Effect of Substituents on the Adsorption of Organic Sulphides at the Mercury/ Solution Interface

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Adsorption of some organic thio compounds at the mercury / solution interface have been studied using capillary electrometer. Thermodynamic parameters such as charge on the metal surface (q^M), surface excess of the organic molecule adsorbed (Γ_{org}), surface coverage (Θ) and free energy of adsorption have been evaluated. It is found that all the compounds are adsorbed more on the positively charged mercury surface, but the various substituent groups present in these organic molecules influence the extent of adsorption on the mercury surface. The order of adsorption among the compounds is found to be: methyl p-tolyl sulphide > methyl phenyl sulphide > methyl p-nitrophenylphenyl sulphide $\geq$ thiophenol.

The adsorption of all these compounds are governed by the Langmuir's adsorption isotherm.

The adsorption of an organic molecule at the metal/ solution interface is primarily a competition for sites on the metal surface between organic molecule and water. The introduction of an electric field arising from the charge imparted to the metal surface is solely responsible for the preferential adsorption of organic molecules on the metal surface. Water molecules from aqueous solutions are attracted more to the interface under high field strength owing to their hyperpolarisability, thus displacing adsorbed organic molecules almost completely [1]. Anions in the aqueous phase are also found to influence the extent of adsorption [2]. In addition to this, different substituent groups present in organic molecules can also alter the extent of adsorption depending on their electron releasing (+I) or electron withdrawing (-I) effects [3-6]. In the present study, the adsorption of thiophenol and a few of its substituted derivatives are reported.

EXPERIMENTAL

The design of the capillary electrometer and the experimental cell used for the interfacial tension measurements are the same as described earlier [5]. The design of the cell is the same as described earlier [6]. Sodium chloride for base solution was of AR (BDH) quality. Thiophenol was of SRL make and was steam distilled with zinc dust and dilute HCl before use. All the other sulphur compounds used in this work were of Aldrich make and were used without further purification. All solutions were prepared in conductivity water. Mercury (AR) was purified electrolytically and distilled in an all glass pyrex Hullet still under reduced pressure. Purified hydrogen was used for the deaeration of the experimental solution. All the measurements were carried out in an air thermostat at 25±0.2°C. The mercury in the capillary was polarised at various values of potentials ranging

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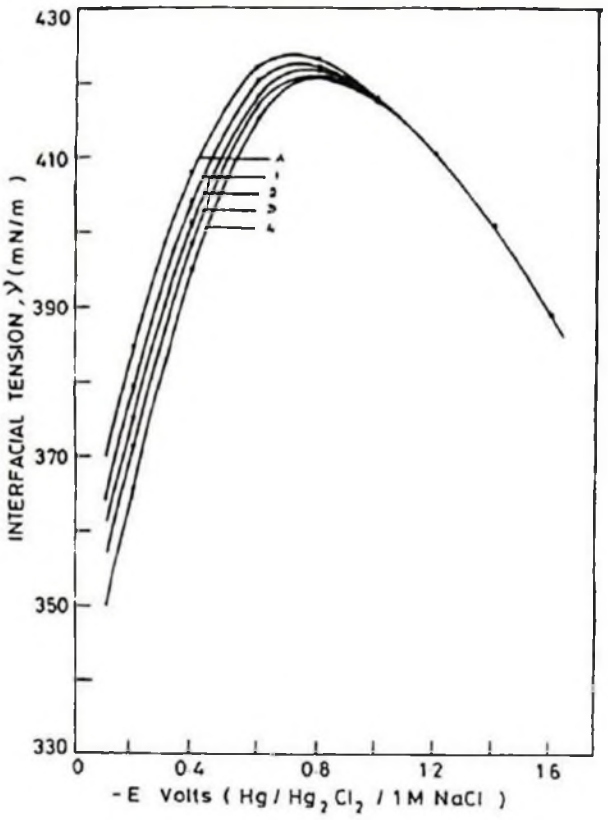


Fig 1 Electrocapillary Curves for 1 M NaCl in presence of 1 x 10^{-3} M Thio Compounds
1 Thiophenol
2 Methyl-p-nitrophenyl sulphide
3. Methyl phenyl sulphide
4. Methyl p-tolyl sulphide

from -0.1 to -1.6 V wrt Hg/Hg_2Cl_2/1 M NaCl using a lead acid battery (6.0 V) and a precision potentiometer (ECIL Ltd, Hyderabad).

RESULTS

Electrocapillary Curves

Electrocapillary curves are obtained in 1 M NaCl solution containing different concentrations of the sulphur compounds ranging from 1 x 10^{-5} to 1 x 10^{-3} M. Typical curves (concentration of sulphur compound = 1 x 10^{-3}) are shown in Fig 1. All the runs were duplicated or triplicated and the results are reproducible to ±0.2 $mN.m^{-1}$ at ecm and ±0.8 $mN.m^{-1}$ (in other words dynes) at the extremes of the curves.

Charge Density on the Metal Surface (q^M)

Charge density on the metal (q^M) has been evaluated [8] by the graphical differentiation of electrocapillary curves at 50 mV intervals. The error limits for the charge density are 0.25 $\mu C.cm^{-2}$ around ecm and 0.5 $\mu C.cm^{-2}$ at the extremes of the curves. The plots of q^M *vs* E at different concentrations of thiophenol are presented in Fig 2. Curves with other sulphur compounds are almost similar.

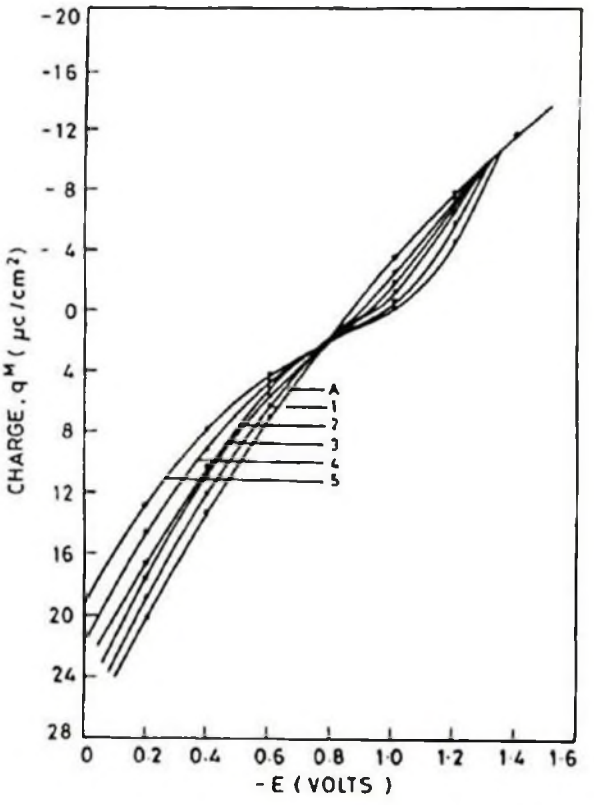


Fig 2 Charge *vs* Potential (E) Curves for Different Concentrations of thiophenol
A. 0 1. 1 x 10^{-5} M 2. 5 x 10^{-5} M
3. 1 x 10^{-4} M 4. 5 x 10^{-4} M 5. 1 x 10^{-3} M

Surface Excess of Organic Molecules Adsorbed (Γ_{org})

Surface excess of organic molecules adsorbed (Γ_{org}) is calculated as described earlier [8]. Surface excess *vs* charge curves are presented in Fig 3.

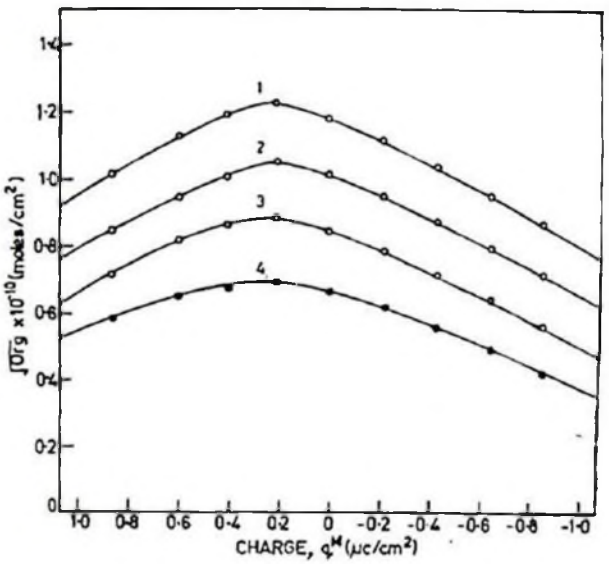


Fig 3 Surface Excess (Γ_{org}) *vs* Charge (q^M) Curves for Adsorption of 1 x 10^{-3} of Thio compounds

1. Methyl p-tolyl sulphide
2. Methyl phenyl sulphide
3 Methyl-p-nitrophenyl sulphide
4 Thiophenol

DISCUSSION

Electrocapillary curves in presence of thio compounds show that all compounds are adsorbed strongly on the positively charged mercury surface and completely desorbed on the negatively charged surface. This is due to the interaction of π-electrons of the aromatic ring and lone pair of electrons on the sulphur atom in the molecule with the positively charged surface and repulsion on the negatively charged surface [8]. Desorption on the negatively charged surface may also be due to the fact that water molecules are more polarisable than the organic molecules on the negatively charged surface and thus displace the organic molecules more easily. The extent of adsorption of the thio compounds from 1 M NaCl solutions is in the order: thiophenol ≤ methyl-p-nitrophenyl sulphide < methyl phenyl sulphide < methyl-p-tolyl sulphide. This order can be explained as follows:

Thiophenol and methyl-p-nitrophenyl sulphide are found to be similar in the extent of adsorption. This may be due to the simultaneous presence of an electron repelling $-CH_3$ (+I effect) and electron attracting $-NO_2$ (-I effect). So the electron density on the sulphur atom in the latter compound remains almost the same as found in the case of the sulphur atom in thiophenol. Even the increased area of the molecule has neglegible effect on the extent of adsorption. The higher adsorption of methyl phenyl sulphide can be ascribed to the increase in electronic charge on the sulphur atom because of the presence of electron repelling $-CH_3$ group in the molecule. This results in larger adsorption. The larger area of methyl phenyl sulphide may further lead to more coverage of the metal surface. In case of methyl-p-tolyl sulphide, presence of two electron releasing $-CH_3$ groups enhances the electron density around sulphur atom considerably. This in turn leads to stronger adsorption of the organic molecule. Increase in molecular area of the compound may lead to more coverage of the metal surface by the molecule.

Charge *vs* Potential Curves

It can be seen from Fig 2 that q^M *vs* E curves for different concentrations of thiophenol intersect at a charge around +2 μC.cm^{-2}, a characteristic shown by most aromatic compounds. q^M *vs* E curves

obtained in the presence of other sulphur containing organic compounds follow a similar pattern as in Fig 2. It can be seen that all compounds are adsorbed strongly on the positively charged metal surface and are completely desorbed on the negatively charged surface.

Surface Excess (Γ_{org}) *vs* Charge (q^M) Curves

All compounds show high values of surface excess on the positively charged mercury surface (Fig 3). The value is very small on the negatively charged surface thereby showing that the compound is completely desorbed on the negatively charged mercury. It can also be observed that the maximum value of surface excess for all values of charge are in the order thiophenol < methyl-p-nitrophenyl sulphide < methyl phenyl sulphide < methyl-p-tolyl sulphide.

Coverage (Θ) *vs* Charge (q^M) Curves

Coverage (Θ) was evaluated using the relation $\Theta = \Gamma/\Gamma_m$ where Γ is the value of the surface excess and Γ_m is the surface excess maximum. The value of Γ_m was obtained from the molecular model supplied by Catalin Products Ltd. U.K. Coverage *vs* charge curves are identical to surface excess *vs* charge curves. These curves for different concentrations of thio compounds have almost similar features. In all cases, coverage confirms the already obseved trend of considerably high adsorption on the positively charged and low on the negatively charged surface.

Application of Adsorption Isotherms

Different isotherms (such as Langmuir, Frumkin and Temkin) were tested graphically for characterising the adsorption of thiophenol and its

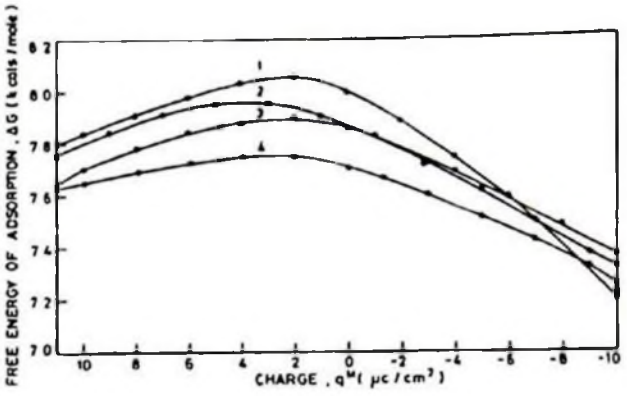


Fig 4 Free Energy *vs* Charge Curves for Adsorption of Thio Compounds
1. Methyl p-tolyl sulphide
2. Methyl phenyl sulphide
3 Methyl-p-nitrophenyl sulphide
4 Thiophenol

derivatives on mercury from NaCl solutions. It is found that a plot of C/Θ *vs* C for various values of charge density gave a family of parallel straight lines with a slope of unity in all cases. This observation shows that the adsorption of thio compound from mercury obeys Langmuir's adsorption isotherm.

Free Energy as a function of q^M

Intercepts of the above parallel lines have been noted for each value of q^M for different isotherm plots from which free energy of adsorption is evaluated. Fig 4 shows the variation of free energy of adsorption (ΔG^o) with q^M for all the thio compounds studied. All the curves are similar. Values of free energy of adsorption for different charges for different compounds follow the order: thiophenol < methyl-p-nitrophenyl sulphide < methyl phenyl sulphide < methyl-p-tolyl sulphide.

This observation is in keeping with the extent of adsorption of these compounds on the mercury surface.

CONCLUSION

A systematic study of the adsorption of thiophenol and its derivatives on the mercury surface from 1 M NaCl brings out the following salient features:

1. All these compounds are adsorbed strongly on the positively charged mercury surface and completely desorbed on the negatively charged surface.

2. The extent of adsorption of the thio compounds from 1 M NaCl solutions is in the order: thiophenol ≤ methyl-p-nitrophenyl sulphide < methyl phenyl sulphide < methyl-p-tolyl sulphide.

3. Langmuir's adsorption isotherm is obeyed in all cases.

REFERENCES

1. M.A.V.Devanathan and B.V.Tilak, *Chem. Rev.*, 65 (1965) 665

2. V.Balaramachandran and S.Venkatakrishna Iyer, *J.Surf. Sci & Tech.*, 10 (1994) 73; *Indian J.Chem.*, 34 (1995) 224; *J.Electrochem. Soc. India*, 45 (1996) 227

3. P.V. Krishnamoorthy, S. Alwarappan, T. Vasudevan, A.Sheik Moideen and S.Venkatakrishna Iyer, *J.Surf. Sci & Tech.*, 8 (1992) 319

4. S.Sankarapandian, M.Anbu Kulandainathan, M Ganesan, T.Vasudevan and S.Venkatakrishna Iyer, *Bull. Electrochem.*, 6 (1990) 469

5. P.V.Krishnamoorthy, M.Anbu Kulandainathan and S.Venkatakrishna Iyer, *Indian J. Chem.*, 30A (1991) 230

6 P.V.Krishnamoorthy and S.Venkatakrishna Iyer, *Bull.Electrochem.*, 7 (1991) 98

7. S. Venkatakrishna Iyer and M.A.V.Devanathan, *Trans. SAEST.* 15 (1980) 28