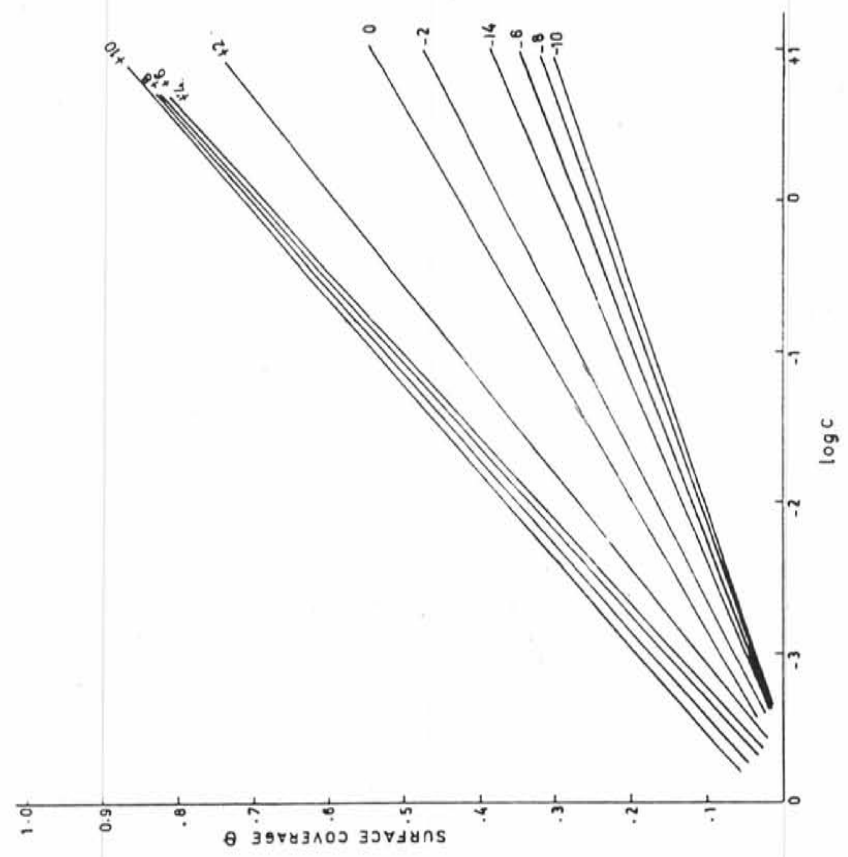


Fig. 3—Variation of surface excess (Γ_{org}) with potential (-E) for the adsorption of thiosemicarbazide on mercury



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Fig. 4—Plot of surface coverage (θ) vs $\log C$ for the adsorption of thiosemicarbazide at positive and negative values of charges q_M ($\mu C/cm^2$)

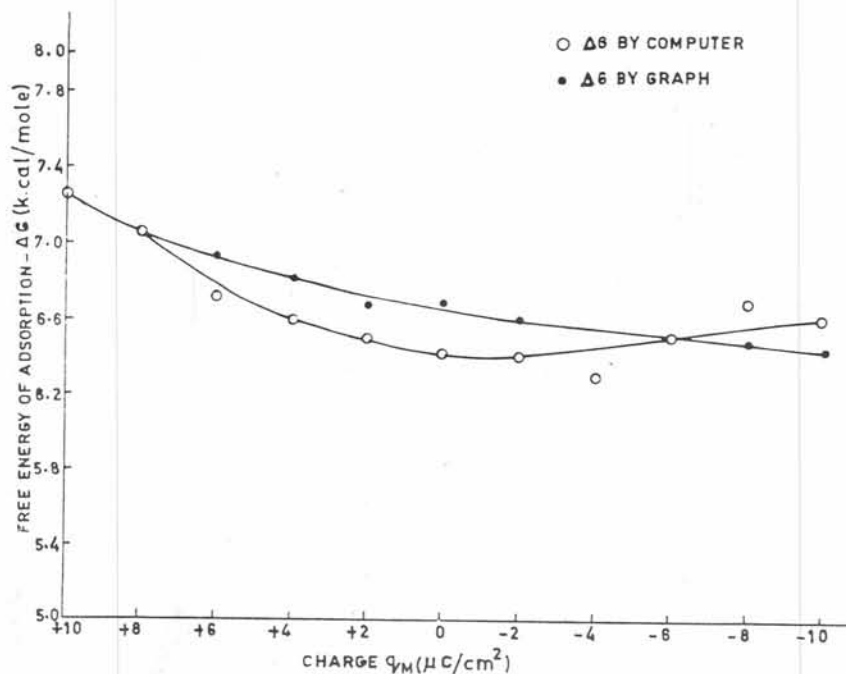


Fig. 5—Plot of variation of free energy of adsorption with charge on the interface for thiosemicarbazide [$0, \Delta G$ by computer; $-\Delta G$ by graph]

Surface excess vs potential curve

The shape of surface excess vs potential curve (Fig.3) is very similar to that observed for thiourea. But the extent of adsorption, as indicated by surface excess values, is found to be more than that for thiourea.

Coverage vs charge curves

The surface coverage has been evaluated using the relation $\Gamma/\Gamma_m = \theta$, where Γ_m is the maximum value of surface excess calculated from the molecular area of the molecule obtained using a molecular model (Catalin Product, England). The value of Γ_m was found to be 9.3×10^{-10} molecules cm^{-2} . Coverage vs charge curves are quite similar to surface excess vs potential curves.

Assignment of the isotherm

The adsorption data were thoroughly analysed using a computer programme¹⁸ and also by a graphical method. It is seen from Fig.4 that a family of straight lines is obtained when coverage (θ) is plotted against C for different values of charges. This observation clearly shows that the adsorption of thiosemicarbazide obeys Temkin adsorption isotherm. The analysis of the adsorption data using computer programme also supports this observation.

Free energy of adsorption as a function of charge

Free energy of adsorption for different values of charge has been evaluated from the values of intercept of isotherm plots and those obtained from computer output data. Fig.5 shows the free energy vs charge curves obtained using the two methods. Both the curves exhibit the same trend. The decrease in free energy with increasing negative charge may be due to the decrease in the interaction of the sulphur atom with the metal surface.

It can be concluded from the present studies that thiosemicarbazide adsorbs more on the mercury surface than thiourea. But both show similar adsorption characteristics. Thiosemicarbazide adsorbs on both the sides of electrocapillary curve and adsorption obeys Temkin's isotherm.

Acknowledgement

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