

THE ADSORPTION BEHAVIOUR OF ETHANOLAMINES IN HYDROCHLORIC ACID SOLUTION

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The adsorption behaviour of mono, di and tri-ethanolamines on the mercury electrode from acidic solution 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 ($-\Delta G^0$) have been evaluated. Ethanolamines in acidic media are found to adsorb on the negatively charged mercury surface and are completely desorbed at more positive electrode charges. The order of adsorption among the ethanolamines is found to be ethanolamine > diethanolamine > triethanolamine. The order of adsorption resembles the order of their basicity. The adsorption of all these compounds are governed by Frumkin's adsorption isotherm.

Keywords: Ethanolamine, adsorption, adsorption isotherm and electrocapillary.

INTRODUCTION

Generally the adsorption of organic molecules at the metal/solution interface is primarily a competition for sites on the metal surface between organic molecules and solvent molecules in the electrolyte. Ions present in the electrolyte have been found to possess significant influence on the extent of adsorption of organic compounds on the metal surface. Such influence of ions on the mercury electrode has been reported by many workers [1-6]. Organic compounds containing nitrogen as the hetero atom have been found to serve very efficiently as corrosion inhibitors both in aqueous phase and vapour phase and as addition agents in electropolishing, electroplating and batteries. The efficacy of these compounds in the above fields of applications can be traced to the presence of lone pairs of electrons in the nitrogen atoms, which enables their strong adsorption on the metal surface. Ethanolamines have been found to serve as vapour phase inhibitors for structural steel [7] and also as

inhibitor for the corrosion of steel in 1 N H_2SO_4 [8]. They also find successful application as addition agents in the $H_3PO_4-H_2SO_4$ bath used for electropolishing of stainless steel [9]. It is of interest to study the adsorption of ethanolamines from 1 M HCl on mercury to understand the influence of structural effects on the extent of adsorption of these compounds on the metal surface. Various thermodynamic parameters have been evaluated to get an idea regarding the extent of adsorption and the nature of adsorption on the metal surface. Results are presented and discussed.

EXPERIMENTAL

The design of the capillary electrometer and the experimental cell design used for the interfacial tension measurements are the same as described elsewhere [10]. All the chemicals were of AR-BDH grade except ethanolamines (E- Merck). All solutions were prepared in conductivity water. Mercury (AR) was purified electrolytically and

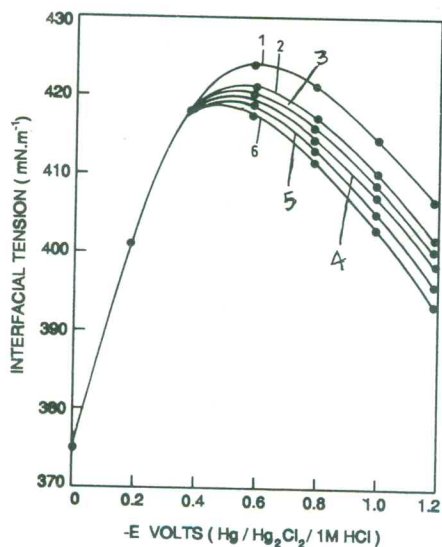


Fig. 1: Electrocapillary curves for 1 M HCl in presence of different concentrations of monoethanolamine
(1) HCl (2) 0.001 M (3) 0.005 M
(4) 0.01 M (5) 0.05 M (6) 0.1 M

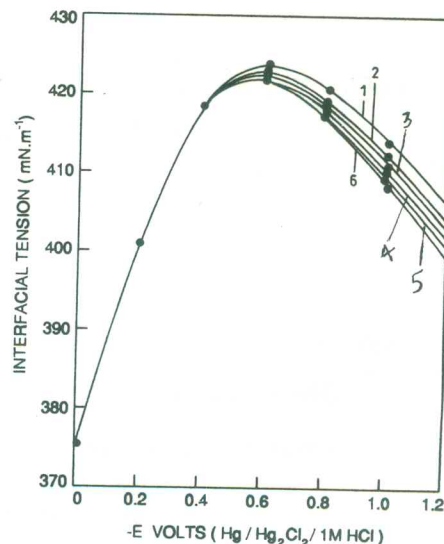


Fig. 3: Electrocapillary curves for 1 M HCl in presence of different concentrations of triethanolamine
(1) HCl (2) 0.001 M (3) 0.005 M
(4) 0.01 M (5) 0.05 M (6) 0.1 M

distilled in an all glass pyrex still [11] under reduced pressure. All the measurements were carried out in an air thermostat at 303 ± 1 K.

Reference electrode used was $\text{Hg}/\text{Hg}_2\text{Cl}_2/1\text{ M HCl}$. Lead acid battery was used for applying the required potential (-0.1 to -1.6 V) to mercury in the capillary electrometer using a precision

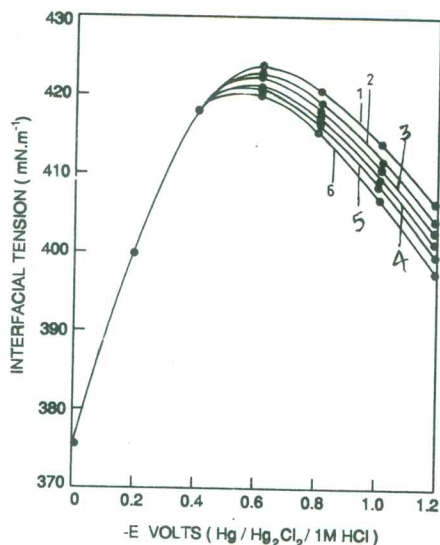


Fig. 2: Electrocapillary curves for 1 M HCl in presence of different concentrations of diethanolamine
(1) HCl (2) 0.001 M (3) 0.005 M
(4) 0.01 M (5) 0.05 M (6) 0.1 M

potentiometer. All the potentials were measured using a digital multimeter (HIL 212).

RESULTS AND DISCUSSION

Electrocapillary curves

Electrocapillary curves obtained in 1 M HCl solution containing various concentrations of ethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA) ranging from 1×10^{-1} to 1×10^{-3} M are shown in Figs. 1-3. All the runs were duplicated and the results are reproducible to $\pm 0.2 \text{ mN.m}^{-1}$ at the ecm and $\pm 0.8 \text{ mN.m}^{-1}$ at the extremes of curves.

Charge on the metal surface (q^M)

The charge on the metal surface was evaluated by the graphical differentiation of electrocapillary curves at 50 mV intervals. The plots of q^M vs E are presented in Fig. 4 for ethanolamine. Curves with other amines are almost similar. The error limits for the charge density are $0.25 \mu\text{C.cm}^{-2}$ at the extremes of the curve.

Surface excess of organic molecules adsorbed (Γ_{org})

The surface excess of organic molecules adsorbed (Γ_{org}) was calculated by the graphical differentiation of the interfacial tension vs

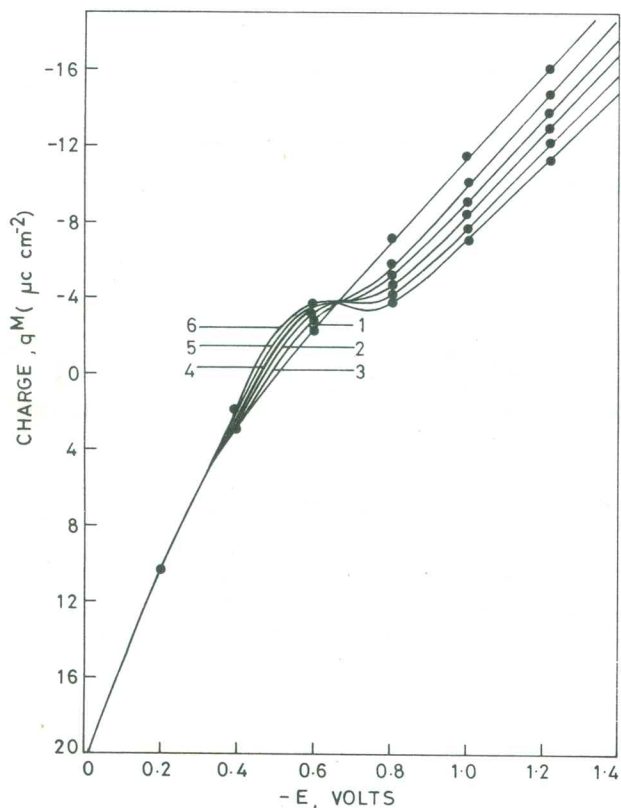


Fig. 4: Variation of charge (q^M) with potential ($-E$) for the adsorption of MEA on mercury from 1 M HCl containing different concentrations of MEA
(1) 0.001 M (2) 0.005 M (3) 0.01 M
(4) 0.05 M (5) 0.1 M

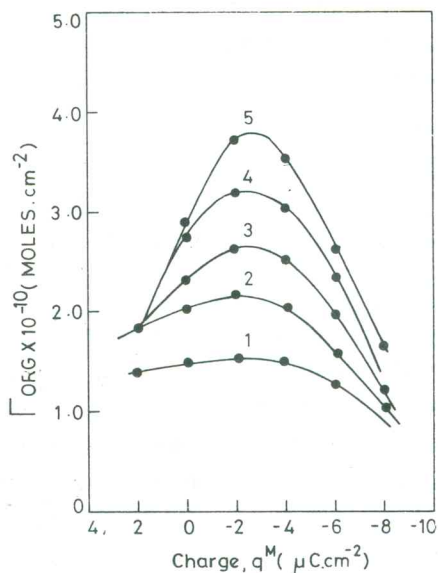


Fig. 5: Variation of surface excess (Γ_{org}) with charge (q^M) for the adsorption of MEA on mercury from 1 M HCl containing different concentrations of MEA
(1) 0.001 M (2) 0.005 M (3) 0.01 M
(4) 0.05 M (5) 0.1 M

concentration curve at constant potential. Values of Γ_{org} obtained for various different concentrations of ethanolamine were plotted as a function of q^M and a representative curve for MEA are shown in Fig. 5.

Electrocapillary curves

It can be seen from Figs. 1-3, that ethanolamines adsorbed more on the negatively charged mercury surface and it gets desorbed on the positively charged surface. It can be seen from Table I that the order of adsorption is MEA > DEA > TEA. The above order can be explained on the basis of the influence of electron withdrawing ability of OH group in alkanol group and the overcrowding on the nitrogen atom.

Surface excess (Γ_{org}) vs charge (q^M) curves

It can be seen from Fig. 5, that when the concentration of adsorbate increases, Γ_{org} value also increases. It is also found that adsorption is more predominant on the negatively charged electrode than on the positive side. This is understandable in terms of the protonation of the alkanolamine and the adsorption being through the positive centre of the molecule and the maximum value of surface excess occurs at a charge of $-2 \mu C.cm^{-2}$.

Coverage (θ) vs charge (q^M) curves

Coverage (θ) was evaluated using the relation Γ/Γ_m , where Γ is the value of surface excess and Γ_m is the surface excess maximum. The value of Γ_m was obtained from the molecular model supplied by the Catalin Products Ltd, UK. Coverage vs charge curves are identical to surface

TABLE I: Interfacial tension for different concentrations of ethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA) at pzc in 1 M HCl

Concn M	MEA		DEA		TEA	
	γ mN.m ⁻¹	-E mV	γ mN.m ⁻¹	-E mV	γ mN.m ⁻¹	-E mV
1×10^{-3}	422.5	588	423.5	590	424.0	600
5×10^{-3}	421.5	575	422.5	565	423.0	585
1×10^{-2}	420.5	550	422.0	550	422.5	575
5×10^{-2}	420.0	530	421.5	540	422.0	560
1×10^{-1}	419.0	520	421.0	525	421.5	550

excess vs charge curves. These curves for different concentrations of MEA have almost similar features. In all cases, coverage confirms the observed trend of considerably high absorption on the negatively charged and low on the positively charged surface.

Application of adsorption isotherms

Different isotherms such as Langmuir, Frumkin and Temkin were tested graphically for characterising the adsorption of ethanolamines on mercury from 1 M HCl solution. A plot of $[\log C - \log (\theta / (1-\theta))]$ vs θ for different values of q^M gave a family of straight lines which clearly supports the fact that the adsorption of the organic compound obeys Frumkin's adsorption isotherm (Fig. 6).

Free energy as a function of q^M

Values of free energy for different charge densities on the metal surface were obtained from Frumkin's isotherm plots. Fig. 7 clearly brings out the fact that $-\Delta G^0$ values for a charge at which maximum adsorption occurs at $-2 \mu\text{C}.\text{cm}^{-2}$ follows the order,

$$\text{MEA} > \text{DEA} > \text{TEA} \quad (2)$$

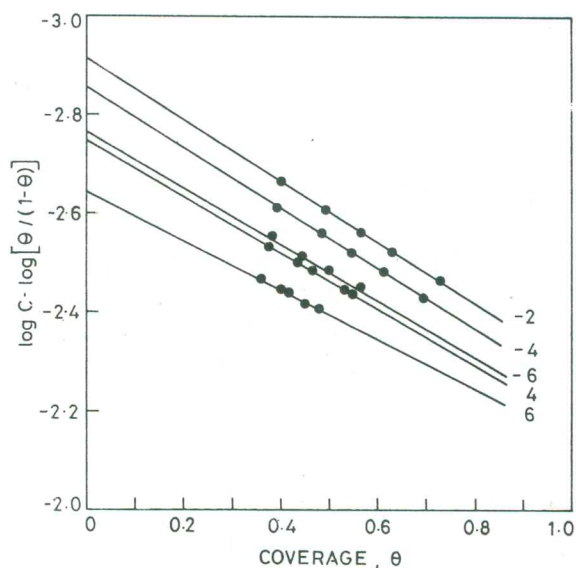


Fig. 6: Frumkin adsorption isotherms for different q^M values for the adsorption of MEA on mercury from 1 M HCl. The numbers near the straight line plots denote the q^M values in $\mu\text{C}.\text{cm}^{-2}$

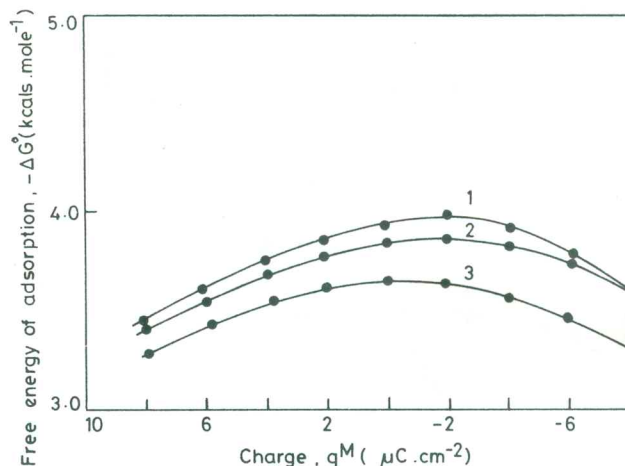


Fig. 7: Variation of energy of adsorption ($-\Delta G^0$) with (q^M) for adsorption of ethanolamines on mercury from 1 M HCl
(1) 0.1 M MEA (2) 0.1 M DEA (3) 0.1 M TEA

CONCLUSION

- ✧ A systematic study of the adsorption of ethanolamine, diethanolamine and triethanolamine from 1 M HCl brings out the following salient features:
- ✧ Alkanolamines adsorb on the negatively charged mercury surface. The ecm is found to shift towards the positive side of the electrocapillary curve thereby indicating more adsorption takes place on the negatively charged metal surface.
- ✧ Frumkin's adsorption isotherm is obeyed in all cases and the maximum adsorption occurs around a charge of $-2 \mu\text{C}.\text{cm}^{-2}$ which is characteristic feature shown by all aliphatic compounds.
- ✧ The electron withdrawing ability of hydroxy group in alkanol compounds and their overcrowding on the nitrogen atom are found to influence the extent of adsorption in the case of di- and tri ethanolamines on the mercury surface. The order of adsorption among the ethanolamines from 1 M HCl is
ethanolamine > diethanolamine > triethanolamine (3)
- ✧ This order of adsorption is also in line with the basicity values of the ethanolamines.

The value of the interaction parameter 'r' calculated from the slope of the isotherm is found to be positive indicating an attractive interaction between adsorbed molecules. This is evident from the nearness of the experimental and theoretical values of Γ_{max} , suggesting close packing of the adsorbed molecules in flat orientation with the hydrocarbon chains and nitrogen atom towards the mercury surface and the -OH group, more or less turned towards the solution in the case of ethanolamines.

REFERENCES

1. K M Joshi and S Rajagopalan, *Indian J Chem*, **10** (1972) 299
2. M A Ghaly and A A Mazhar, *Surf Tech*, **16** (1982) 31
3. R K Jaworsky, M Goldezinowski and Z Galus, *J Electroanal Chem*, **252** (1988) 425

4. S Alwarappan, A Sheik Mideen, M Anbukulandainathan, P V Krishnamoorthy, T Vasudevan and S Venkatakrishna Iyer, *J Electrochem Soc India*, **39** (1990) 170
5. K Madhavan, A Sheik Mideen, M Anbukulandainathan, M Ganesan and S Venkatakrishna Iyer, *J Surf Sci & Tech*, **8** (1992) 257
6. V Balaramachanran and S Venkatakrishna Iyer, *J Surf Sci & Tech*, **10** (1994) 73; *Indian J Chem*, **24** (1994) 224 and *J Electrochem Soc India*, **45** (1996) 227
7. C A Mann, *Trans Electrochem Soc*, **69** (1936) 116
8. T P Viswanathan, *Ind J Tech*, **16** (1978) 408
9. G Jayashree, A Subramanian, S Mohan and T Vasudevan, *7th National Conference of Electrochemists, SAEST, Kolhapur* (1996)
10. S Venkatakrishna Iyer and M A V Devanathan, *Ind J Chem*, **20A** (1981) 648
11. G H Hullet and H P Minahin, *Phys Rev*, **21** (1905) 388