Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2014, 6(12):575-581

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Interfacial behaviour of glutaric acid at the mercury electrode from 0.1M Na_2SO_4 solution

A. Sheik Mideen

Department of Chemistry, Sathyabama University, Chennai, Tamil Nadu, India

---

ABSTRACT

The adsorption of glutaric acid on mercury in aqueous solution of 0.1M Na_2SO_4 has been investigated by capillary electrometer. Thermodynamic parameters such as surface charge density (q_M), surface excess of organic molecule adsorbed (Γorg) and coverage (θ) have been evaluated. The adsorption of glutaric acid occurs both on positively and negatively charged mercury surface. Maximum adsorption occurs at negative charges and desorption occurs at extremes of positive and negative charges. It is found from q_M versus potential (–E) plot that the glutaric acid at various concentrations intersects one another at 950 mV which is negative to the electrocapillary maximum (ecm) and at a charge density of –2.5 $\mu C\ cm^{-2}$. The adsorption of glutaric acid obeys Langmuir's adsorption isotherm. The maximum coverage occurs at a charge density of –1.2 $\mu C\ cm^{-2}$. The free energy changes of adsorption of glutaric acid with coverage were ascribed to the dipole-dipole interaction at the surface.

Key words: Adsorption, Capillary electrometer, Interfacial tension, Glutaric acid, Adsorption isotherm.

INTRODUCTION

The adsorption characteristics of many organic compounds at the mercury solution interface have been described in the literature [1-5]. Organic adsorption plays key roles not only in electrochemical energy conversion, but also in electroorganic synthesis, corrosion protection, electrodeposition, electrochemical sensors, etc. In general, organic adsorption may be represented by a displacement of adsorbed water molecules according to the reaction: $[organic]_{sol} + nH_2O_{ads} \leftrightarrow [organic]_{ads} + nH_2O_{sol}$. The organic molecules will have to be dissociated from any water molecules with which they are hydrated because they have polar groups. In general, the lower the solubility of the organic compounds in the electrolyte, the higher the adsorbability on the electrode.

Glutaric acid is a dicarboxylic acid with odd carbon number. It is used to decrease polymer elasticity, as scale removers, water treatment chemicals, tanning agents, corrosion inhibitors, and in the synthesis of pharmaceuticals, surfactants, and metal finishing compounds. An understanding of the adsorption behavior of neutral organic molecules is essential in elucidating the reaction kinetics across electrode/electrolyte interfaces. Kang and Xing [6] examined the adsorption of dicarboxylic acids by kaolinite and montmorillonite at different pH conditions. The magnitude of adsorption of succinic acid, glutaric acid, adipic acid and azelaic acid on such minerals was the highest at pH 4 as compared to those at pH 7 and 9. Marcin et al. [7] studied the adsorption of phthalic acid on mercury electrode in the pH range 0.5-11.5 using surface tension, double layer capacity, and zero charge potential measurements. The calculated adsorption isotherms indicate a reorientation of phthalic acid molecules from flat to vertical orientation with increase of phthalic acid concentration in the solution. These results combined with the change of the zero charge potentials suggest that in the vertical position -COOH groups are directed to the surface of the metal. Morrison and Miller [8] determined the maximum adsorptions of the lower members of the mono- and di-carboxylic acids from aqueous solutions for coconut charcoals of different degrees of activation. They concluded that acids with an even number of carbon atoms had larger adsorptions than acids with an odd number. The alternation was much more marked for the di- than for the mono-carboxylic acids. Adsorption equilibria of glutaric acid and glyoxylic acid on weakly basic ion-exchanger Amberlite IRA-67 were theoretically and experimentally investigated [9]. The equilibrium isotherms were significantly dependent on initial acid concentration and the adsorption of both acids followed pseudo second order kinetics. Shinjiro Yagyu et al. [10] investigated the adsorption structure of glutaric acid on the Cu(110) surface as a function of sample temperature and concluded that glutaric acid adsorbs as mono-glutarate form at 400 K and changes to a bi-glutarate structure at 600 K. The several studies carried out about the adsorption behaviour of dicarboxylic acids to establish relationships between molecular properties and of these compounds. The aim of the present study was to determine the structure of the mercury/solution interface for glutaric acid and to analyse how the presence of carboxyl groups affect the adsorption process in presence of sodium sulphate as supporting electrolyte.

EXPERIMENTAL SECTION

The design of capillary electrometer and the experimental cell set up used for the measurement of interfacial tension are described elsewhere [11]. Mercury used was Analar grade and it is further purified electrolytically and distilled in an all glass pyrex still under reduced pressure. The base electrolyte sodium sulphate (BDH) was of AR grade used after recrystallisation twice from triple distilled water. Glutaric acid (Sigma) of AR grade was used without further purification. Purified hydrogen was used for the deaeration of experimental solution. All the measurements were carried out in an air thermostat at 25 ± 0.2°C. The mercury in the capillary electrometer was polarized at various values of potentials ranging from –0.1 to –1.6 V applied with reference to Hg/Hg_2SO_4/0.1M Na_2SO_4 using a precision potentiometer in combination with a 6 V lead acid battery. All the potentials are measured using a digital multimeter (HIL 212).

RESULTS AND DISCUSSION

Electrocapillary curves:

Electrocapillary curves for various concentrations of glutaric acid using 0.1M Na_2SO_4 as the base electrolyte at 25 ± 0.2°C are shown in figure 1. Values of interfacial tension (γ) were determined between the potentials, 0 and –1.6 V of the mercury electrode with respect to Hg/$HgSO_4$/0.1M Na_2SO_4 electrode. All the runs were duplicated and the results are reproducible to 0.2 mN m^{-1} at the electrocapillary maximum and ± 0.8 mN m^{-1} at the extremes of the curves. Fig.1 shows that the adsorption of glutaric acid occurs both on positively and negatively charged mercury surface. At negative charges, adsorption is slightly more and desorption occurs at extreme negative and positive charges. The adsorption on positive side may be due to the interaction of the mercury with the carboxyl groups of glutaric acid molecules in flat configuration. The adsorption on the negative side may be due to the interaction of positively charged hydrocarbon group with negatively charged metal surface. Further the change of ecm with glutaric acid concentration in the solution indicates a reorientation of -COOH groups which are directed to the surface of the metal from flat to vertical orientation. Similar observations were reported for the adsorption of phthalic acid on mercury electrode [8].

Charge density on metal surface:

Figure 2 shows the relation between electrode charge density (q_M) and potential (–E). It is found from the figure that glutaric acid at various concentrations intersects one another at 950mV which is negative to the electrocapillary maximum (ecm) and at a charge density of –2.5 μC cm^{-2}. It is clear that at extreme negative (–1.6 V) and positive (–0.35 V) potentials, desorption is complete for different concentrations adsorbate. The negative shift of ecm reveals that maximum adsorption of dipoles of glutaric acid are adsorbed with their negative dicarboxyl ends oriented towards the electrode surface. The more positive value obtained for glutaric acid suggests that adsorption occurs with the alkyl group in contact with the mercury surface. Further, glutaric acid adsorbs as mono-glutarate with initial concentration and changes to a bi-glutarate structure with higher concentration.

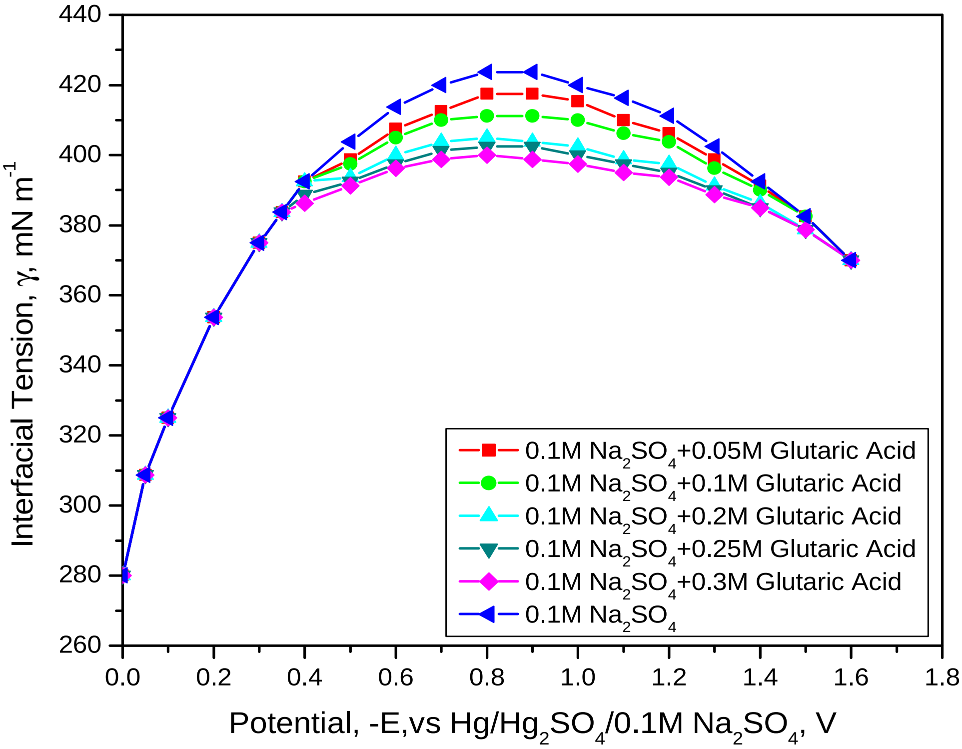

Fig.1 Electrocapillary curves of glutaric acid in 0.1M Na_2SO_4

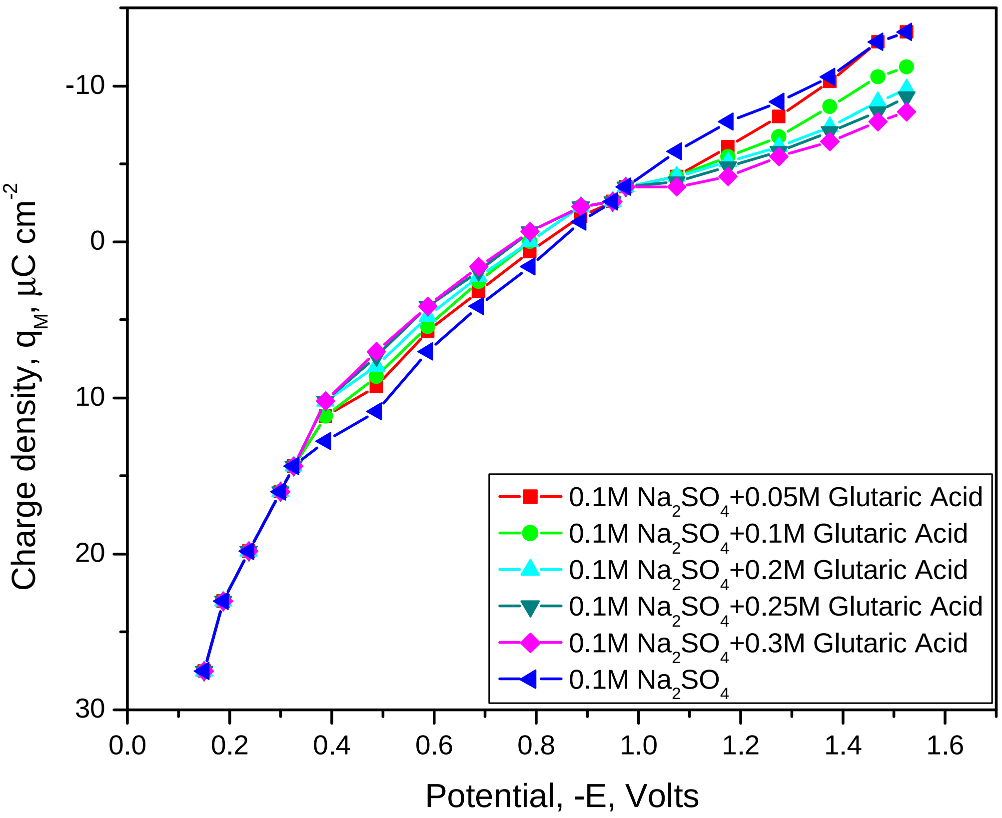

Fig.2 Variation of charge density (q_M, µC cm^{-2}) with potential (–E, Volts) for the adsorption of glutaric acid on Hg

Surface excess (Γ_{org}) versus charge density (q_M) curve:

Surface excess values for different concentrations of glutaric acid were plotted as a function of q_M is shown in figure 3. It is seen from the figure that it is bell shaped and when the concentration of the adsorbate increases Γ_{org} value also increases. Maximum adsorption occurs at negative charges and desorption occurs at extremes of positive and negative charges. These curves exhibit a maximum value of surface excess near to the ecm at a charge density of –1.2 μC cm^{-2}.

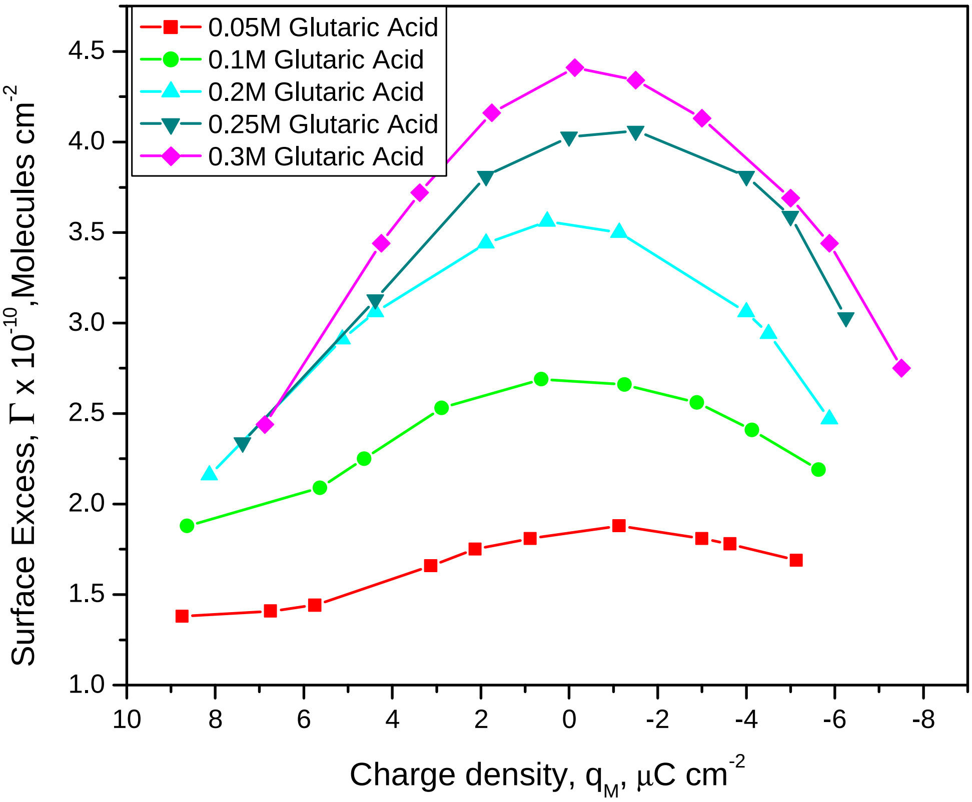

Fig.3 Variation of surface excess (Γ_{org}) with charge density (q_M, μC cm^{-2}) for the adsorption of various concentrations glutaric acid on Hg from 0.1M Na_2SO_4

Coverage (θ) versus charge density (q_M) curve:

Surface excess maximum (Γ_m) used in the determination of surface coverage had been evaluated from the initial slope of c/Γ vs c curve for $q_M = 0$. It was found to be equal to 5.1×10^{-10} molecules cm^{-2}. This value of Γ_m was used for the calculation of surface coverage ($\theta = \Gamma/ \Gamma_{max}$). Figure 4 shows the coverage vs charge density curves have a bell shape for the adsorption of glutaric acid from 0.1M Na_2SO_4 solution. The maximum coverage occurs at a charge density of –1.2 μC cm^{-2}.

Application of isotherms:

The application of the isotherms for the adsorption of glutaric acid on mercury from 0.1M Na_2SO_4 as the electrolyte was tested by analysing the adsorption data graphically to find the best fit of the isotherm. The adsorption data obtained was used to try various isotherms like Langmuir, Frumkin, Temkin and Virial isotherms for characterizing the adsorption of glutaric acid 0.1M Na_2SO_4. It was found that a family of parallel straight line with unit gradient was obtained when values of c/θ were plotted against c for various values of q_M (Figure 5 and Figure 6). It was found that adsorption data satisfies Langmuir's adsorption isotherm.

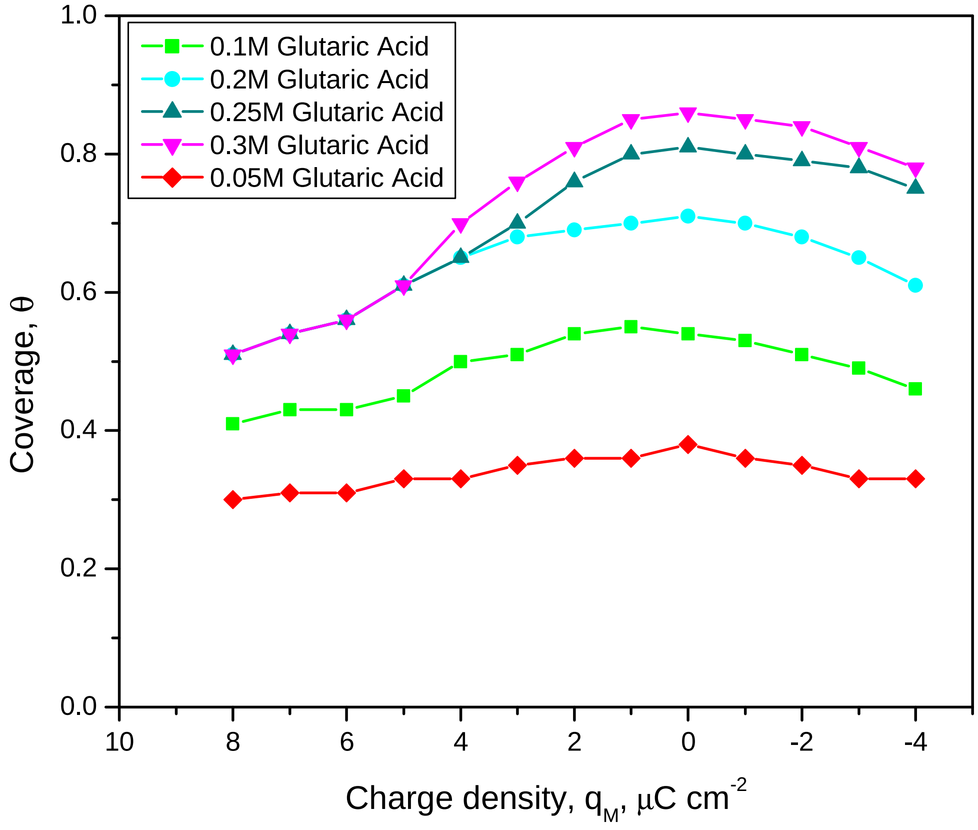

Fig.4 Variation of coverage (θ) with charge density (q_M, μC cm^{-2}) on the interface for the adsorption of glutaric acid on Hg from 0.1M Na_2SO_4

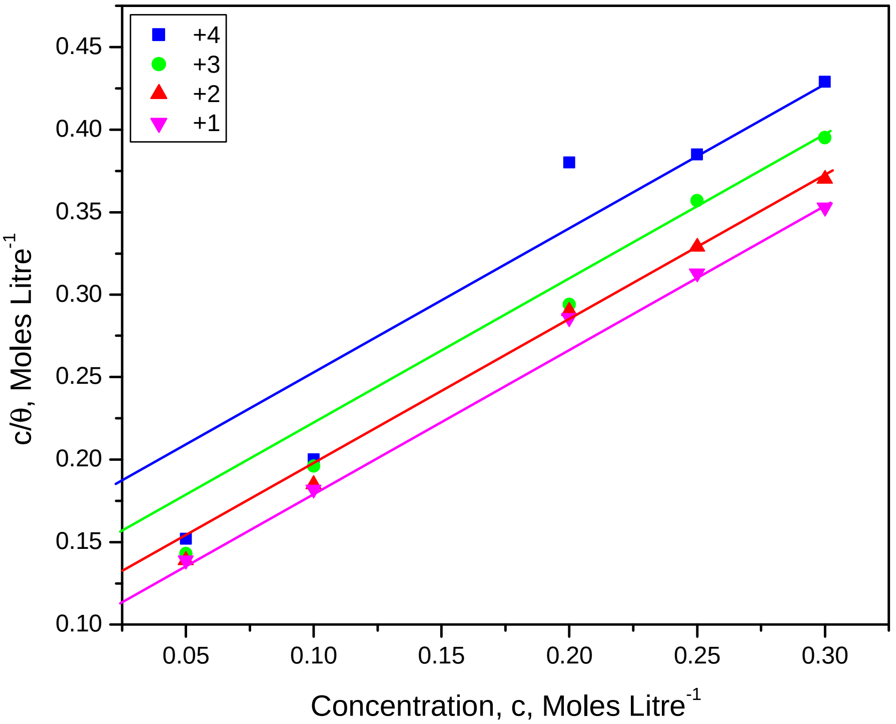

Fig.5 Plot of c/θ versus for the adsorption of glutaric acid at some positive values charge (q_M, μC cm^{-2})

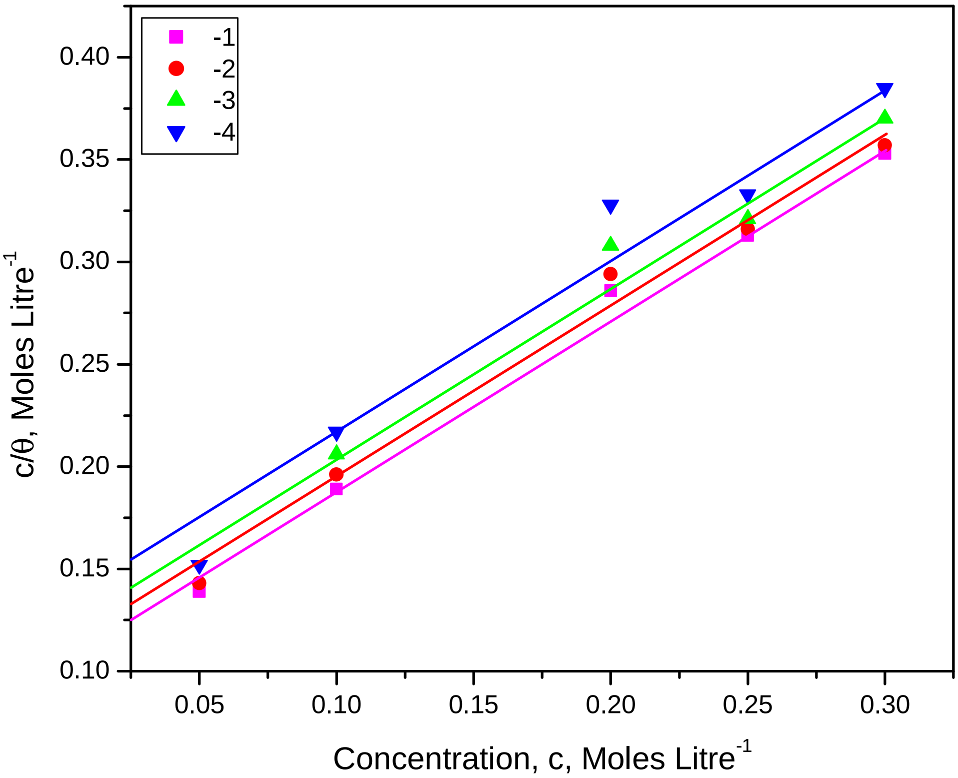

Fig.6 Plot of c/θ versus for the adsorption of glutaric acid at some negative values charge (q_M, μC cm^{-2})

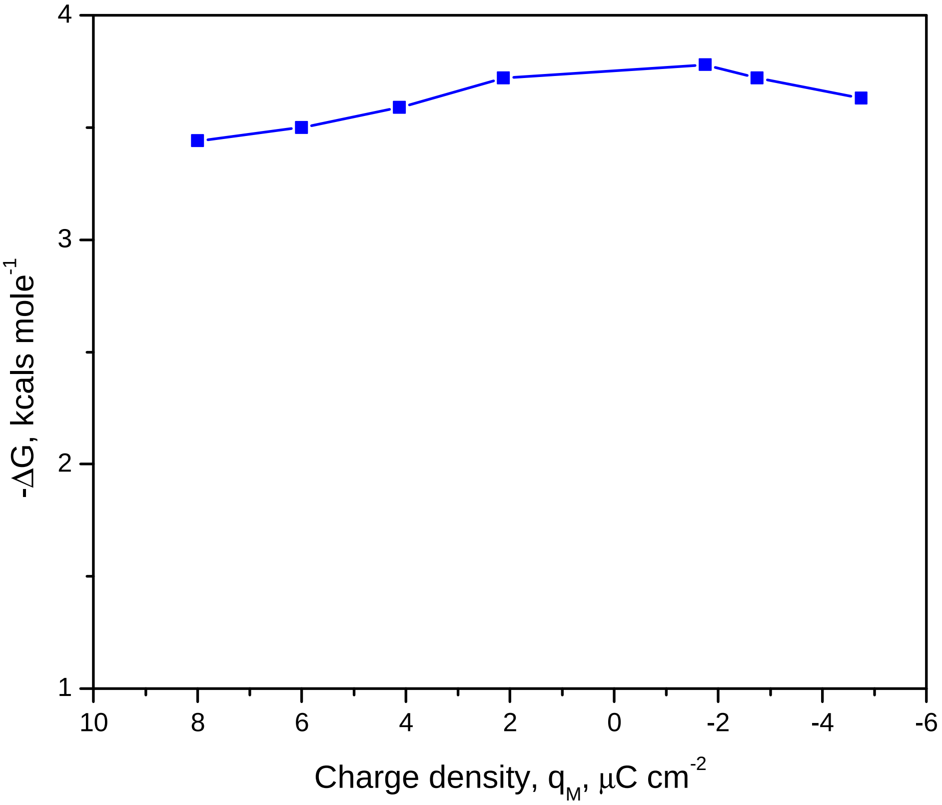

Fig.7 Plot of the variation of free energy of adsorption with charge density of the interface for the adsorption of glutaric acid

Free energy of adsorption as a function of charge density:

Free energy values for different charge densities on the metal surface were obtained from Langmuir's plots. Figure 7 shows a plot of free energy of adsorption versus charge density for the adsorption of glutaric acid from 0.1M Na_2SO_4. Free energy can be explained by considering that glutaric acid adsorbs on negative charges than at positive charges. The maximum free energy occurs at a charge density of $-2\ \mu C\ cm^{-2}$. The free energy changes of adsorption of glutaric acid with coverage were ascribed to the dipole-dipole interaction at the surface.

CONCLUSION

The study of adsorption of glutaric acid at the mercury solution interface leads to the following conclusions.

1. Glutaric acid adsorbs more on the negative side of the electrocapillary curve. The change of ecm with glutaric acid concentration in the solution indicates a reorientation of -COOH groups which are directed to the surface of the metal from flat to vertical orientation.
2. Maximum adsorption occurs around the charge density of $-1.2\ \mu C\ cm^{-2}$. Glutaric acid adsorbs as mono-glutarate with lower concentration and changes to a bi-glutarate structure with higher concentration.
3. The adsorption of glutaric acid from 0.1M Na_2SO_4 solution is found to obey Langmuir's isotherm.
4. The free energy changes of adsorption of glutaric acid with coverage were ascribed to the dipole-dipole interaction at the surface. The free energy of adsorption has a maximum value at $-2\ \mu C\ cm^{-2}$.

Acknowledgement

The author is thankful to the Directors, Sathyabama University, Chennai for their kind permission to publish this paper.

REFERENCES

[1] RMA Ramanathan; A Subramanian; S Alwarappan; T Vasudevan; SVK Iyer, *Bull. Electrochem.,* **2001,** 17(1), 01-05.

[2] B Muralidharan; G Paruthimalkalaignan; T Vasudevan; S Alwarappan; SVK Iyer, *Bull. Electrochem.*, **2000,** 16(12), 539-543.

[3] AS Mideen; PV Krishnamoorthy; M Ganesan; SVK Iyer, *J. Surface Sci. Technol.*, **1991,** 7(2), 197-203.

[4] K Madhavan; AS Mideen; M Anbukulandainathan; M Ganesan; SVK Iyer, *J. Surface Sci. Technol.,* **1992,** 8(3), 257-270.

[5] B Muralidharan; S Alwarappan; T Vasudevan; SVK Iyer, *Bull. Electrochem.,* **1998,** 14(6-7), 231-234.

[6] S Kang; B Xing, *Langmuir,* **2007,** 23(13), 7024-7031.

[7] JL Morrison; DM Miller, *Can. J. Chem.,* **1955,** 33(2), 330-343.

[8] O Marcin; D Jadwiga; G Zbigniew, *Can. J. Chem.*, **1981,** 59(13), 1918-1924.

[9] SS Bayasit; I Insi; H Uslu, *J. Chem, Eng. Data,* **2010,** 55(2), 679-684.

[10] S Yagyu; M Yoshitake; T Chikyow, *Shinku,* **2008,** 50(5), 386-389.

[11] AS Mideen, Ph.D thesis, Madurai Kamaraj University, **1992**.