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Adsorption of organic molecules at the mercury-solution interface: effect of anion specific adsorption on double layer properties

John Joseph Buckfelder III
Iowa State University

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Adsorption of organic molecules
at the mercury-solution interface:
Effect of anion specific adsorption
on double layer properties

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by

John Joseph Buckfelder, III

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
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DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Physical Chemistry

Signatures have been redacted for privacy

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1980

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TABLE OF CONTENTS

| | Page |
|--|------|
| INTRODUCTION | 1 |
| Adsorption of Background Electrolyte | 10 |
| Organic Adsorption | 13 |
| EXPERIMENTAL | 19 |
| Capillary Electrometer | 19 |
| Capacitance Bridge | 23 |
| Materials | 26 |
| RESULTS AND DISCUSSION | 30 |
| Preliminary Data Treatment | 30 |
| Model for the Covered Portion of the Surface | 56 |
| Aliphatic Compounds | 63 |
| Benzyl Alcohol | 78 |
| Summary and Suggestions for Future Work | 86 |
| BIBLIOGRAPHY | 89 |
| ACKNOWLEDGEMENTS | 93 |
| APPENDIX A | 94 |
| Polynomial Coefficients | 94 |
| APPENDIX B | 100 |
| Charge and Surface Excess | 100 |
| APPENDIX C | 111 |
| Capacity Data | 111 |

INTRODUCTION

The study of the interfacial region between a metal electrode and an electrolyte solution is of interest to a wide variety of disciplines. The kinetics of electrochemical reactions are dependent on the properties of this so-called double layer region. Weaver and Anson (1-3) have shown how different electrolytes can change the rates of oxidation of simple metal cations. Corrosion of metals can be prevented by additives, usually organic molecules, which adsorb onto the metal, blocking any reaction. The mechanism of this inhibition is not completely understood, and certainly depends on double layer properties. Most recently, the use of semiconductors for photoproduction of electricity (4-7) has been studied; the electron transfer across the interface is very much dependent on the properties of the double layer.

Various methods have recently been developed to determine the properties of the double layer. Electroreflectance spectroscopy (8,9) has been used on lead and mercury electrodes in solutions of sodium fluoride. Changes in reflectance can be related to changes in the double layer region. Raman spectroscopy (10-12) shows promise in being able to elucidate surface structures by the so-called "giant Raman" effect. So far, however, the technique seems to be largely limited to silver surfaces and pyridine-

type molecules. Both these techniques are still in early development stages, and as yet are not quantitative methods of analysis.

The great majority of work done on the double layer region has been done using mercury electrodes. There are several reasons for this choice. First, there is a region of 1.3 to 1.6 volts over which mercury behaves very nearly as an ideally polarizable electrode (one for which no faradaic current flows as the potential is varied). Second, the mercury surface can be continuously renewed, providing a clean surface to the electrolyte. This is important, since any impurities which can adsorb onto the surface will affect the measurements. The periodic renewing of the mercury surface is an easy method of cleaning which is not available for solid electrodes. The classical Lippmann capillary electrometer (13), which measures surface tension as function of potential, is still used today with only minor modification.

Plots of surface tension vs. potential are called electrocapillary curves; addition of an adsorbate to the background electrolyte will decrease the surface tension. The family of curves for iso-pentanol in 0.1 N HClO_4 is shown in Figure 1; the top curve is for the background electrolyte, with increasing amounts of adsorbate in the lower curves. The potential at the maximum (electrocapillary

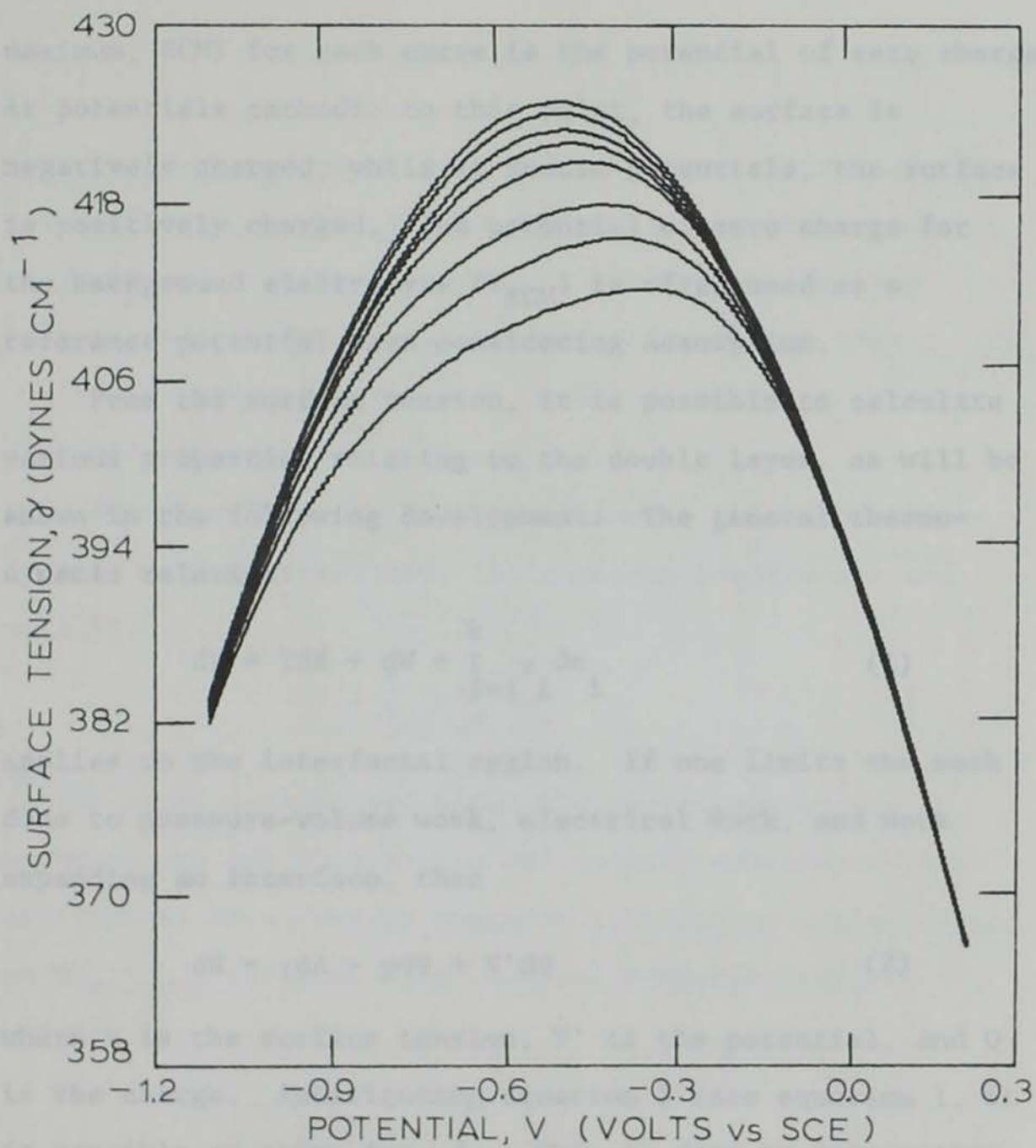


Figure 1. Electrocapillary curves for iso-pentanol
in 0.1 N HClO₄

maximum, ECM) for each curve is the potential of zero charge. At potentials cathodic to this point, the surface is negatively charged, while at anodic potentials, the surface is positively charged. The potential of zero charge for the background electrolyte (V_{ECM}) is often used as a reference potential when considering adsorption.

From the surface tension, it is possible to calculate various properties relating to the double layer, as will be shown in the following development. The general thermodynamic relation:

$$dE = TdS + dW + \sum_{i=1}^k \mu_i dn_i \quad (1)$$

applies to the interfacial region. If one limits the work done to pressure-volume work, electrical work, and work expanding an interface, then

$$dW = \gamma dA - pdV + V'dQ \quad (2)$$

where γ is the surface tension, V' is the potential, and Q is the charge. Substituting equation 2 into equation 1, it is possible to solve for $-d\gamma$. This is done by integrating the result of the substitution, holding γ , p , V' , and μ_i constant, differentiating generally, comparing the result with equation 1, and then using the Gibbs-Duhem equations for the two phases to eliminate dp and $d\mu_1$. The resulting equation appears below.

$$-d\gamma = SdT + qdV + \sum_{i=2}^k \Gamma_i^{(1)} d\mu_i \quad (3)$$

where S is a surface entropy per unit area, q is a charge per unit area, and Γ_i is the surface excess per unit area of component i . The superscript 1 indicates that the interfacial boundary plane has been chosen such that $\Gamma_{H_2O} = 0$. Γ_i then represents the excess amount of material present over that in the bulk solution.

Equation 3 is the basic equation by which the experimental data are analyzed. At constant temperature and potential:

$$-d\gamma = \sum_{i=2}^k \Gamma_i^{(1)} d\mu_i \quad (4)$$

In the studies presented here, the components of the solution are the electrolyte and organic substance. All experiments were done at constant electrolyte concentration, so $d\mu_{\text{electr.}}$ is zero. The chemical potential can be written as:

$$\mu = \mu_0 + RT \ln a \quad \text{so,} \quad (5)$$

$$d\mu = RT \, d \ln a \quad (6)$$

and equation 4 becomes:

$$-d\gamma = \Gamma_{\text{org}} RT \, d \ln a_{\text{org}} \quad (7)$$

and a plot of γ vs. $\ln a$ will have a slope related to the surface excess of the organic substance. In

practice, one defines the spreading pressure (π) as $(\gamma_o - \gamma)_V$ where γ_o is the surface tension of the pure electrolyte solution, and γ is the surface tension of the electrolyte containing organic. Substituting into equation 7, one arrives at:

$$d\pi = \Gamma_{\text{org}} RT \, d \ln a_{\text{org}} \quad (8)$$

and a plot of π vs. $\ln a$ will have a slope of $RT\Gamma_{\text{org}}$. At high concentrations of organic substance, the π vs. $\ln a$ plots become linear; the slope corresponds to a maximum surface excess, Γ_m . The surface coverage (θ) is defined as Γ/Γ_m .

At constant temperature and concentration of organic material:

$$-d\gamma = qdV \quad (9)$$

and a plot of γ vs. V will have a slope equal to $-q$, the charge on the metal. The second derivative of γ with respect to potential gives the differential capacity (C):

$$C = \frac{dq}{dV} = - \frac{d^2\gamma}{dV^2} \quad (10)$$

The capacity can also be measured directly using a capacitance bridge; curves have the characteristic shape shown in Figure 2. Curve A is for the background electrolyte alone; curves B-H are for increasing amounts of organic material. The peaks at the potential extremes are desorption

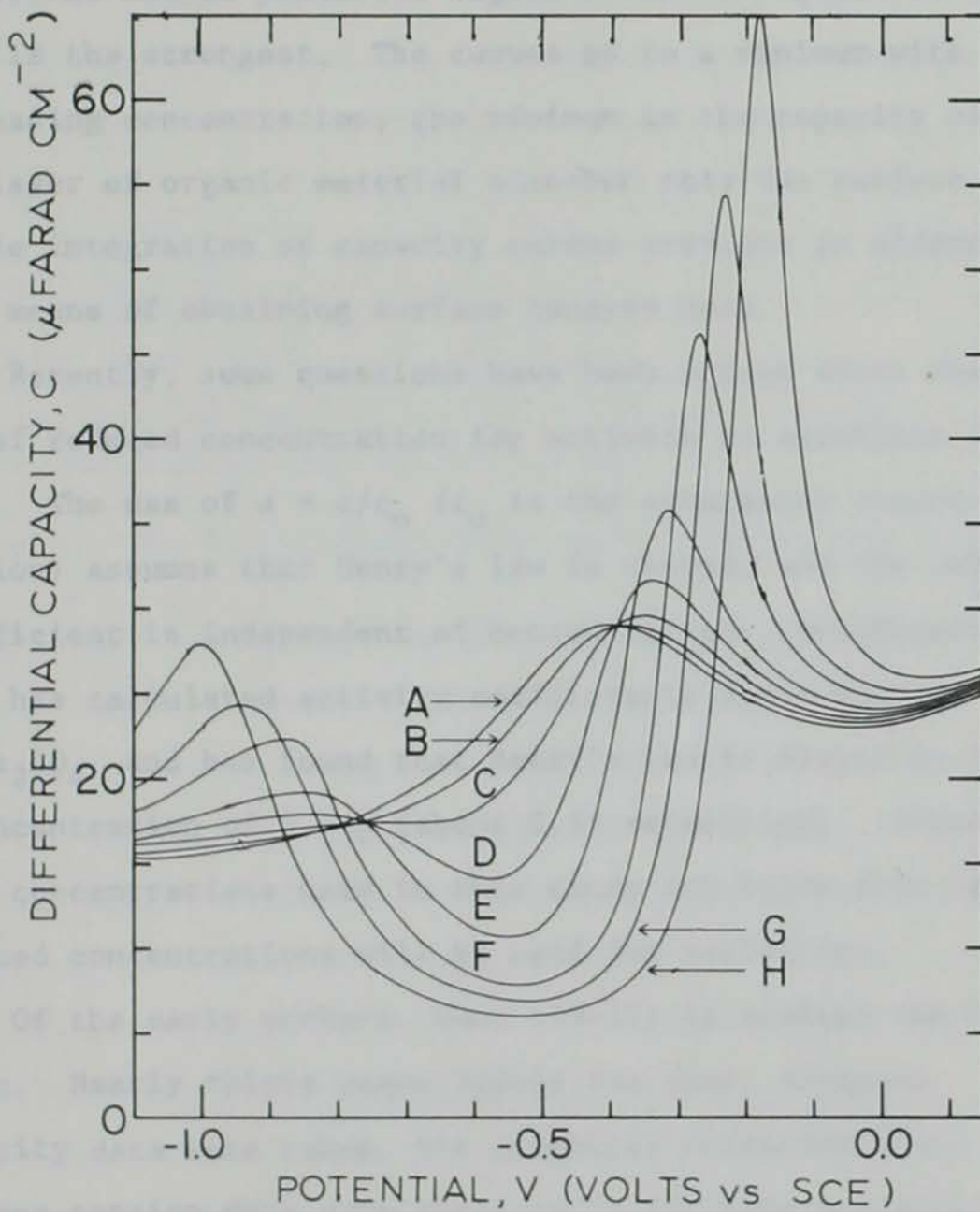


Figure 2. Capacity curves for iso-pentanol in 0.1 N HClO₄
 Reduced concentration (A) 0.0, (B) 0.0123,
 (C) 0.0244, (D) 0.0336, (E) 0.0476, (F) 0.0698,
 (G) 0.0909, (H) 0.1304

peaks; the middle potential region is where organic adsorption is the strongest. The curves go to a minimum with increasing concentration; the minimum is the capacity of a monolayer of organic material adsorbed onto the surface. Double integration of capacity curves provides an alternative means of obtaining surface tension data.

Recently, some questions have been raised about the use of reduced concentration for activity in equations 5-8 (14). The use of $a = c/c_0$ (c_0 is the saturation concentration) assumes that Henry's law is obeyed, and the activity coefficient is independent of concentration. Nakadomari (14) has calculated activity coefficients for 2-butanol in Na_2SO_4 , and has found that Henry's law is obeyed up to a concentration of 0.7 N (about 0.35 saturation). Since most concentrations used in this study are below this value, reduced concentrations will be used for activities.

Of the early workers, Gouy (15-17) is perhaps the best known. Nearly thirty years before the first accurate capacity data were taken, his graphical differentiation of surface tension data gave capacity in striking agreement with experiment. The Gouy-Chapman theory of the double layer (18-19) is based on a model of point charges in a dielectric medium. When applied to real systems, the theory gave unrealistically high values of charge. Stern (20) modified this theory by realizing molecules and ions have

a plane of closest approach to the electrode; they are not point charges. The model for the interface for a background electrolyte is shown in Figure 3. Region I is called the

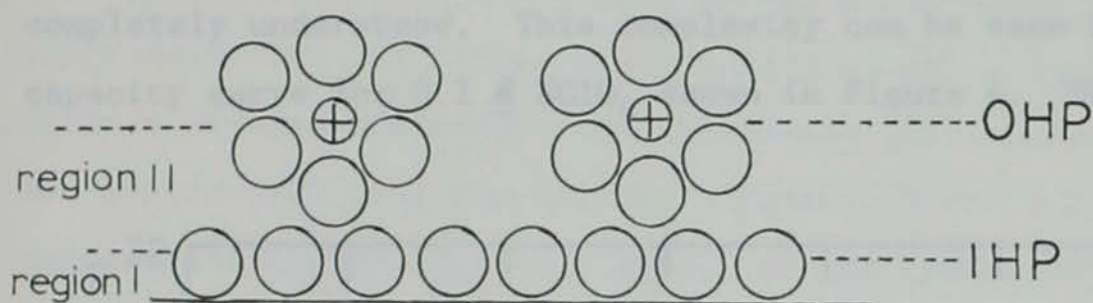


Figure 3. The Gouy-Chapman-Stern model for the double layer inner layer, bounded by the inner Helmholtz plane (IHP), and is restricted to water and specifically adsorbed ions.

(The term specific adsorption refers to the fact that some ions can form a covalent-like bond to the electrode. In general, specific adsorption refers to anions, which can adsorb on the electrode without a hydration sheath). Region II, the outer layer, is bounded by the outer Helmholtz plane (OHP), and contains hydrated species. The major use of the Gouy-Chapman-Stern theory has been to determine the amount of adsorption; Grahame (21) has made extensive use of this theory to calculate charges and capacities for background electrolytes.

Adsorption of Background Electrolyte

Even in the absence of organic solutes, the structure of the double layer for background electrolytes is not completely understood. This complexity can be seen in the capacity curve for 0.1 N HClO₄ shown in Figure 4. The

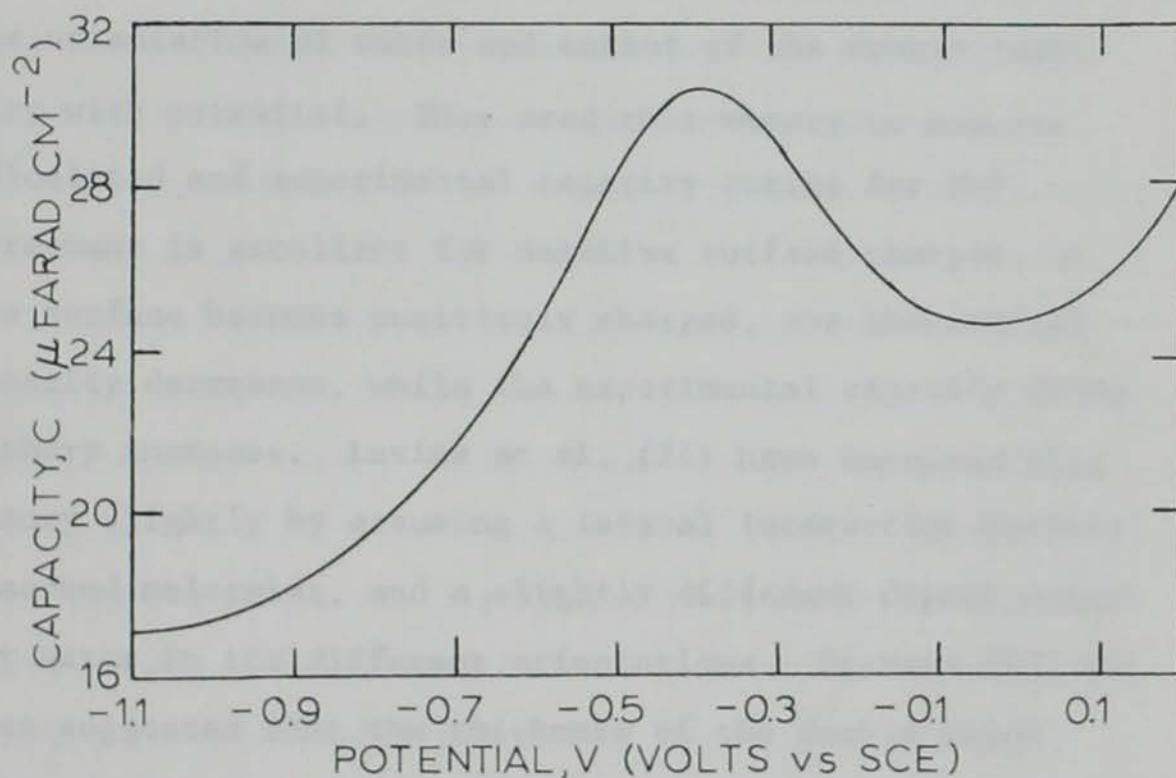


Figure 4. Capacity curve for 0.1 N HClO₄

capacity rises from a minimum of about 17 $\mu\text{F cm}^{-2}$, through a hump near the potential of zero charge, then to a steadily rising portion at most anodic potentials. The hump is characteristic of most background electrolytes; it may be larger or smaller depending on electrolyte, and decreases

in size with decreasing electrolyte concentration. This highly structured capacity curve indicates a changing double layer structure with potential.

Reorientation of water with changing potential is one explanation for the structured capacity curves. In the absence of specific adsorption; MacDonald (22), and MacDonald and Barlow (23) have put forward a theory in which both the orientation of water and extent of the double layer vary with potential. They used this theory to compare calculated and experimental capacity curves for NaF. Agreement is excellent for negative surface charges; as the surface becomes positively charged, the theoretical capacity decreases, while the experimental capacity shows a sharp increase. Levine et al. (24) have improved this theory slightly by assuming a lateral interaction between adsorbed molecules, and a slightly different dipole moment for water in its different orientations. Grahame (25) has also suggested that the thickness of the double layer changes with potential. However, no model for the double layer in the absence of specific adsorption can reproduce the capacity curve for the entire potential region.

In electrolytes where specific adsorption is present, the situation is even more complex. Grahame (21) has used the Gouy-Chapman-Stern model to calculate amounts of adsorption. In calculating the amount of specific

adsorption, he considered specifically adsorbed anions to have a covalent-like bond to the metal. Other workers, most notably Levine et al. (26) proposed a model which accounts for specific adsorption in terms of discreteness of charge potentials. The model takes into account the actual microscopic nature of the interface, and does not treat the adsorbed charge as a smeared out distribution. Rangarajan (27) has reviewed some of these microscopic models, and has indicated the types of interactions which must be considered in modeling the interface, and several approaches which might be tried.

Several statistical mechanical approaches have been taken to model the double layer. Buff and Stillinger (28) used a cluster theory of inhomogeneous fluids to calculate potential distributions in the double layer. Using partition functions, Badiali and Goodisman (29) have derived the Gibbs adsorption isotherm and the Lippmann equation. The diffuse layer has been modeled by Stillinger and Kirkwood (30) using a moment expansion. They arrive at the conclusion that for high electrolyte concentrations, ions tend to align themselves in a lattice-like grid; as one moves away from the electrode, the charge alternates sign for each lattice layer.

Unfortunately, none of the above models has been applied to real systems, so a test of their validity has

not been made. Cooper and Harrison, in a series of papers (31-33), have suggested that the models based on the Gouy-Chapman theory of the double layer need to be reexamined. According to these workers, the separation of the interface into an inner and outer layer is based on unrealistic assumptions and approximations. They put forward a preliminary theory in which the capacity of the electrode is accounted for by a change in effective distance from the electrode for ionic species. This can qualitatively account for the capacity curves, as anions are adsorbed at a position nearer the surface than are cations. This will result in an increasing capacity as the potential is made more positive, the general trend shown in Figure 4. However, the detailed structure of the capacity curves cannot be easily explained using this model. While it is true that models for the double layer for background electrolytes have reached a state of great complexity, abandoning the underlying theory seems to be too drastic a remedy.

Organic Adsorption

Frumkin, in the 1920's, developed a theory for organic adsorption (34), which is an extension of the classical Langmuir isotherm. His modification takes into account the lateral interaction between adsorbed organic molecules, and

can be written as:

$$Ba = \frac{\theta}{(1-\theta)} e^{-2\alpha\theta} \quad (11)$$

where B is an adsorption equilibrium constant, and takes into account metal-adsorbate interactions; α is an interaction parameter and represents adsorbate-adsorbate interactions. B is potential dependent, α is a constant, independent of potential. Frumkin (35) has also shown that if one considers adsorption to be replacement of a capacitor containing water molecules with one containing organic molecules as the dielectric, B will contain the following terms:

$$W_1 = \frac{1}{2}(C - C_{\text{org}})V^2 \quad (12a)$$

$$W_2 = C_{\text{org}} V_n V \quad (12b)$$

where W_1 is the work necessary to replace a water dielectric with an organic one, and W_2 is due to the change in charge produced by the oriented dipoles of the adsorbed organic molecules. Here C is the capacity of the uncovered surface, C_{org} is the capacity of the covered surface, and V_n is the change in the point of zero charge as one goes from an uncovered to a covered surface.

Hansen and co-workers (36) have shown that B can be written as:

$$B = B_o \exp - \left(\frac{G(V) + C_{\text{org}} V_n V - \frac{1}{2} C_{\text{org}} V^2}{\Gamma_m RT} \right) \quad (13)$$

where B_0 is the value of B at $V = V_{ECM}$, and $G(V)$ is the difference in surface tension between $V = V_{ECM}$ and $V = V$ in the absence of organic adsorption. In fitting data to the Frumkin isotherm, values for C_{org} and V_n can be calculated. The Frumkin isotherm has been used extensively in studies of adsorption of organic molecules; for a review of recent literature, see references (37-39).

The Frumkin isotherm implies several relationships between experimental quantities; two of these will be discussed. The equation of state

$$\pi = -RT\Gamma_m (\ln(1-\theta) + \alpha\theta^2) \quad (14)$$

follows from the Frumkin isotherm. π is a function of activity and potential; if θ is a function of π alone, independent of potential, then a specific value of π (and θ) can be obtained either by varying the potential or activity of the organic substance. This means that plots of π vs. $\ln a$ at different potentials should be superimposable by translation along the $\ln a$ axis.

The Frumkin isotherm equation also implies a linear relation between charge and surface excess at constant potential:

$$q = (1-\theta)q_w + \theta Q \quad (15)$$

where q is the charge on the metal, q_w is the charge on the uncovered surface, and Q is the charge on the organically

covered surface. This will be shown in the following development. The Frumkin isotherm equation can be written in the form:

$$Ba = f(\theta) \quad (16)$$

Taking the logarithm of both sides, and differentiating with respect to potential at constant θ , one obtains:

$$\frac{d \ln B}{d V} = - \frac{\partial \ln a}{\partial V} \quad (17)$$

$-dq$ in equation 3 is an exact differential, from this one obtains:

$$-RT\Gamma_m \frac{\partial \ln a}{\partial V} = \frac{\partial q}{\partial \theta} \quad (18)$$

substituting equation 18 into equation 17:

$$\frac{\partial q}{\partial \theta} = RT\Gamma_m \frac{d \ln B}{d V} \quad (19)$$

$$dq = RT\Gamma_m \frac{d \ln B}{d V} d\theta \quad (20)$$

Integrating equation 20 indefinitely, one obtains:

$$q = RT\Gamma_m \left(\frac{d \ln B}{d V} \right) \theta + q' \quad (21)$$

When θ is zero, $q' = q_w$, the charge for the background electrolyte. At $\theta = 1$, $q = Q$ and:

$$Q - q_w = RT\Gamma_m \frac{d \ln B}{d V} \quad (22)$$

Substituting equation 22 into equation 21, one gets:

$$q = (1-\theta)q_w + \theta Q \quad (15)$$

Parsons (40) has used a similar derivation to obtain equation 15. In the absence of specific adsorption, one can model the covered surface as a capacitor with organic substance as the dielectric; in this case, $Q = C_{\text{org}}(V - V_n)$.

Extensive use has been made of the superimposability of π vs. $\ln a$ curves both as a test of the applicability of the Frumkin isotherm and to calculate surface excesses (41-45). The linear charge vs. surface excess plots have not been used to any great extent; in most cases (46,47), they are simply used as a further test of applicability of the Frumkin theory. Breiter and Delahay (48) have used this linear relation to compare surface excesses calculated from equation 15 to those determined thermodynamically from equation 8. However, they used charge vs. potential plots to estimate a value for Q , and made no assumptions about the components of this charge.

The effect of anion specific adsorption on organic adsorption has received surprisingly little attention. The purpose of this study will be to model the double layer on the covered part of the surface, and to allow for specific adsorption on this part of the surface. The linear charge vs. surface excess plots provide a means of determining Q ,

the charge on the covered surface; from these values and the model proposed, an estimate of the amount of anion specific adsorption will be made.

Pentanoic acid and iso-pentanol were chosen for this study due to the fact that earlier work has shown them to be well-represented by the Frumkin equation. Perchloric acid was used as the background electrolyte due to previous experience in this laboratory which has shown HClO_4 to be an electrolyte for which no sticking of the mercury in the capillary occurs. The mercury moves smoothly in the capillary as the pressure is changed; electrocapillary curves taken in HClO_4 are extremely reproducible. Sulfuric acid was chosen as an electrolyte which is less strongly adsorbed than perchloric acid, to provide a further test of the theory. The amount of specific adsorption calculated for sulfuric acid should be less than that for perchloric acid. The study of adsorption of aromatic compounds at the mercury-solution interface has not been done as extensively as for aliphatic compounds; for this reason, benzyl alcohol was studied. Sodium nitrate was used as a background electrolyte to compare capacity curves taken here with results reported previously.

EXPERIMENTAL

Capillary Electrometer

The capillary electrometer used in this study is a modification (49) of the classical apparatus employed by Lippmann (13); it is shown schematically in Figure 5. The apparatus is composed of three sections: the cell containing the capillary, a pressure application and measuring system, and a potentiometer to apply a potential difference across the interface. These sections will be briefly discussed.

The potentiometer applies a known potential between the mercury capillary and a saturated calomel electrode (SCE). The SCE is isolated from the cell in order to minimize contamination of the test solution by chloride ion. Since potassium ion forms an insoluble salt with perchlorate ion, sodium chloride is used in the SCE.

Pressure was applied to the mercury reservoir from a nitrogen tank; fine adjustment of the pressure was made by means of a large (50 ml) syringe. A fused quartz pressure gauge (Texas Instruments) was used to measure the gas pressure over the mercury.

The cell was made from a glass cylinder sealed at each end with optically plane glass to permit viewing of the capillary with a microscope; the capillary was illuminated from the rear to facilitate viewing. Inlets are for the

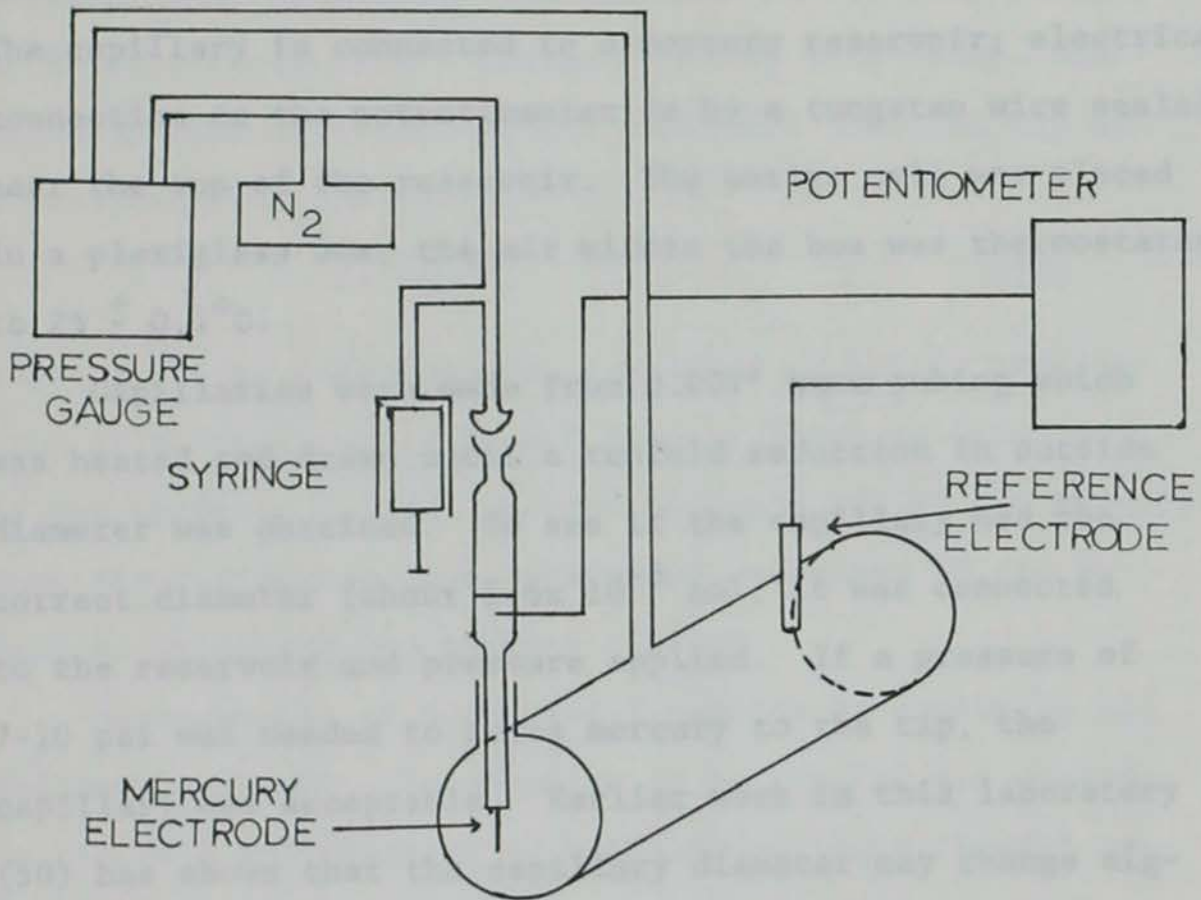


Figure 5. Block diagram for capillary electrometer

reference electrode, a reference pressure for the pressure gauge, and a nitrogen bubbler to deoxygenate solutions. The capillary is connected to a mercury reservoir; electrical connection to the potentiometer is by a tungsten wire sealed near the top of the reservoir. The entire cell was placed in a plexiglass box; the air within the box was thermostated to $25 \pm 0.1^{\circ}\text{C}$.

Capillaries were made from 0.007" bore tubing which was heated and drawn until a tenfold reduction in outside diameter was obtained. To see if the capillary had the correct diameter (about 1.6×10^{-3} cm), it was connected to the reservoir and pressure applied. If a pressure of 7-10 psi was needed to force mercury to the tip, the capillary was acceptable. Earlier work in this laboratory (50) has shown that the capillary diameter may change significantly during the first few weeks of use. Therefore, before any measurements were made with a new capillary, it was allowed to stand in distilled water for at least three weeks. With periodic cleaning in warm, concentrated sulfuric acid, capillaries were usable for several years.

Before using the capillary, it was necessary to determine the radius at some specific position. A scale in the eyepiece of the microscope was used to measure a distance from the capillary tip; the mercury thread was always brought to this position. From earlier work in

this laboratory (49), the surface tension of mercury in contact with 0.1 N HClO₄ was found to be 425.6 dynes cm⁻¹ at the electrocapillary maximum. Using this value, the radius of the capillary at the reference position can be determined from the equation:

$$r = \frac{2\gamma}{F} \quad (23)$$

where r is the radius of the capillary, F is the pressure (sum of nitrogen pressure and mercury head) applied, and γ is the surface tension. A contact angle of 180° is assumed. Once the radius has been determined, equation 23 can be used to calculate the surface tension.

Measurements of interfacial tension were made in the following manner. The solution to be studied was placed in the cell and degassed by bubbling nitrogen through it. In order to minimize loss of volatile organic material, the nitrogen was first passed through a presaturation cell containing a solution of the same composition as that in the cell. The cell was air thermostatted at 25°C for at least one hour to ensure thermal equilibrium.

The electrode was then polarized to a specific potential and several drops of mercury expelled to ensure a clean surface. The mercury was then brought to a position near the reference point until the meniscus became stable. A final pressure adjustment was made to bring the meniscus precisely to the reference point, at which time the

pressure was recorded. A new potential was applied, and the procedure repeated. Measurements were generally made at 50 mV intervals over the region -1.1 V to + 0.2 V vs. SCE. Data were taken starting at -1.1 V in 100 mV intervals to + 0.2 V, then the intermediate 50 mV data were taken starting at + 0.15 V. When data were taken at 25 mV intervals, a similar procedure was followed. At the end of each experiment, the height of the mercury reservoir was measured to determine the pressure head due to mercury.

Capacitance Bridge

The circuit for the capacitance bridge is shown in Figure 6; details of construction have been given previously (47). Its design is similar to that used by Grahame (51) and Damaskin (52). The phase sensitive amplifier produces pulses to start and stop the timer at the birth of a drop and at the balance point. Drop times measured in this manner were reproducible to about 0.01 seconds in an 8-10 second drop. The reference electrode (SCE) was isolated from the cell in a manner similar to that for the capillary electrometer.

The dropping mercury electrode was constructed from 0.85 mm bore tubing which was drawn in the following manner. One end of the tubing was sealed and a portion of the tube

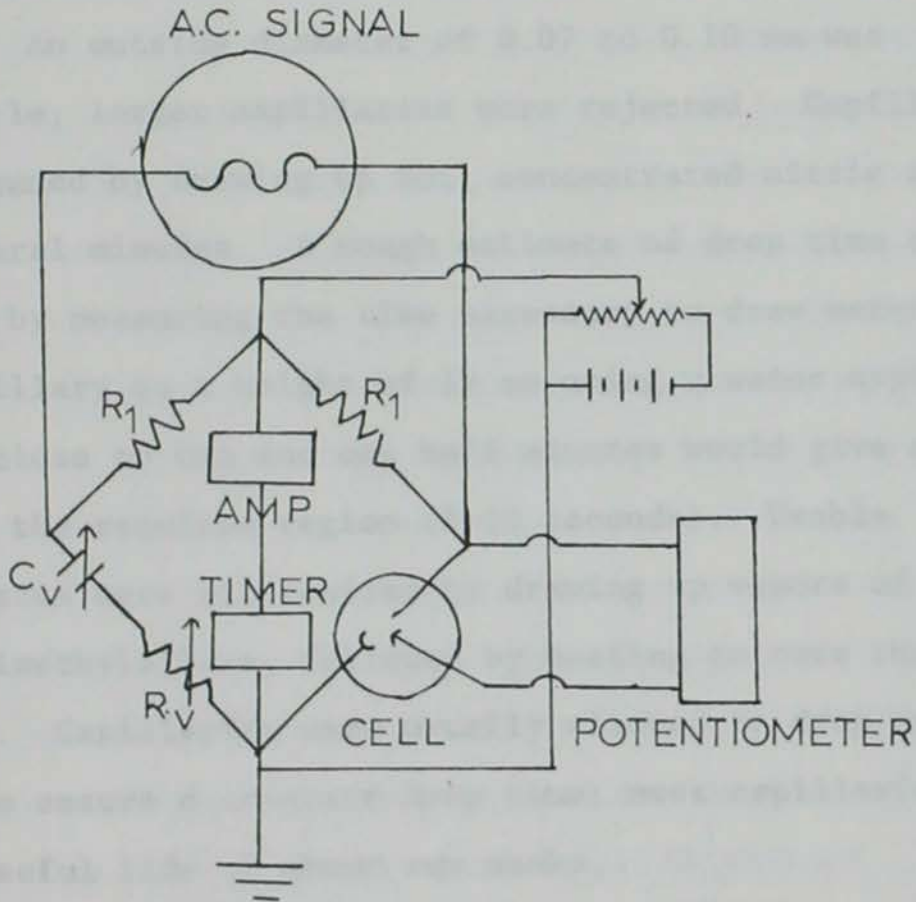


Figure 6. Block diagram for capacitance bridge

was heated and pulled slightly, reducing the outside diameter by about 50%. A small bulb was then blown in this region, increasing the bore to about the original size. This portion of the tube was heated strongly and rapidly pulled. An outside diameter of 0.07 to 0.10 mm was acceptable; larger capillaries were rejected. Capillaries were cleaned by drawing up hot, concentrated nitric acid for several minutes. A rough estimate of drop time could be made by measuring the time necessary to draw water up the capillary to a height of 17 cm using a water aspirator. A time close to two and one half minutes would give a drop time in the required region (8-10 seconds). Usable capillaries were siliconized by drawing up vapors of dichlorodimethylsilane, followed by heating to cure the coating. Capillaries were usually allowed to drop overnight to ensure a constant drop time; most capillaries had a useful life of about two weeks.

Preparation for capacity experiments was basically the same as described for electrocapillary experiments, however, the cell was not thermostated. The lock-in amplifier was tuned by placing a simulated cell in the circuit. This cell consisted of a 500 μ F capacitor and a 90 ohm resistor connected in series. With this system in place, the amplifier was adjusted for maximum response. The A. C. signal was 400 Hz at 3 mV rms; the in phase and

quadrature components were detected by the amplifier. With the amplifier tuned, the simulated cell was replaced by the dropping mercury electrode.

Measurements were again made over the potential range -1.1 V to + 0.2 V (-1.50 V to + 0.2 V for NaF and NaNO₃). In general, measurements were made at 50 mV intervals, but in the region of the capacity peaks, this was reduced to 25 or 12.5 mV. The capacity and resistance were balanced at about 90% of the drop life; measurements made at shorter times agreed within experimental error, indicating that diffusion of adsorbate was complete by the time measurements were made. The drop time, capacity, and resistance at the balance point were recorded; the mercury flow rate was assumed to be constant and was calculated by weighing mercury collected for a known period of time. From the flow rate and drop time, the area of the drop was calculated and the capacity per square centimeter determined.

Materials

The mercury used in both electrocapillary and capacity measurements was triply distilled under vacuum by the Ames Laboratory. It was used as received with no further purification. Water used in preparation of solutions and for glassware cleaning was quadruply distilled, the second stage from alkaline potassium permanganate. Perchloric

acid and sulfuric acid were analytical reagent grade (Fisher Scientific Co.) and were used without further treatment. Sodium fluoride and sodium nitrate were reagent grade (J. T. Baker) and were used without purification. All organic compounds (iso-pentanol, pentanoic acid, and benzyl alcohol) were reagent grade (J. T. Baker) and were used after simple distillation.

All solutions were prepared in the following manner. Stock perchloric and sulfuric acids were titrated to obtain their concentrations in order to make up 0.1 N solutions. Sodium fluoride and sodium nitrate solutions were made by weighing appropriate amounts to make up the required concentrations. The solutions containing organic material were made by adding known volumes of the solute to the background electrolyte. This procedure was used instead of diluting a stock saturated solution so that fresh solutions could be made for each experiment. This was particularly important for the benzyl alcohol studies due to problems described below. Saturation concentrations were 0.227 M, 0.363 M, and 0.381 M for iso-pentanol, pentanoic acid and benzyl alcohol respectively (53).

Initially a stock saturated benzyl alcohol solution (approx. 21) was made, and diluted as necessary for the experiments. After a period of about three weeks, results showed significantly larger errors than earlier experiments

made with fresh solution. When the benzyl alcohol was redistilled and new solution made, these errors disappeared. To check for the presence of oxidizable or reducible species, a crude dropping mercury electrode was constructed and scans taken of perchloric acid, and fresh and old benzyl alcohol solutions; the perchloric acid and three week old benzyl alcohol solutions are shown in Figure 7. The fresh

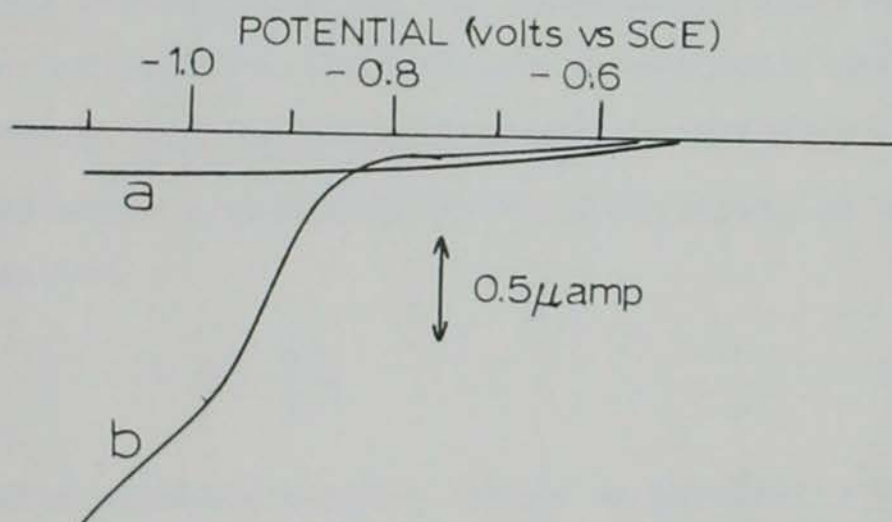


Figure 7. Polarograms of: (a) 0.1 N HClO_4 , (b) 0.1 N HClO_4 and a reduced concentration of benzyl alcohol of 0.0909

solution gave a polarogram which was substantially the same as that for 0.1 N HClO_4 . There is some reducible species present in the old solution not detectable in fresh solution. Benzaldehyde is a starting material for the preparation of benzyl alcohol; a polarogram of this material in perchloric acid was similar to curve b in

Figure 7. It is possible that some air oxidation of benzyl alcohol accounts for the appearance of the impurity after a period of time. When freshly distilled benzyl alcohol was used, periodic checks with the dropping mercury electrode detected no impurity.

These data were converted to differential resistance, and fit by a computer program to a polynomial of degree ten or less. The polynomial with the lowest root mean square deviation between observed and calculated points which had no point of inflection was chosen to represent the data. A polynomial with an inflection point would have a zero (and elsewhere a positive) second derivative; as seen from the equation

$$C = - \frac{d^2}{dx^2} \quad (19)$$

a negative capacity results, which is physically impossible. Using the above equation, it has been shown (34) that double differentiation of the polynomial gives capacities which compare well with experimental capacities for several electrolyte solutions. The coefficients of the polynomials fit to the data are given in Appendix A. Figures 8-11 show the electrocapillary curves for the systems studied.

For each electrode, operating pressure (x) vs. activity (y) plots (at constant potential) were made. Plots for the aliphatic compounds were superimposable

RESULTS AND DISCUSSION

Preliminary Data Treatment

Raw electrocapillary data were taken as degrees of deflection (DOD, output from pressure gauge) vs. potential. These data were converted to interfacial tensions, and fit by a computer program to a polynomial of degree ten or less. The polynomial with the lowest root mean square deviation between observed and calculated points which had no point of inflection was chosen to represent the data. A polynomial with an inflection point would have a zero (and elsewhere a positive) second derivative; as seen from the equation

$$C = - \frac{\partial^2 \gamma}{\partial V^2} \quad (10)$$

a negative capacity results, which is physically impossible. Using the above equation, it has been shown (54) that double differentiation of the polynomial gives capacities which compare well with experimental capacities for several electrolyte solutions. The coefficients of the polynomials fit to the data are given in Appendix A. Figures 8-12 show the electrocapillary curves for the systems studied.

For each adsorbate, spreading pressure (π) vs. $\ln a$ plots (at constant potential) were made. Plots for the aliphatic compounds were superimposable

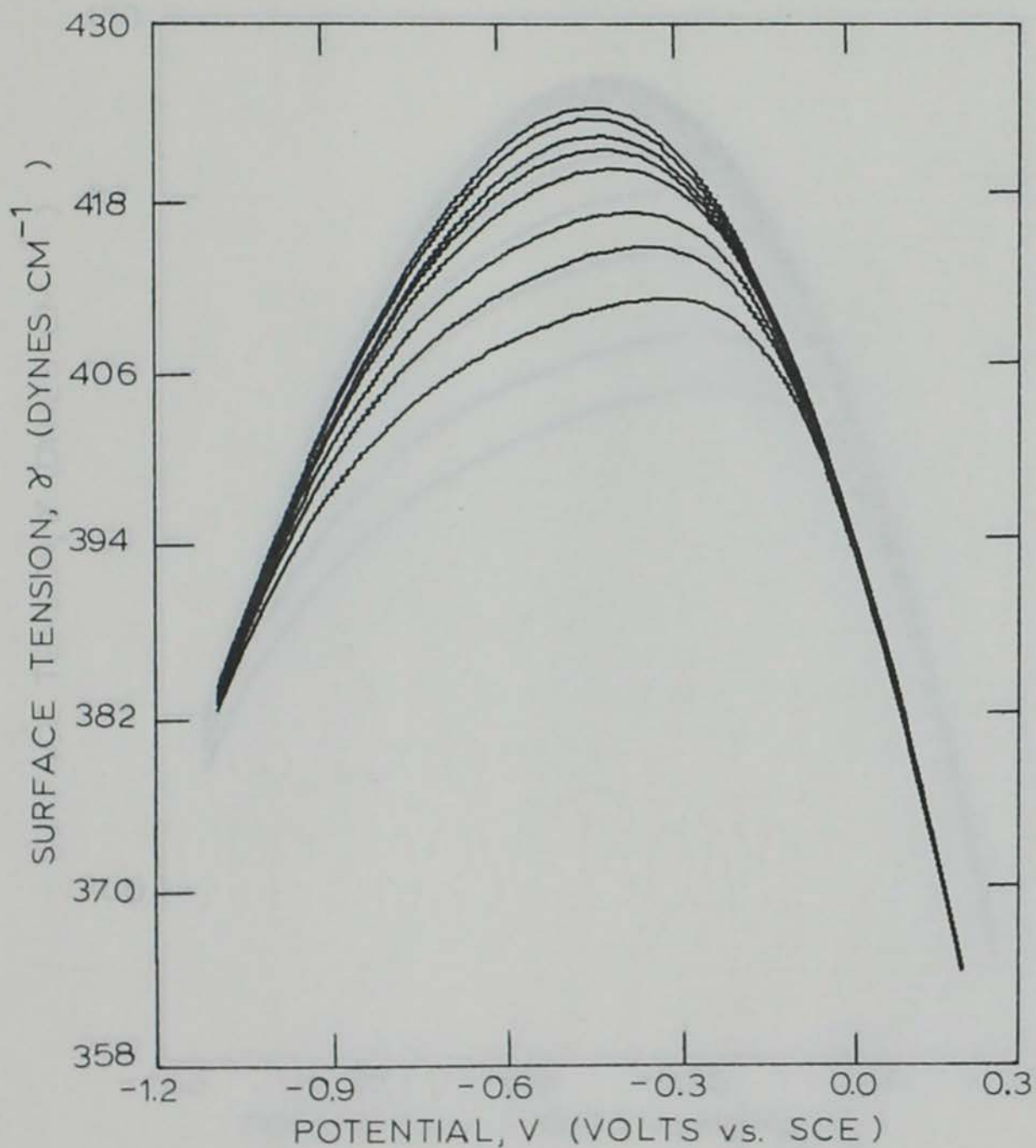


Figure 8. Electrocapillary curves for iso-pentanol in 0.1 N HClO₄. Reduced concentrations (from top) 0.0, 0.0123, 0.0244, 0.0361, 0.0476, 0.0698, 0.0909, 0.1304

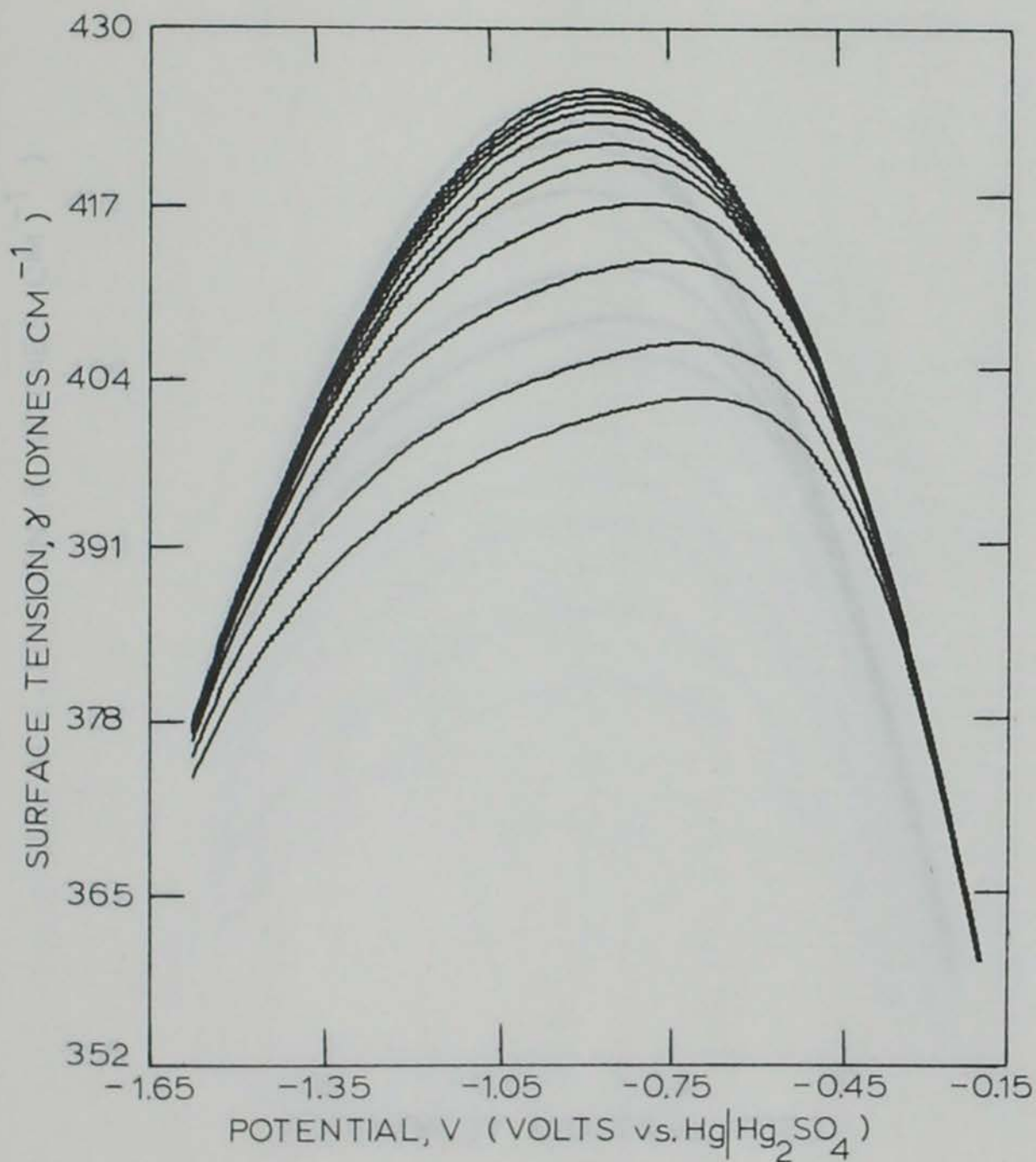


Figure 9. Electrocapillary curves for iso-pentanol in $0.1 \text{ N H}_2\text{SO}_4$. Reduced concentrations (from top) 0.0, 0.0123, 0.0244, 0.0361, 0.0476, 0.0698, 0.0909, 0.1304, 0.2000, 0.3548, 0.5000

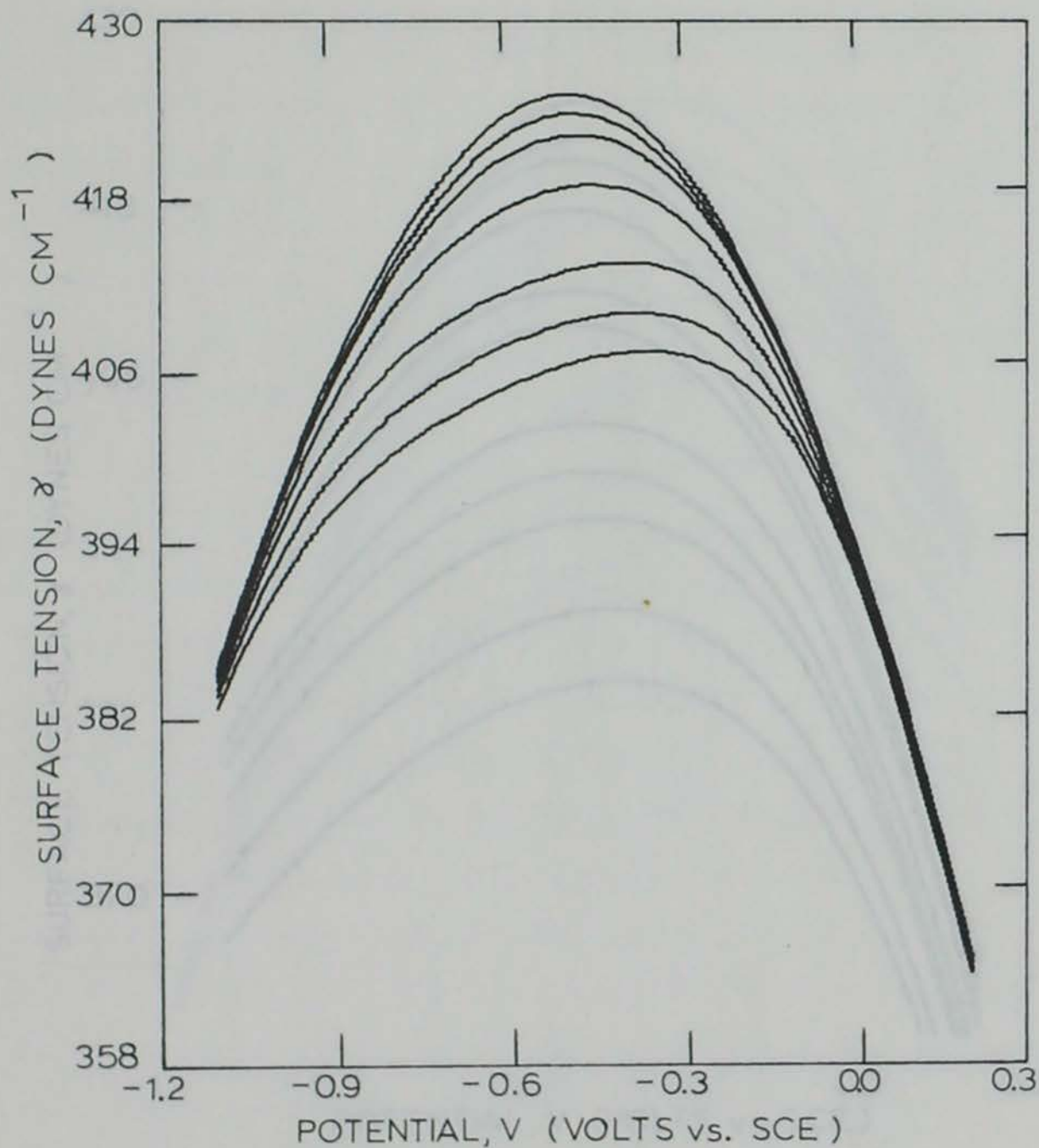


Figure 10. Electrocapillary curves for pentanoic acid in 0.1 N HClO₄. Reduced concentrations (from top) 0.0, 0.0123, 0.0244, 0.0476, 0.0909, 0.1304, 0.1666

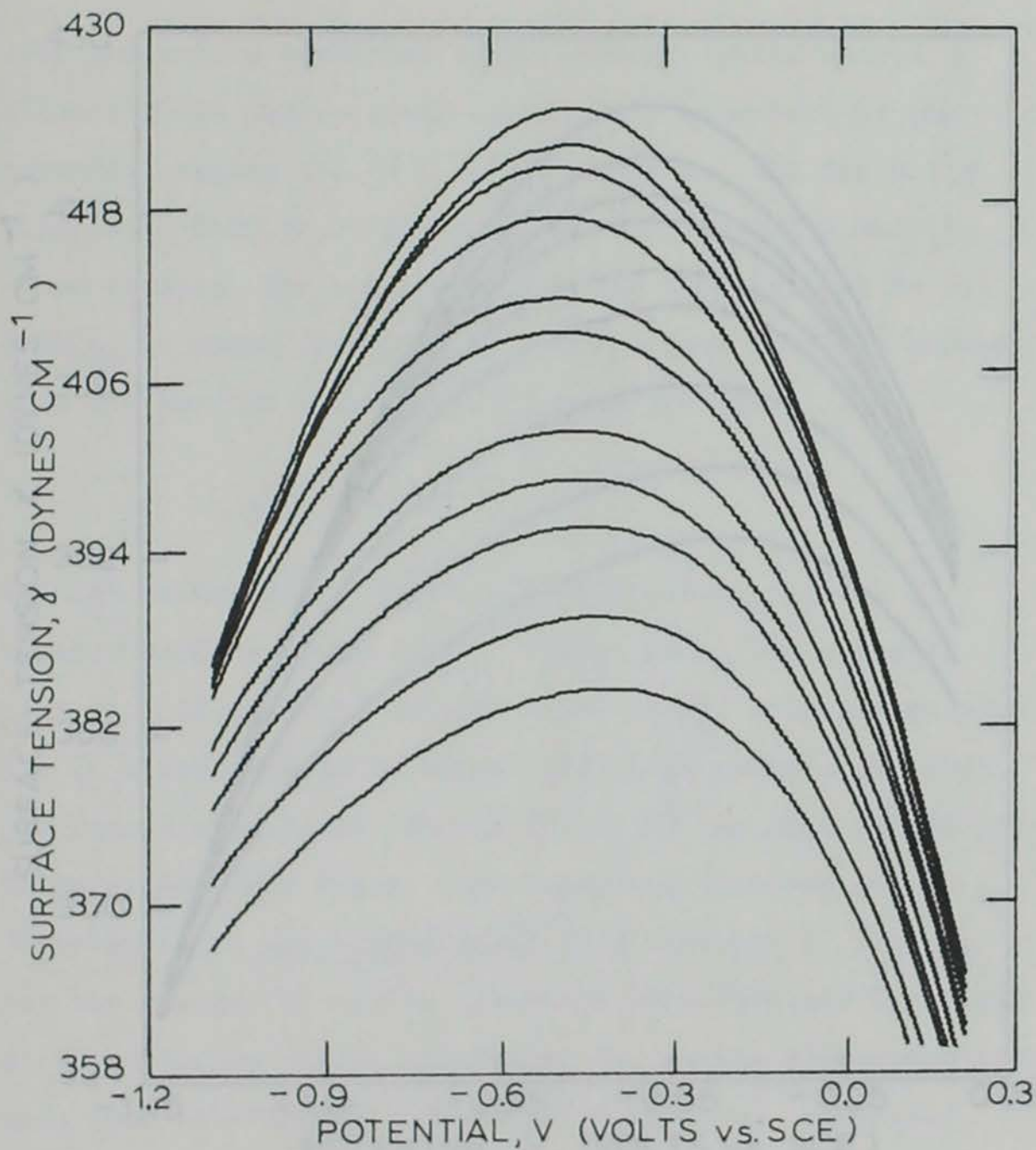


Figure 11. Electrocapillary curves for benzyl alcohol in 0.1 N $HClO_4$. Reduced concentrations (from top) 0.0, 0.0024, 0.0048, 0.0101, 0.0254, 0.0354, 0.0677, 0.1063, 0.1517, 0.2625, 0.3884

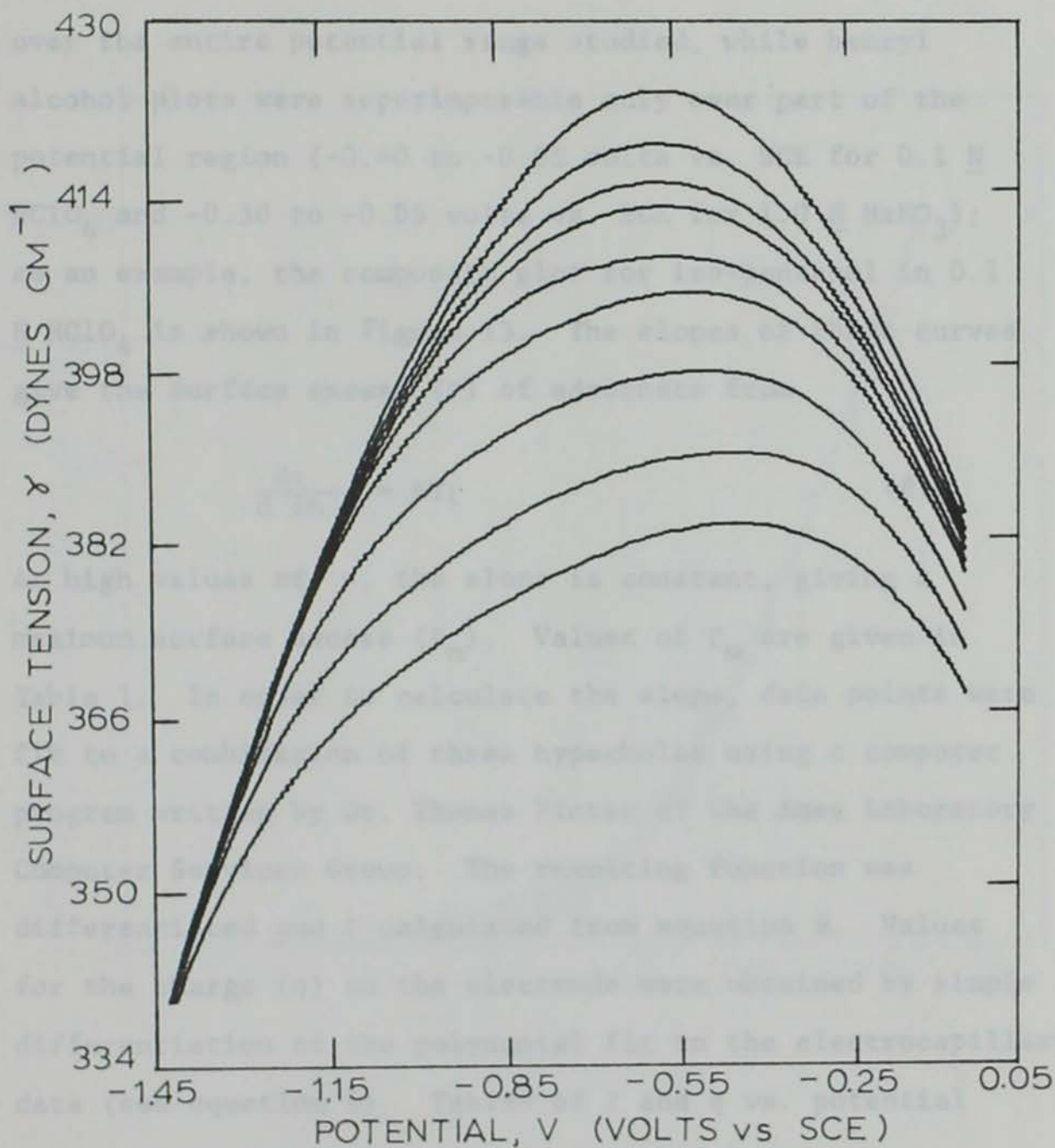


Figure 12. Electrocapillary curves for benzyl alcohol in 1.0 N NaNO_3 . Reduced concentrations (from top) 0.0, 0.0051, 0.0101, 0.0177, 0.0310, 0.0507, 0.1013, 0.2024, 0.3543

over the entire potential range studied, while benzyl alcohol plots were superimposable only over part of the potential region (-0.40 to -0.05 volts vs. SCE for 0.1 N HClO₄ and -0.30 to -0.05 volts vs. SCE for 1.0 N NaNO₃); as an example, the composite plot for iso-pentanol in 0.1 N HClO₄ is shown in Figure 13. The slopes of these curves give the surface excess (Γ) of adsorbate from

$$\frac{d\pi}{d \ln a} = RT\Gamma \quad (8)$$

At high values of π , the slope is constant, giving a maximum surface excess (Γ_m). Values of Γ_m are given in Table 1. In order to calculate the slope, data points were fit to a combination of three hyperbolas using a computer program written by Dr. Thomas Pinter of the Ames Laboratory Computer Services Group. The resulting function was differentiated and Γ calculated from equation 8. Values for the charge (q) on the electrode were obtained by simple differentiation of the polynomial fit to the electrocapillary data (see equation 9). Tables of Γ and q vs. potential for each adsorbate are given in Appendix B.

The data for each adsorbate system were fit to the Frumkin equation using the method of Broadhead, Baikerikar, and Hansen (47). The Frumkin isotherm

$$Ba = \frac{\theta}{1-\theta} e^{-2\alpha\theta} \quad (11)$$

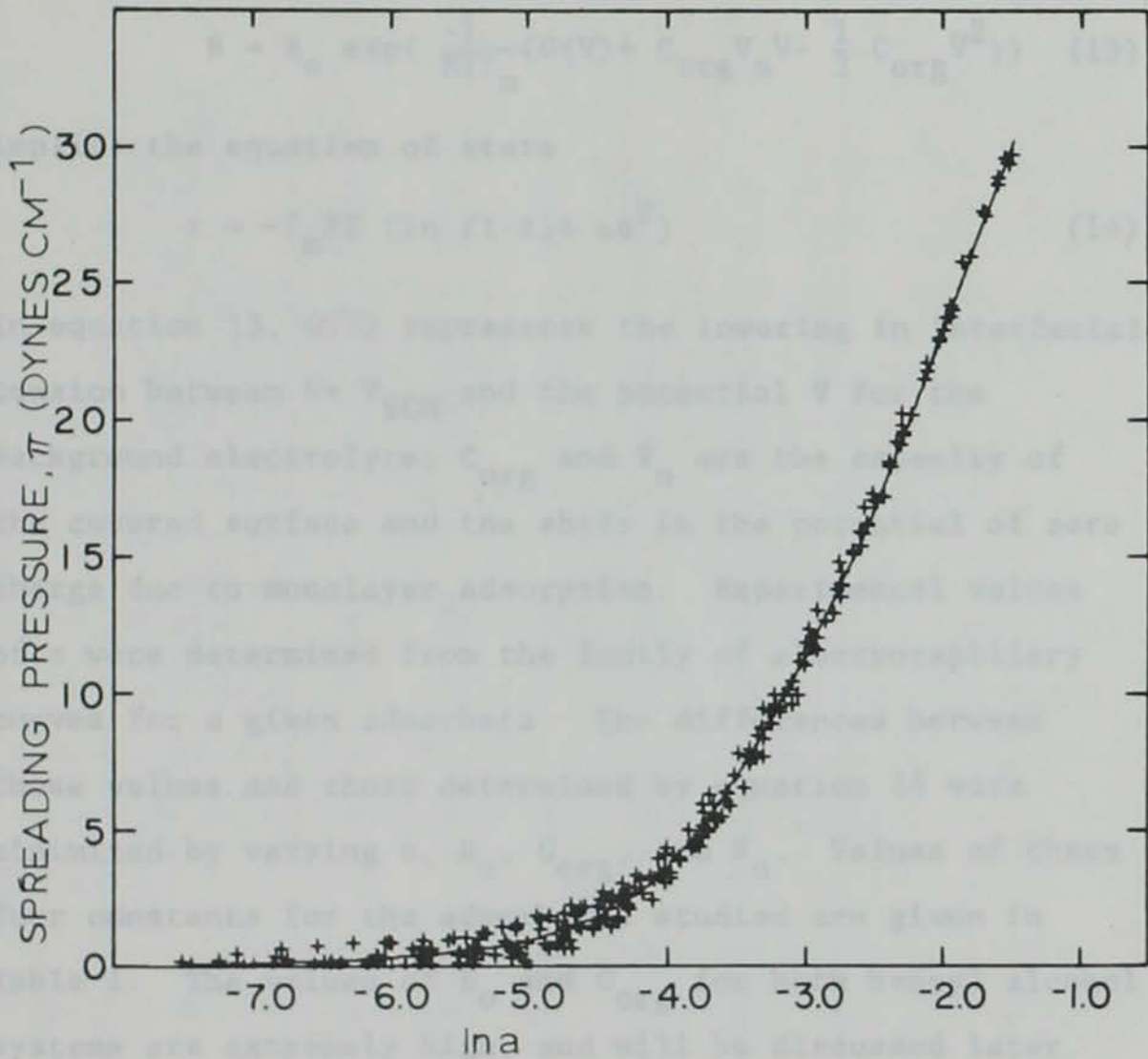


Figure 13. Composite π vs. $\ln a$ plots for iso-pentanol
in 0.1 N HClO_4

with

$$B = B_o \exp\left(\frac{-1}{RT\Gamma_m}(G(V) + C_{org} V_n V - \frac{1}{2} C_{org} V^2)\right) \quad (13)$$

implies the equation of state

$$\pi = -\Gamma_m RT (\ln(1-\theta) + \alpha\theta^2) \quad (14)$$

In equation 13, $G(V)$ represents the lowering in interfacial tension between $V = V_{ECM}$ and the potential V for the background electrolyte; C_{org} and V_n are the capacity of the covered surface and the shift in the potential of zero charge due to monolayer adsorption. Experimental values of π were determined from the family of electrocapillary curves for a given adsorbate. The differences between these values and those determined by equation 14 were minimized by varying α , B_o , C_{org} , and V_n . Values of these four constants for the adsorbates studied are given in Table 1. The values of B_o and C_{org} for both benzyl alcohol systems are extremely high, and will be discussed later. The negative values of α are unusual, but have been observed by Damaskin et al. for pyridine (55) and phenol (56). According to these workers, a negative value of α is explained by a smaller interaction as molecules shift orientation from flat to vertical on the surface.

The Frumkin equation implies a linear relation between charge and surface excess at constant potential,

Table 1. Values of α , B_0 , C_{org} , and V_n as calculated from the Frumkin isotherm

| Adsorbate | α | B_0 | $\frac{C_{org}}{\mu F \text{ cm}^{-2}}$ | $\frac{V_n}{\text{volts vs. ECM}}$ | $\frac{V_{ECM}}{\text{volts vs. SCE}}$ | $\frac{\Gamma_m \times 10^{10}}{\text{moles cm}^{-2}}$ |
|---|----------|-------|---|------------------------------------|--|--|
| iso-pentanol 0.1 N $\underline{\text{HClO}}_4$ | 1.34 | 6.02 | 4.51 | 0.335 | -0.477 | 4.76 |
| iso-pentanol 0.1 N $\underline{\text{H}_2\text{SO}}_4$ | 1.27 | 3.66 | 5.83 | 0.200 | -0.900 | 5.10 |
| pentanoic acid 0.1 N $\underline{\text{HClO}}_4$ | 1.16 | 8.39 | 4.55 | 0.270 | -0.487 | 4.80 |
| benzyl alcohol 0.1 N $\underline{\text{HClO}}_4$ | -0.92 | 173.0 | 16.28 | 0.163 | -0.478 | 4.79 |
| benzyl alcohol 1.0 N $\underline{\text{NaNO}}_3$ | -0.93 | 228.0 | 19.65 | 0.185 | -0.529 | 4.79 |

$$q = (1-\theta) q_w + \theta Q \quad (15)$$

with $Q = C_{\text{org}}(V - V_n)$ and $\theta = \frac{\Gamma}{\Gamma_m}$. The charge on the solution side of the double layer is equal, but of opposite sign, to that on the metal. Plots of charge on the metal vs. Γ are shown in Figures 14-23; except for benzyl alcohol plots made at potentials negative to the ECM, all are linear. (Unless otherwise stated, all potentials will be with respect to the potential of the ECM in the base electrolyte; values of this potential are given in Table 1). The benzyl alcohol q vs. Γ plots are linear over the potential region for which the π vs. $\ln a$ curves are superimposable; it has been proposed (55) that aromatic molecules may have two orientations of adsorption (with ring parallel and perpendicular to the surface), and the curvature may be due to this fact. An additional fact pointing to two-state adsorption can be seen in the movement of the ECM. While it is not apparent in Figures 11 and 12, the potential of the ECM initially moves to more negative potentials for the lowest two or three concentrations before making the usual move to positive potentials with increasing concentration. This initial movement could indicate the presence of a low coverage orientation which is not favored as the surface excess increases.

The least squares slopes and intercepts of the lines

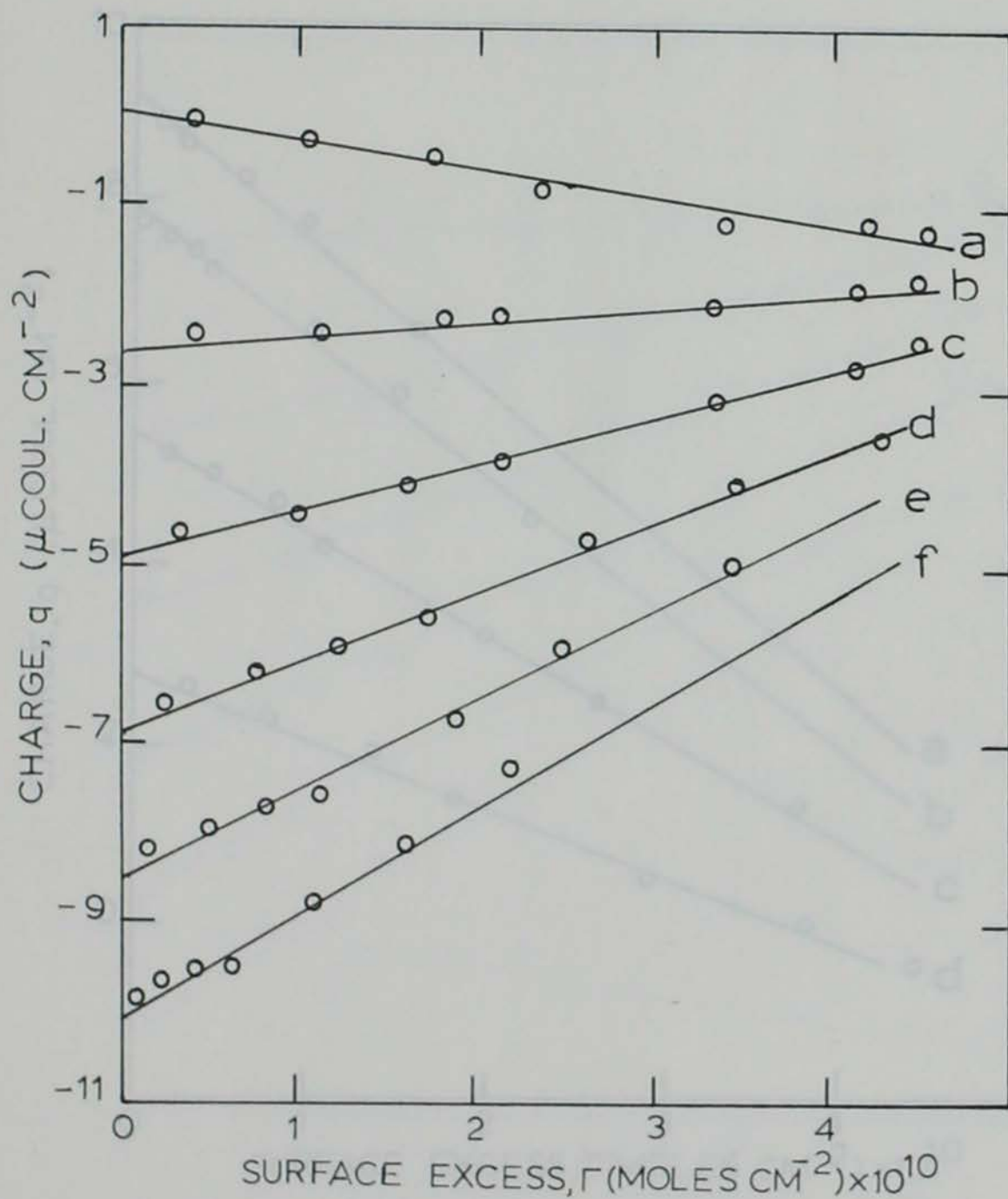


Figure 14. q vs. Γ plots for iso-pentanol in 0.1 N $HClO_4$. Potentials negative to ECM. (a) 0.0, (b) -0.10, (c) -0.20, (d) -0.30, (e) -0.40, (f) -0.50 volts vs. ECM

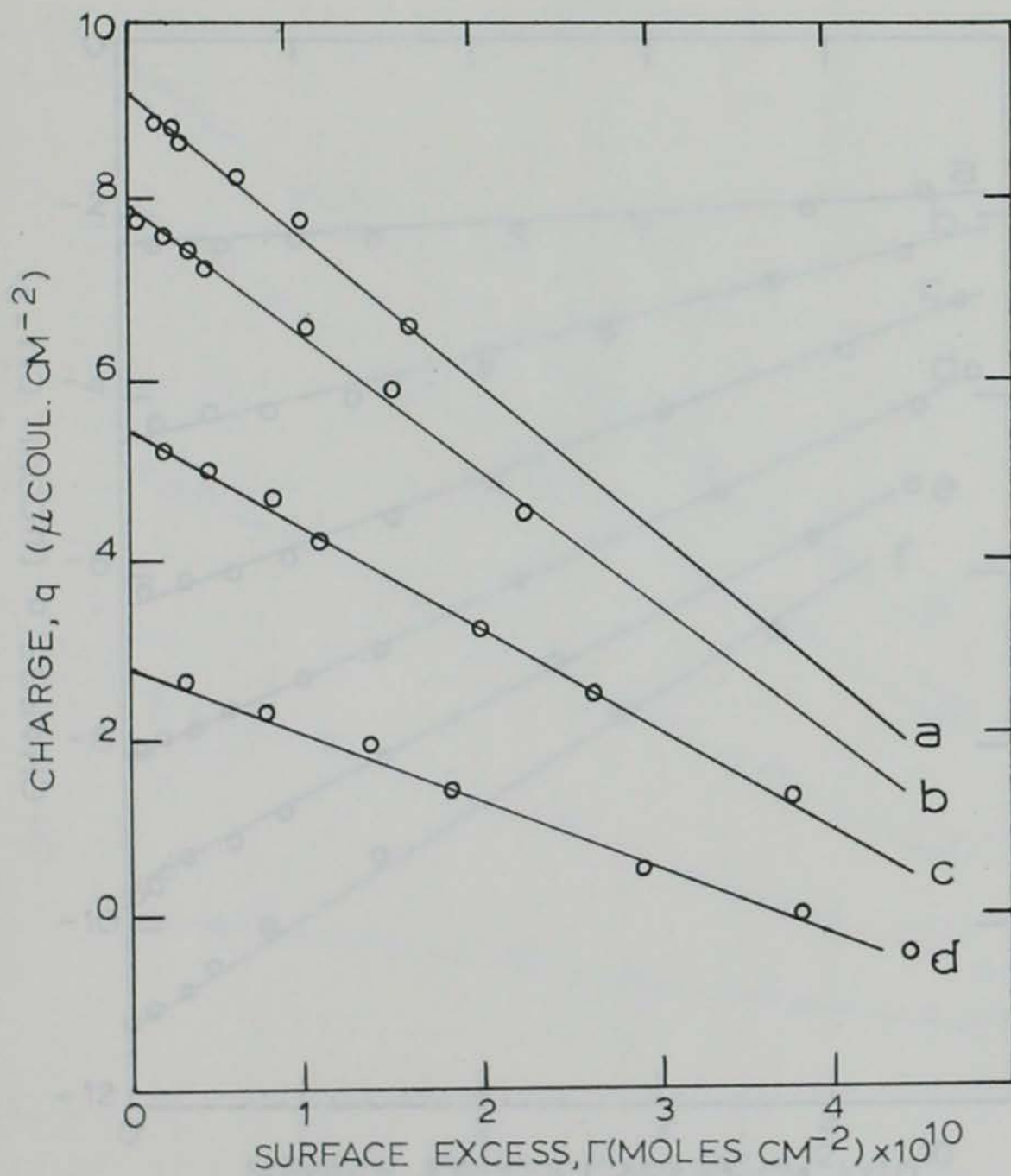


Figure 15. q vs. Γ plots for iso-pentanol in 0.1 N HClO_4 . Potentials positive to ECM. (a) 0.35, (b) 0.30 (c) 0.20, (d) 0.10 volts vs. ECM

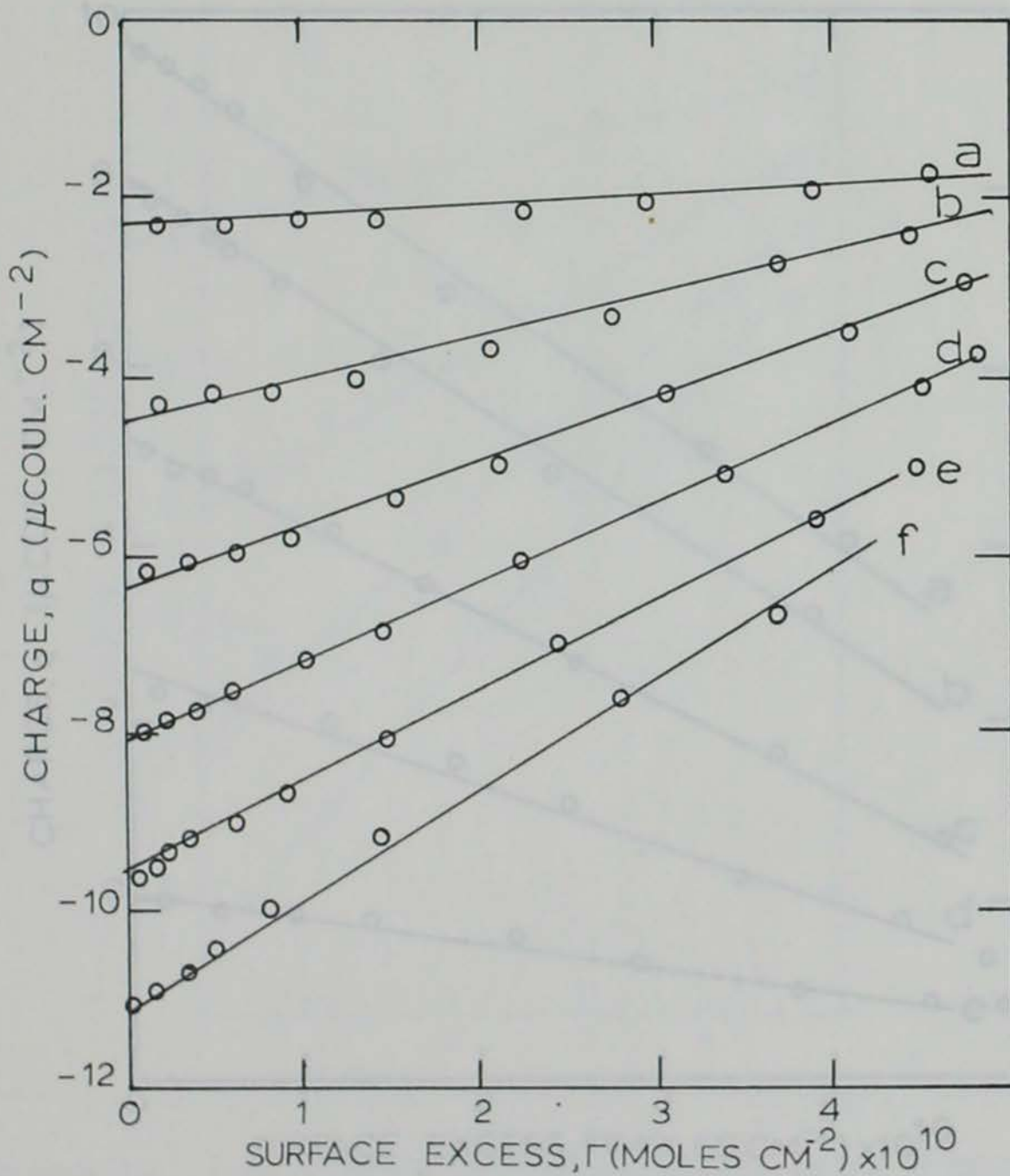


Figure 16. q vs. Γ plots for iso-pentanol in 0.1 N H_2SO_4 . Potential negative to ECM. (a) -0.10, (b) -0.20 (c) -0.30, (d) -0.40, (e) -0.50, (f) -0.60 volts vs. ECM

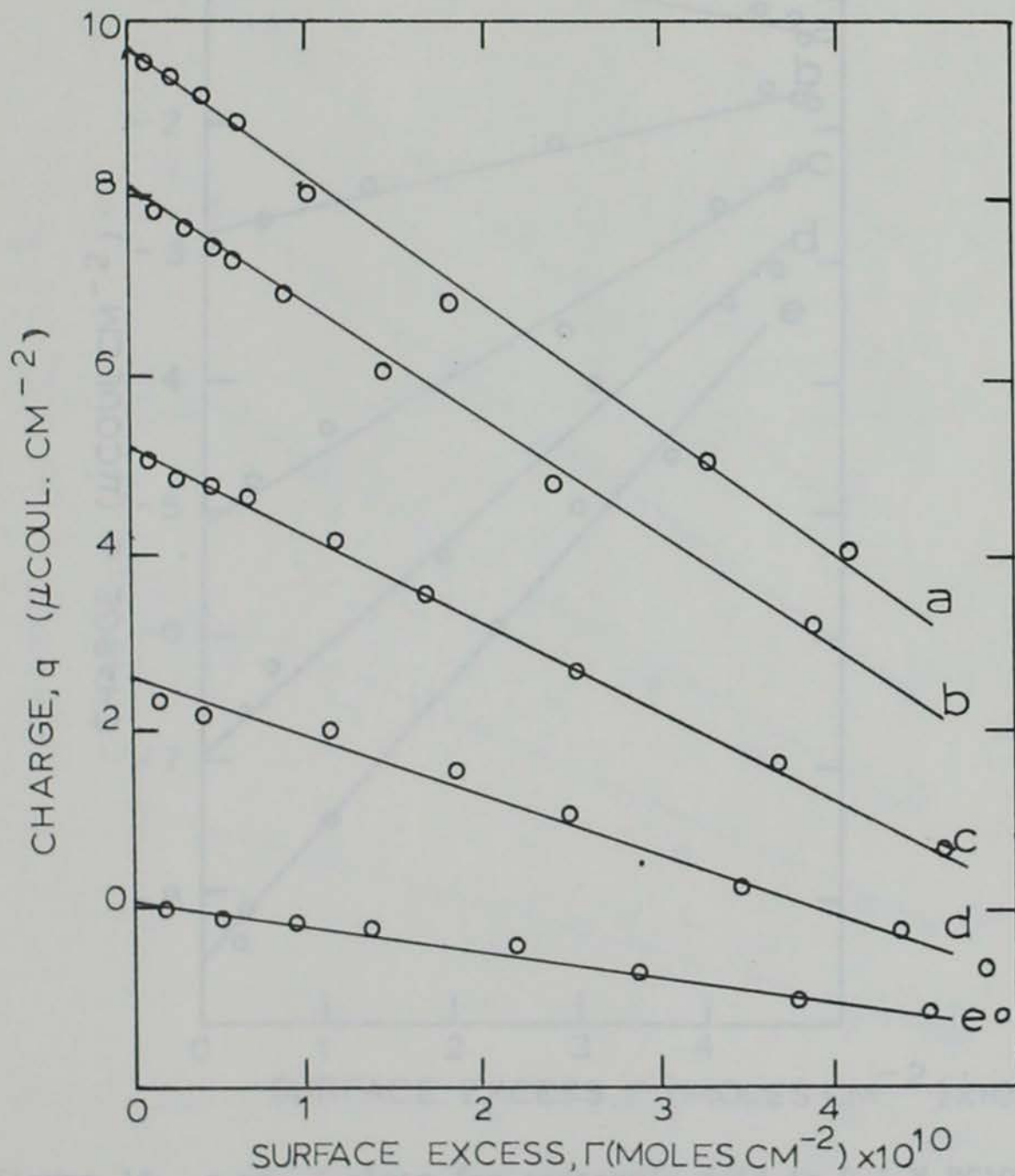


Figure 17. q vs. Γ plots for iso-pentanol in 0.1 N H_2SO_4 . Potentials positive to ECM. (a) 0.35, (b) 0.30, (c) 0.20, (d) 0.10, (e) 0.0 volts vs. ECM

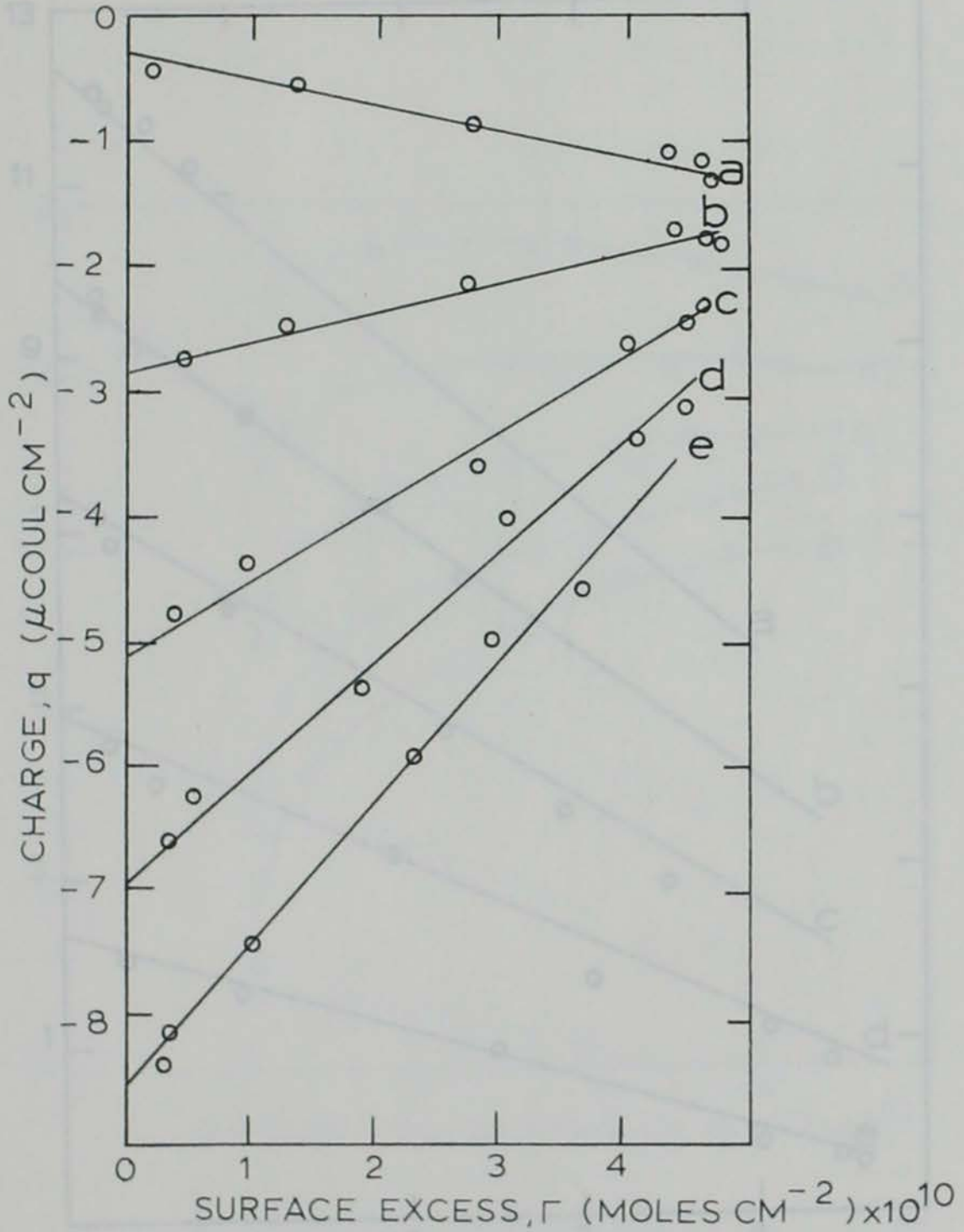


Figure 18. q vs. Γ plots for pentanoic acid in 0.1 N HClO_4 . Potentials negative to ECM. (a) -0.013, (b) -0.113, (c) -0.213, (d) -0.313, (e) -0.413 volts vs. ECM

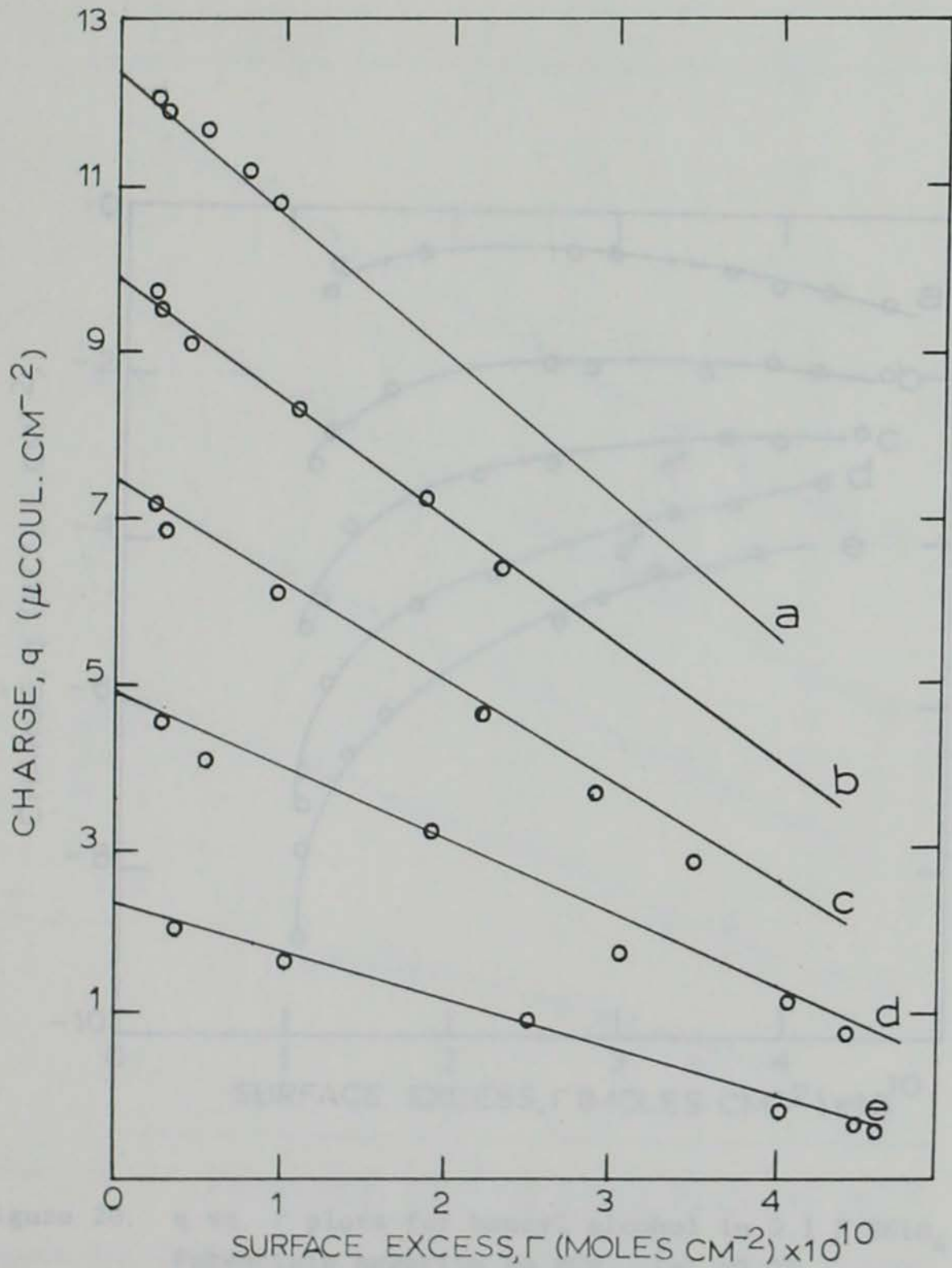


Figure 19. q vs. Γ plots for pentanoic acid in 0.1 N HClO_4 . Potentials positive to ECM. (a) 0.487, (b) 0.387, (c) 0.287, (d) 0.187, (e) 0.087 volts vs. ECM

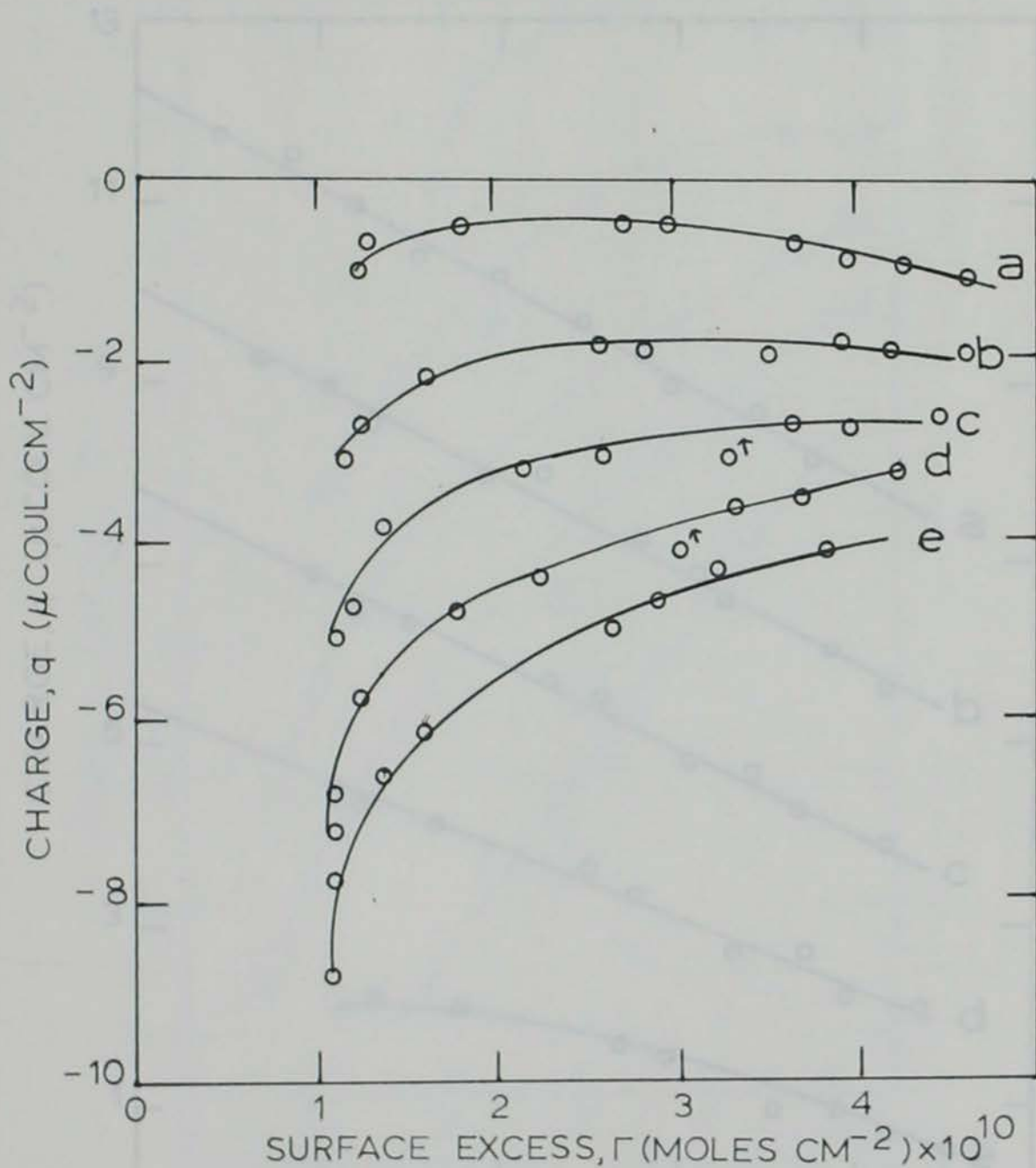


Figure 20. q vs. Γ plots for benzyl alcohol in 0.1 N HClO_4 . Potentials negative to ECM. (a) -0.05, (b) -0.15, (c) -0.25, (d) -0.35, (e) -0.45 volts vs. ECM

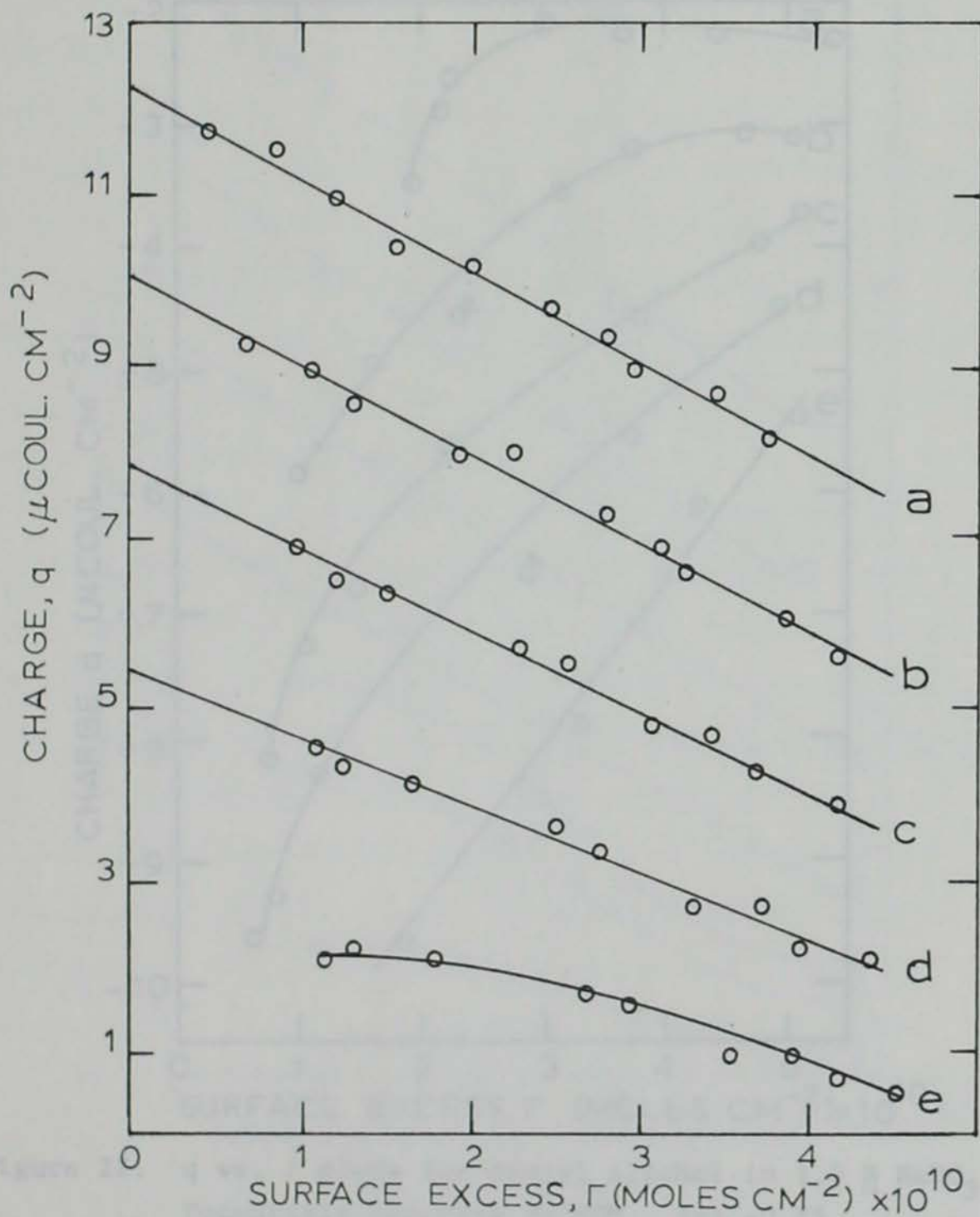


Figure 21. q vs. Γ plots for benzyl alcohol in 0.1 N HClO_4 . Potentials positive to ECM. (a) 0.487, (b) 0.387, (c) 0.287, (d) 0.187, (e) 0.087 volts vs. ECM

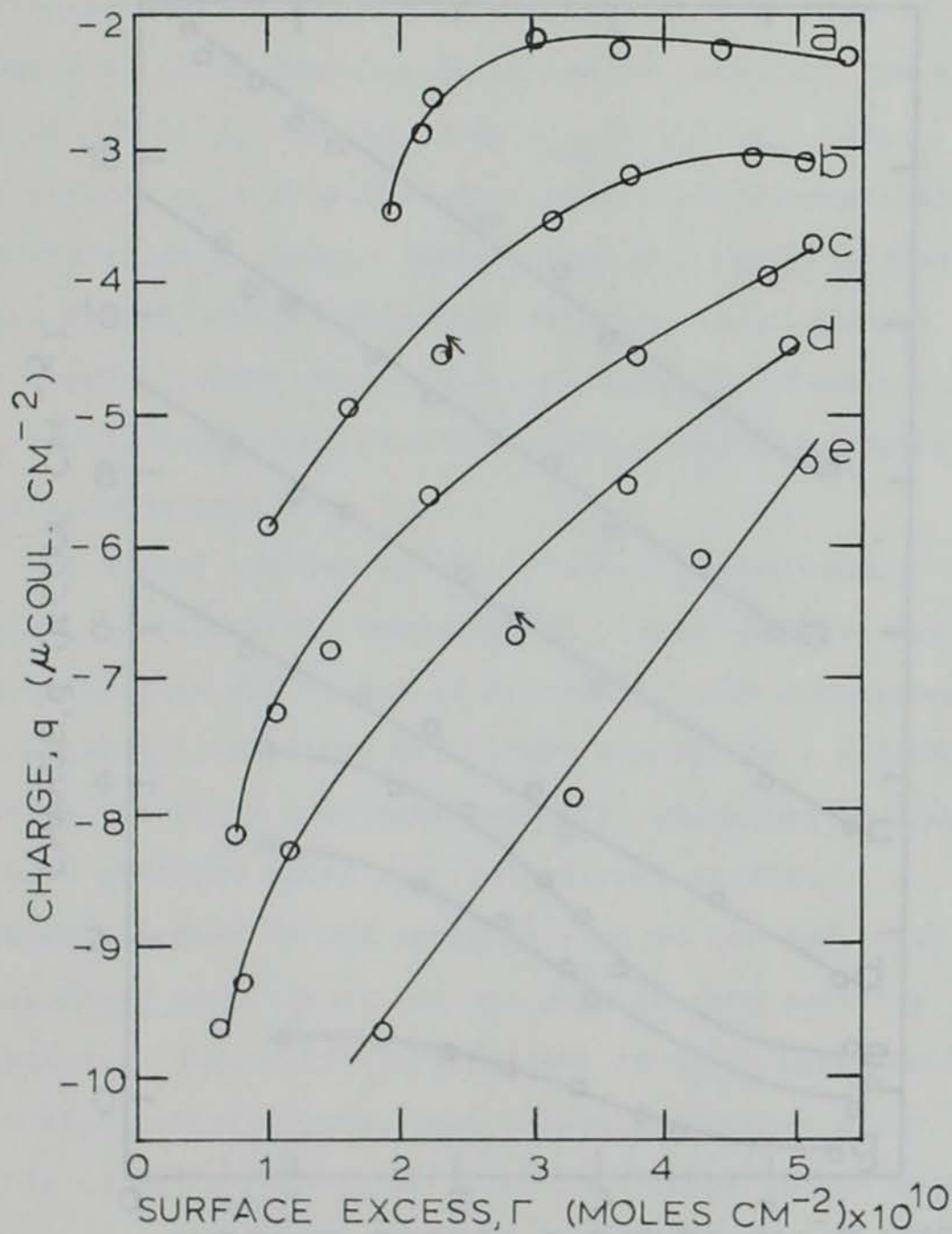


Figure 22. q vs. Γ plots for benzyl alcohol in 1.0 N NaNO_3 . Potentials negative to ECM. (a) -0.15, (b) -0.25, (c) -0.35, (d) -0.45, (e) -0.55 volts vs. ECM

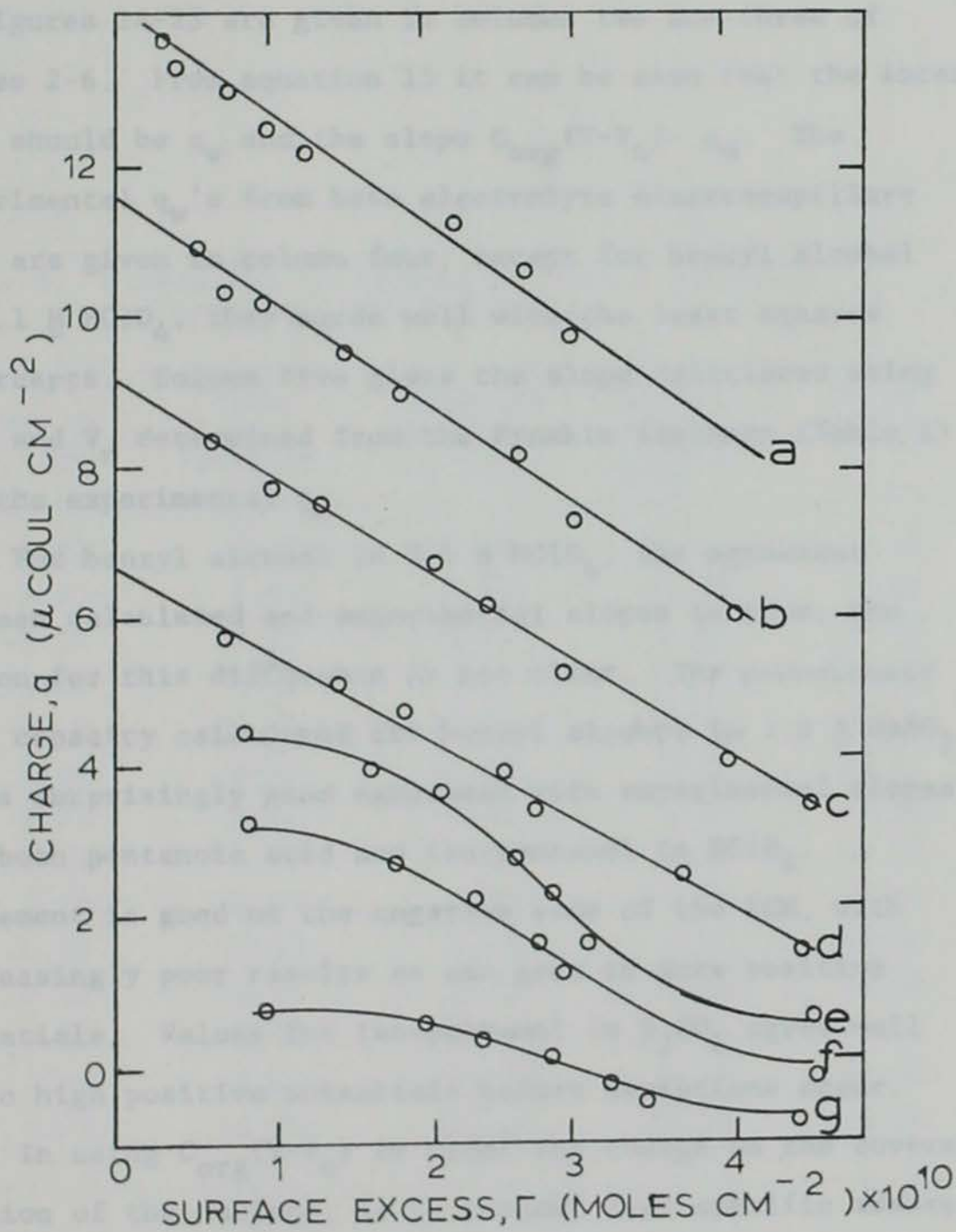


Figure 23. q vs. Γ plots for benzyl alcohol in 1.0 N NaNO_3 . Potentials positive to ECM. (a) 0.530, (b) 0.430, (c) 0.330, (d) 0.230, (e) 0.180, (f) 0.130, (g) 0.030 volts vs. ECM

in Figures 14-23 are given in columns two and three of Tables 2-6. From equation 15 it can be seen that the intercept should be q_w and the slope $C_{org}(V-V_n) - q_w$. The experimental q_w 's from base electrolyte electrocapillary data are given in column four; except for benzyl alcohol in 0.1 N $HClO_4$, they agree well with the least squares intercepts. Column five gives the slope calculated using C_{org} and V_n determined from the Frumkin isotherm (Table 1), and the experimental q_w .

For benzyl alcohol in 0.1 N $HClO_4$, the agreement between calculated and experimental slopes is poor; the reason for this difference is not clear. The anomalously high capacity calculated for benzyl alcohol in 1.0 N $NaNO_3$ gives surprisingly good agreement with experimental slopes. For both pentanoic acid and iso-pentanol in $HClO_4$, agreement is good on the negative side of the ECM, with increasingly poor results as one goes to more positive potentials. Values for iso-pentanol in H_2SO_4 agree well up to high positive potentials before deviations occur.

In using $C_{org}(V-V_n)$ to model the charge on the covered portion of the surface, it is assumed that specific adsorption is absent. Cations are more highly hydrated than anions, so specific adsorption of cations is unlikely. This accounts for the excellent agreement between calculated and experimental slopes at potentials negative to the ECM.

Table 1. Slopes and intercepts of q vs. Γ lines for iso-pentanol in 0.1 N HClO_4

Table 2. Slopes and intercepts of q vs. Γ lines for iso-pentanol in 0.1 N HClO_4

| $\frac{V}{\text{volts}}$ vs. ECM | Slope least sq. | Intercept least sq. $\mu\text{C cm}^{-2}$ | Intercept exptl. $\mu\text{C cm}^{-2}$ | Slope exptl. |
|-------------------------------------|--------------------|---|--|-----------------|
| -0.50 | 1.24 | -10.10 | -10.03 | 1.32 |
| -0.40 | 1.01 | -8.53 | -8.38 | 1.06 |
| -0.30 | 0.77 | -7.84 | -6.67 | 0.80 |
| -0.20 | 0.52 | -4.91 | -4.76 | 0.49 |
| -0.10 | 0.16 | -2.63 | -2.52 | 0.12 |
| 0.00 | -0.31 | 0.03 | 0.01 | -0.32 |
| 0.05 | -0.54 | 1.42 | 1.36 | -0.56 |
| 0.10 | -0.76 | 2.80 | 2.72 | -0.79 |
| 0.15 | -0.95 | 4.12 | 4.08 | -1.03 |
| 0.20 | -1.13 | 5.43 | 5.41 | -1.26 |
| 0.25 | -1.33 | 6.72 | 6.70 | -1.49 |
| 0.30 | -1.49 | 7.94 | 7.94 | -1.71 |
| 0.35 | -1.63 | 9.14 | 9.13 | -1.90 |
| 0.40 | -1.73 | 10.34 | 10.29 | -2.10 |

Table 3. Slopes and intercepts of q vs. Γ lines for iso-pentanol in $0.1 \text{ N H}_2\text{SO}_4$

| $\frac{V}{\text{volts}}$ vs. ECM | Slope least sq. | Intercept least sq. $\mu\text{C cm}^{-2}$ | Intercept exptl. $\mu\text{C cm}^{-2}$ | Slope exptl. |
|-------------------------------------|--------------------|---|--|-----------------|
| -0.60 | 1.19 | -10.98 | -11.11 | 1.24 |
| -0.55 | 1.09 | -10.29 | -10.36 | 1.17 |
| -0.50 | 1.02 | -9.57 | -9.59 | 1.08 |
| -0.45 | 0.95 | -8.80 | -8.81 | 0.99 |
| -0.40 | 0.87 | -8.02 | -7.99 | 0.89 |
| -0.35 | 0.79 | -7.23 | -7.14 | 0.79 |
| -0.30 | 0.70 | -6.36 | -6.25 | 0.67 |
| -0.25 | 0.59 | -5.48 | -5.52 | 0.55 |
| -0.20 | 0.46 | -4.51 | -4.54 | 0.42 |
| -0.15 | 0.31 | -3.46 | -3.42 | 0.27 |
| -0.10 | 0.13 | -2.34 | -2.25 | 0.11 |
| -0.05 | -0.07 | -1.15 | -1.13 | -0.07 |
| 0.00 | -0.27 | 0.06 | 0.05 | -0.24 |
| 0.05 | -0.46 | 1.32 | 1.27 | -0.43 |
| 0.10 | -0.67 | 2.61 | 2.55 | -0.62 |
| 0.15 | -0.84 | 3.88 | 3.89 | -0.81 |
| 0.20 | -1.00 | 5.21 | 5.27 | -1.01 |
| 0.25 | -1.09 | 6.54 | 6.71 | -1.26 |
| 0.30 | -1.25 | 8.07 | 8.20 | -1.45 |
| 0.35 | -1.42 | 9.67 | 9.74 | -1.70 |

Table 4. Slopes and intercepts of q vs. r lines for pentanoic acid in 0.1 N HClO_4

| $\frac{V}{\text{volts}}$ vs. ECM | Slope least sq. | Intercept least sq. $\mu\text{C cm}^{-2}$ | Intercept exptl. $\mu\text{C cm}^{-2}$ | Slope exptl. |
|-------------------------------------|--------------------|---|--|-----------------|
| -0.413 | 1.13 | -8.53 | -8.54 | 1.13 |
| -0.313 | 0.84 | -6.76 | -6.89 | 0.88 |
| -0.213 | 0.57 | -4.97 | -5.03 | 0.59 |
| -0.113 | 0.23 | -2.78 | -2.82 | 0.22 |
| -0.013 | -0.18 | -0.33 | -0.31 | -0.20 |
| 0.037 | -0.42 | 1.10 | 1.01 | -0.43 |
| 0.087 | -0.57 | 2.23 | 2.32 | -0.66 |
| 0.137 | -0.75 | 3.50 | 3.63 | -0.88 |
| 0.187 | -0.90 | 4.73 | 4.92 | -1.11 |
| 0.237 | -1.07 | 6.03 | 6.19 | -1.32 |
| 0.287 | -1.27 | 7.37 | 7.43 | -1.53 |
| 0.337 | -1.42 | 8.67 | 8.67 | -1.75 |
| 0.387 | -1.48 | 9.92 | 9.89 | -1.95 |
| 0.437 | -1.58 | 11.20 | 11.10 | -2.16 |
| 0.487 | -1.65 | 12.44 | 12.30 | -2.36 |

Table 5. Slopes and intercepts of q vs. Γ lines for benzyl alcohol in 0.1 N HClO_4

| $\frac{V}{\text{volts}}$ vs. ECM | Slope least sq. | Intercept least sq. $\mu\text{C cm}^{-2}$ | Intercept exptl. $\mu\text{C cm}^{-2}$ | Slope exptl. |
|-------------------------------------|--------------------|---|--|-----------------|
| 0.128 | -0.68 | 4.23 | 3.81 | -0.91 |
| 0.178 | -0.80 | 5.44 | 5.11 | -1.02 |
| 0.228 | -0.90 | 6.68 | 6.34 | -1.10 |
| 0.278 | -0.96 | 7.81 | 7.51 | -1.18 |
| 0.328 | -1.03 | 9.01 | 8.61 | -1.24 |
| 0.378 | -1.04 | 10.05 | 9.85 | -1.33 |
| 0.428 | -1.09 | 11.24 | 11.08 | -1.42 |
| 0.478 | -1.08 | 12.27 | 12.35 | -1.51 |

Table 6. Slopes and intercepts of q vs. Γ lines for benzyl alcohol in 1.0 N NaNO_3

| $\frac{V}{\text{volts}}$ vs. ECM | Slope least sq. | Intercept least sq. $\mu\text{C cm}^{-2}$ | Intercept exptl. $\mu\text{C cm}^{-2}$ | Slope exptl. |
|-------------------------------------|--------------------|---|--|-----------------|
| 0.23 | -1.09 | 6.73 | 6.61 | -1.20 |
| 0.28 | -1.19 | 7.99 | 7.92 | -1.26 |
| 0.33 | -1.23 | 9.14 | 9.15 | -1.32 |
| 0.38 | -1.30 | 10.38 | 10.37 | -1.36 |
| 0.43 | -1.34 | 11.57 | 11.58 | -1.41 |
| 0.48 | -1.42 | 12.81 | 12.84 | -1.47 |
| 0.53 | -1.40 | 13.99 | 14.15 | -1.54 |

It has been shown (57) that while both sulfate and perchlorate anions are specifically adsorbed, perchlorate is more strongly adsorbed at potentials near the ECM. Comparison of slopes in Table 3 for iso-pentanol in 0.1 \underline{N} H_2SO_4 indicate that no specific adsorption occurs until about 0.25 volts vs. ECM, while for perchloric acid solutions, specific adsorption is present at about 0.10 volts vs. ECM (Tables 2 and 4).

Based on the above data, a modification in equation 15 is made to account for the presence of specific adsorption on the organically covered part of the surface:

$$q = (1-\theta) q_w + \theta(q_{org} + q'_{sp}) \quad (24)$$

where q'_{sp} represents the charge due to specifically adsorbed anions. The model for the double layer which will be discussed next will consider only the covered part of the surface. Any values of charge or capacity pertaining to the uncovered surface will be taken from the experimental background electrolyte data.

Model for the Covered Portion of the Surface

The following model for the double layer on the covered portion of the electrode is proposed (see Figure 24). The entire potential is dropped across regions I and II; a diffuse layer is not considered. Region I contains only water molecules and specifically adsorbed anions.

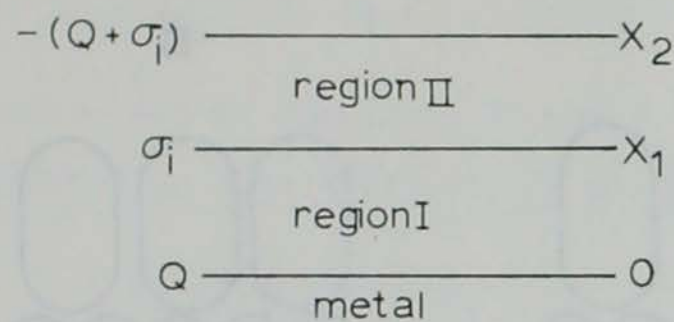


Figure 24. Model for the double layer showing distribution of charges

Since this model is only for the covered part of the surface, region II contains organic molecules exclusively. Cations or anions necessary to balance the surface charge are outside region II. X_1 and X_2 are the distances from the electrode for the boundaries of regions I and II. Q is the charge on the electrode, σ_i is the charge at the boundary for region I (in the absence of specific adsorption, σ_i is zero), and $-(Q + \sigma_i)$ is the charge at the boundary for region II. For the concentrations of background electrolyte used, this charge can be considered to be in a monolayer at the boundary, and a distribution of excess charge in the diffuse layer is ignored. The physical arrangement of molecules would be as shown in Figure 25.

For a region of uniform electric field, one can write the electric displacement D as:

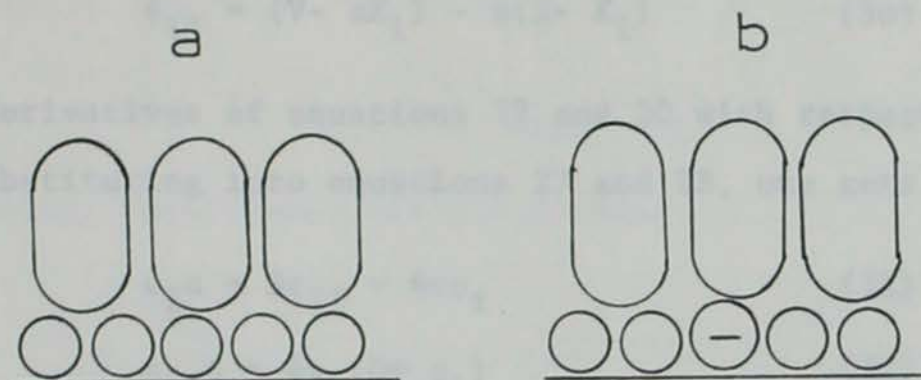


Figure 25. Physical arrangement of molecules within the double layer. (a) absence of specific adsorption, (b) presence of specific adsorption

$$D_i = D_{i+1} - 4\pi q_{i+1} \quad (25)$$

where i and $i+1$ are adjoining regions and q_{i+1} is the charge on the $i+1$ boundary, with D_i defined as:

$$D_i = -\epsilon_i \frac{d\psi}{dx} \quad (26)$$

where ϵ is the dielectric constant of the region and $\frac{d\psi}{dx}$ is the potential gradient. The following equations can be written for D in regions I and II of Figure 24:

$$-\epsilon_I \left(\frac{d\psi}{dx} \right)_I = -\epsilon_{II} \left(\frac{d\psi}{dx} \right)_{II} - 4\pi\sigma_i \quad (27)$$

$$-\epsilon_{II} \left(\frac{d\psi}{dx} \right)_{II} = 0 + 4\pi(Q + \sigma_i) \quad (28)$$

Assuming a linear potential drop in both regions,

$$\psi_I = V - \alpha x \quad (29)$$

$$\psi_{II} = (V - \alpha X_1) - \beta(X_2 - X_1) \quad (30)$$

Taking derivatives of equations 29 and 30 with respect to x and substituting into equations 27 and 28, one gets

$$\epsilon_I \alpha = \beta \epsilon_{II} - 4\pi \sigma_i \quad (31)$$

$$\epsilon_{II} \beta = 4\pi (Q + \sigma_i) \quad (32)$$

Solving for β and α

$$\beta = \frac{4\pi (Q + \sigma_i)}{\epsilon_{II}} \quad (33)$$

$$\alpha = \frac{4\pi Q}{\epsilon_I} \quad (34)$$

The potential applied to the electrode is then:

$$V = \alpha X_1 + \beta(X_2 - X_1) \quad \text{or,} \quad (35)$$

$$V = \left[\frac{4\pi X_1}{\epsilon_I} \right] Q + \left[\frac{4\pi (X_2 - X_1)}{\epsilon_{II}} \right] (Q + \sigma_i) \quad (36)$$

The terms in brackets are of capacity form, and equation 36 can be written:

$$V = \frac{Q}{C_1} + \frac{Q + \sigma_i}{C_2} \quad (37)$$

From the model for the charge distribution discussed

previously:

$$q = (1-\theta) q_w + \theta(q_{org} + q'_{sp}) \quad (24)$$

the following identifications can be made.

$$q'_{sp} = -\sigma_i \quad (38a)$$

$$q_{org} = (Q + \sigma_i) \quad (38b)$$

$$q'_{sp} + q_{org} = Q \quad (38c)$$

The slope $(\frac{dq}{d\theta})$ of equation 24 is $q_{org} + q'_{sp} - q_w$; using the least squares slope calculated previously and equation 38c, one can calculate Q:

$$Q = \left(\frac{dq}{d\theta}\right)_V + q_w \quad (39)$$

Solving equation 37 for σ_i ,

$$\sigma_i = C_2 V - Q \left(\frac{C_2}{C_1} + 1\right) \quad (40)$$

Assuming values for C_1 and C_2 , one can calculate the amount of specifically adsorbed charge on the covered portion of the electrode. A method of estimating C_1 and C_2 will be discussed next.

In the absence of specific adsorption, σ_i is zero, and equation 40 can be written:

$$Q = \frac{C_2 C_1}{C_1 + C_2} V \quad (41)$$

Comparing this equation with that proposed by Frumkin, equation 15, they are identical with $C_{org} = C_2 C_1 / (C_2 + C_1)$, and $V - V_n = V$. The use of V_n as a reference potential for the covered part of the surface is analogous to using V_{ECM} as the reference potential on the uncovered surface. Plotting Q vs. V , one should get a straight line whose slope is C_{org} , and whose intercept is $C_{org} V_n$. This provides an alternative means of determining C_{org} and V_n . Having calculated C_{org} in this manner, it is necessary to estimate either C_1 or C_2 in order to obtain the other capacity.

In the absence of specific adsorption, region I is composed solely of water molecules, and its capacity can be estimated from the equation for a parallel plate capacitor

$$C = \frac{\epsilon}{4\pi d} \quad (42)$$

with ϵ being the dielectric constant, and d the plate separation (about 3 \AA for water). The theoretical calculation of the dielectric constant for water has always presented a problem; the bulk value of 80 is far above that which is calculated by statistical theory for independent water dipoles ($\epsilon = 13$). Kirkwood (58) proposed a model in which several hydrogen bonded molecules acted as if they were a single "supermolecule". His calculations indicated that a group of five molecules would bring the

dielectric constant up to 80. Dr. Sam Liu of the Ames Laboratory extended this calculation to include the effect of the intense electric fields near the interface and calculated a value of between 6 and 10 for ϵ in the first layer of water (59); this agrees with estimates suggested previously (60-62). Bockris and Reddy (63) have modeled the double layer in the far cathodic potential region where the capacity is about $16 \mu\text{F cm}^{-2}$, independent of electrolyte. A value of 6 for the dielectric constant of the first water layer gives excellent agreement with experimental capacities. A dielectric constant of 6 will be used in the calculations done here; which results in a value of $17.7 \mu\text{F cm}^{-2}$ for C_1 . Having estimated C_1 , C_2 and σ_1 can easily be calculated.

In addition to the assumption made about the dielectric constant of water, two other assumptions are made. The use of V_n as a reference potential for the covered part of the surface has been described before. It is also assumed that C_1 and C_2 are constant over the entire potential region studied. Since the organic molecules (region II) are assumed to have a constant orientation, a constant capacity might be expected. Water molecules are expected to change orientation with changing potential, causing a change in ϵ_1 . This would lead to a change in the capacity C_1 with potential; use of a constant C_1 is

a first approximation.

Aliphatic Compounds

The following method will be used to calculate σ_i for iso-pentanol in 0.1 N HClO₄ and 0.1 N H₂SO₄ and pentanoic acid in 0.1 N HClO₄. From the slopes of the charge vs. surface excess plots (Table 2-4), and experimental q_w 's (charge for the background electrolyte), Q , the charge on the covered part of the surface will be calculated from equation 39. Q will be plotted vs. potential (V); values for C_{org} and V_n will be taken from the slope and intercept of the linear portion of the curve as indicated previously. With the estimate of $C_1 = 17.7 \mu\text{F cm}^{-2}$ C_2 will be calculated (see equation 41); σ_i will then be determined from equation 40.

Plots of q vs. V are shown in Figures 26-28 for the three aliphatic systems studied. All three have a linear portion at negative potentials, with deviations occurring at positive potentials. While the scatter is somewhat greater for the H₂SO₄ data, deviation from linearity does not appear to occur until about + 0.25 V. The slope and intercept for the linear portion of the curves (indicated by arrows) were determined, and C_{org} and V_n calculated. These values are given in Table 7.

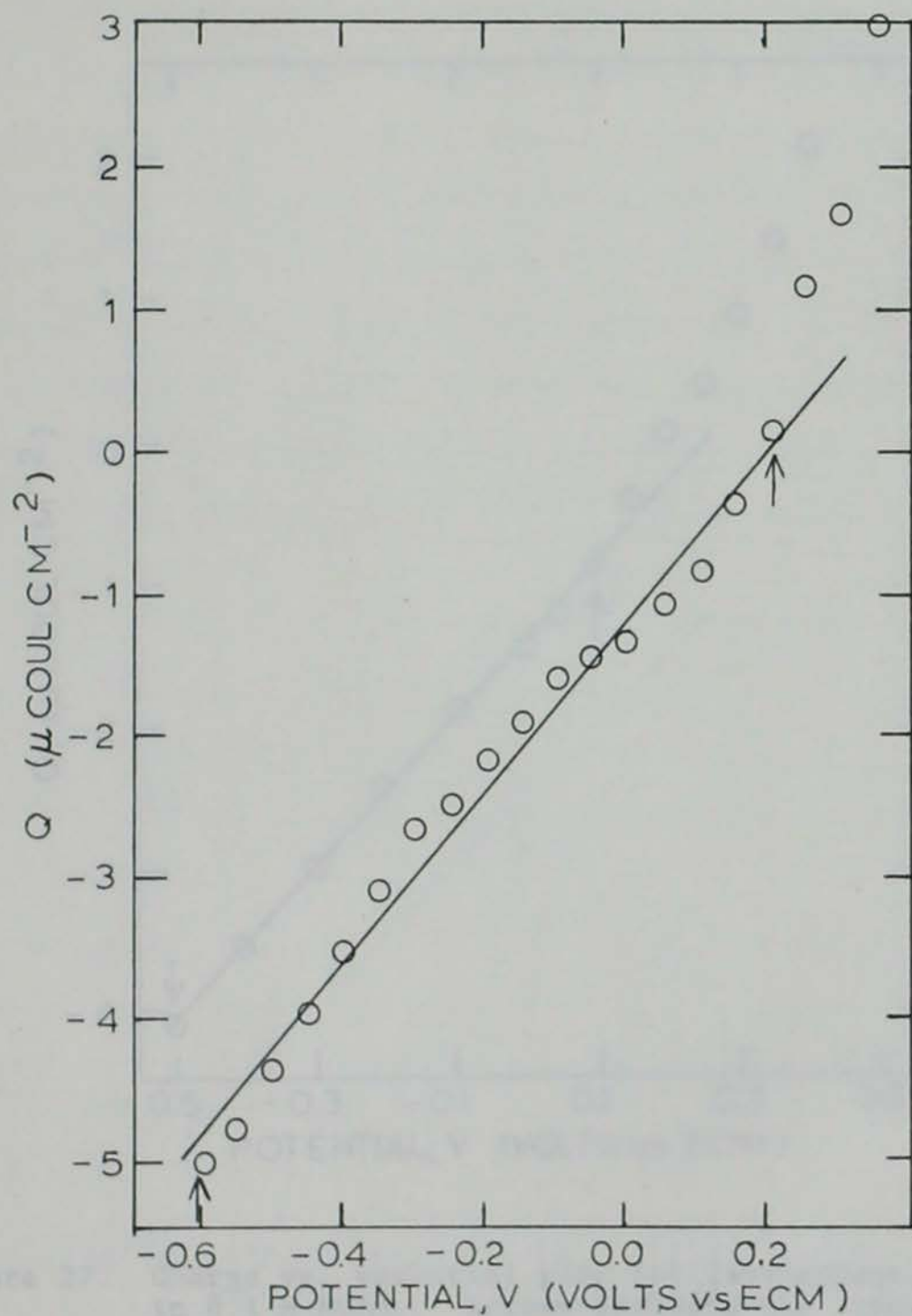


Figure 26. Charge vs. potential plot for iso-pentanol in 0.1 \underline{N} H_2SO_4 . Arrows indicate the linear portion of the curve

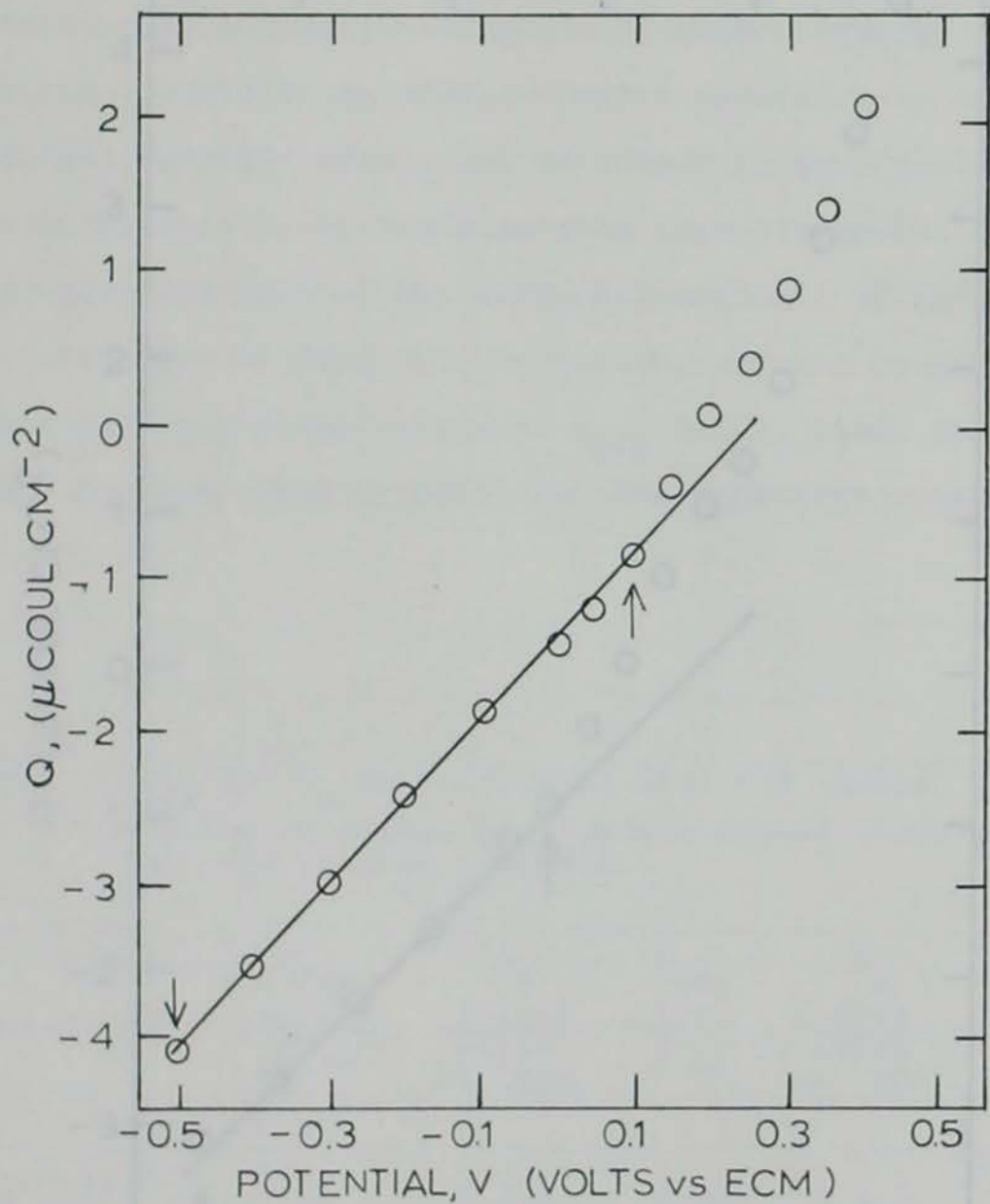


Figure 27. Charge vs. potential plot for iso-pentanol in 0.1 N HClO₄. Arrows indicate the linear portion of the curve

Figure 28. Charge vs. potential plot for pentanoic acid in 0.1 N HClO₄. Arrows indicate the linear portion of the curve

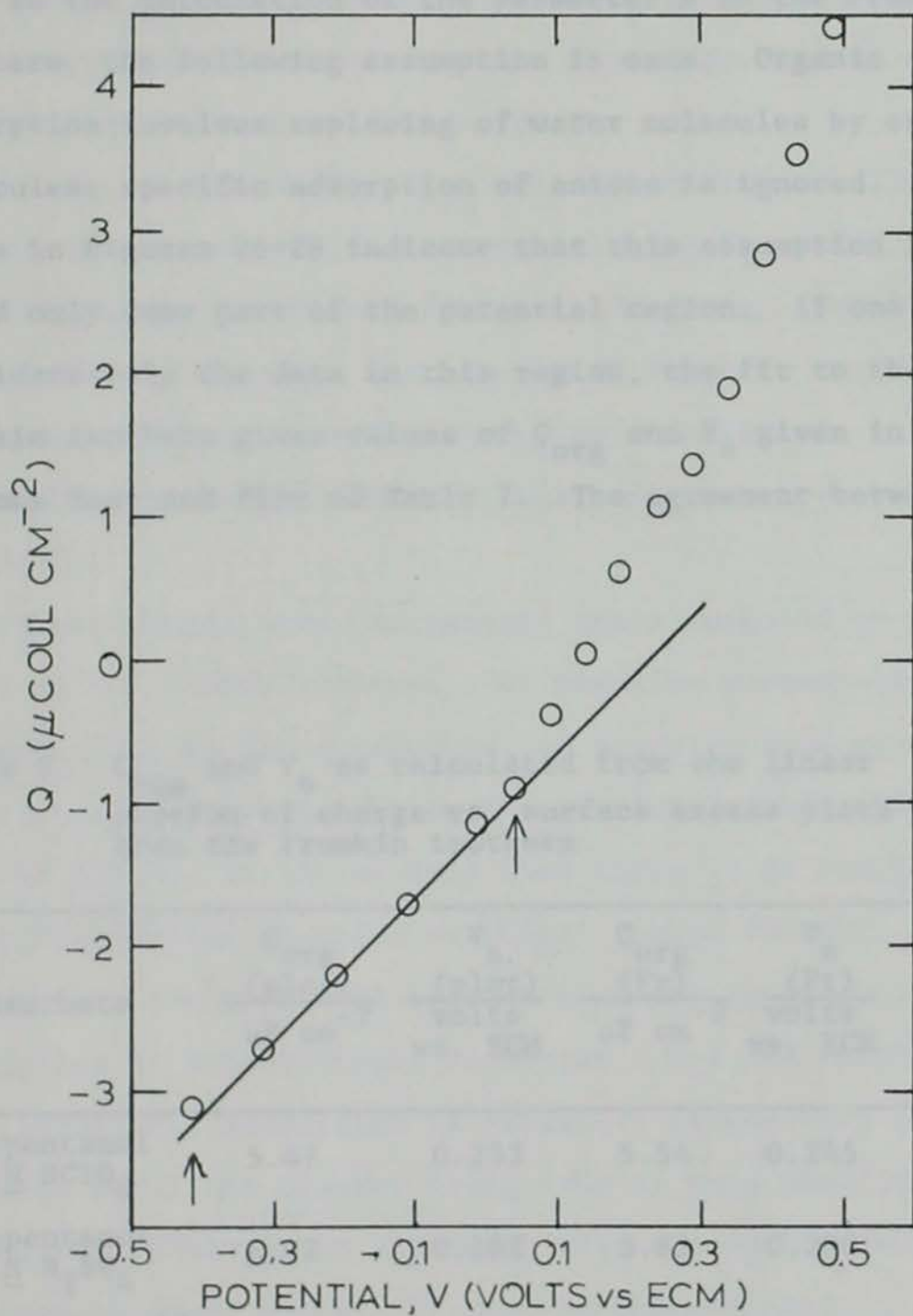


Figure 28. Charge vs. potential plot for pentanoic acid in 0.1 N HClO_4 . Arrows indicate the linear portion of the curve

In the calculation of the parameter B in the Frumkin isotherm, the following assumption is made. Organic adsorption involves replacing of water molecules by organic molecules; specific adsorption of anions is ignored. The plots in Figures 26-28 indicate that this assumption is valid only over part of the potential region. If one considers only the data in this region, the fit to the Frumkin isotherm gives values of C_{org} and V_n given in columns four and five of Table 7. The agreement between

Figure 29

These curves have the general shape expected on the basis of the theory proposed. At negative potentials,

Table 7. C_{org} and V_n as calculated from the linear portion of charge vs. surface excess plots and from the Frumkin isotherm

| Adsorbate | $\frac{C_{org}}{\mu F \text{ cm}^{-2}}$ (plot) | $\frac{V_n}{\text{volts vs. ECM}}$ (plot) | $\frac{C_{org}}{\mu F \text{ cm}^{-2}}$ (Fr) | $\frac{V_n}{\text{volts vs. ECM}}$ (Fr) | $\frac{C_2}{\mu F \text{ cm}^{-2}}$ |
|---|---|--|---|--|-------------------------------------|
| iso-pentanol 0.1 N HClO_4 | 5.47 | 0.253 | 5.54 | 0.245 | 7.92 |
| iso-pentanol 0.1 N H_2SO_4 | 6.02 | 0.198 | 5.83 | 0.200 | 9.10 |
| pentanoic acid 0.1 N HClO_4 | 5.03 | 0.233 | 4.87 | 0.230 | 7.03 |

values of C_{org} and V_n shown in Table 7 is excellent, indicating that the model fits the experimental data well in the absence of specific adsorption.

Using the values for C_{org} calculated from the linear portion of the curves (Figures 26-28), and $C_1 = 17.7 \mu\text{F cm}^{-2}$, C_2 was determined for each adsorbate. Values for C_2 are given in the last column of Table 7. Equation 40 can now be used to calculate σ_i as function of potential; results of these calculations are shown in Figure 29.

These curves have the general shape expected on the basis of the theory proposed. At negative potentials σ_i is zero; this is to be expected, as positive ions are not specifically adsorbed. While the scatter in the sulfuric acid is larger, it can be said that there is no specific adsorption in the negative potential region for this system. As the potential becomes more positive, specific adsorption of anions starts to appear. For the perchloric acid solutions, adsorption is initially larger than for sulfuric acid, the reverse being true at more positive potentials. This is in agreement with adsorption data obtained by Bauer et al. (57) for perchlorate and sulfate anions.

For all three systems studied, the amount of specific adsorption is much less than for the uncovered surface.

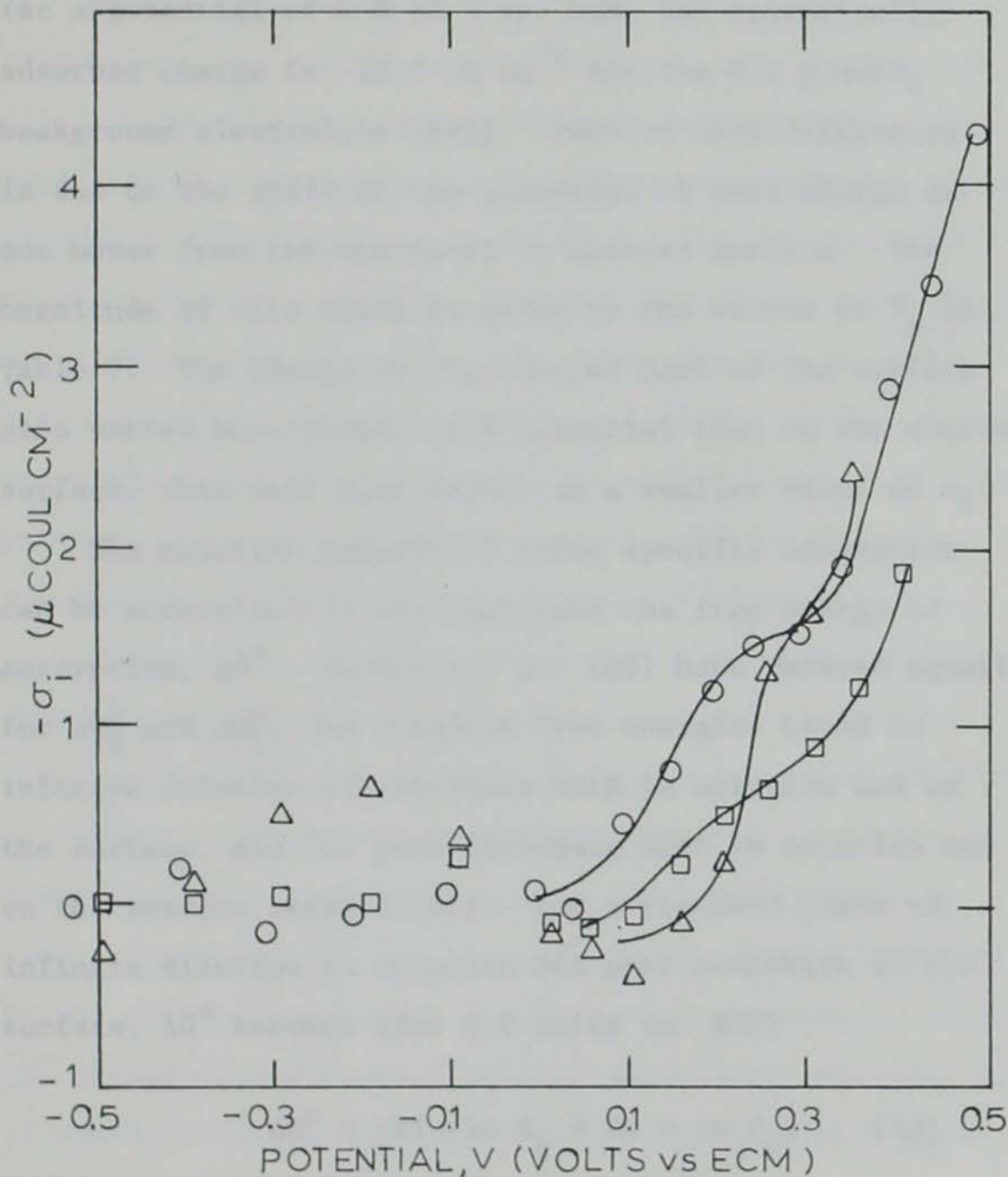


Figure 29. Specifically adsorbed charge vs. potential plots. \triangle iso-pentanol in 0.1 N H_2SO_4 \square iso-pentanol in 0.1 N HClO_4 \circ pentanoic acid in 0.1 N HClO_4

(at a potential of + 0.30 V vs. ECM, the specifically adsorbed charge is $-10.3 \mu\text{C cm}^{-2}$ for the 0.1 N HClO_4 background electrolyte (64)). Part of this difference is due to the shift in the potential of zero charge as one moves from the uncovered to covered surface. The magnitude of this shift is given by the values of V_n in Table 7. The charge on the covered part of the surface also varies more slowly with potential than on the uncovered surface; this will also result in a smaller value of σ_i .

The relative amounts of anion specific adsorption can be understood if one considers the free energy of adsorption, ΔG° . Hansen et. al. (65) have derived equations for ΔG°_0 and ΔG°_1 , the standard free energies based on infinite dilution of adsorbate both in solution and on the surface, and for pure adsorbate both in solution and on the surface respectively. For a standard state of infinite dilution in solution and pure adsorbate on the surface, ΔG° becomes (for 0.0 volts vs. ECM)

$$\Delta G^\circ = -RT (\ln B_0 + 2\alpha + \ln f_0) \quad (43)$$

where B_0 is the value of B at the ECM, α is the interaction parameter in the Frumkin equation (both given in Table 1), and $f_0 = 55.5/c_0$ is the activity coefficient of the adsorbate at infinite dilution, referred to a pure liquid adsorbate standard state. Using equation 43, values for

ΔG° were calculated and found to be -5.91, -5.62, and -5.54 kcal mole⁻¹ for iso-pentanol, pentanoic acid, both from 0.1 N HClO₄, and for iso-pentanol in 0.1 N H₂SO₄ respectively. In comparing the two perchloric acid systems, iso-pentanol, being held more strongly to the electrode, should allow less specific adsorption; this is indeed true. The iso-pentanol in 0.1 N H₂SO₄, with the lowest free energy of adsorption should show the most specific adsorption; at positive potentials this is true. At lower potentials, sulfate is less strongly adsorbed, making comparison with perchlorate systems difficult.

While the qualitative aspects of the curves in Figure 29 can be explained, some features cannot be accounted for. With the uncertainty in the dielectric constant for the water layer, the magnitude of specifically adsorbed charge is only an estimate. Also, the small plateau, especially prominent for pentanoic acid, cannot be explained by the theory at present. However, the calculation of Q , the charge on the covered surface allows for the calculation of the differential capacity (C) by a method which does not depend on any adsorption isotherm.

The first derivative of charge with respect to potential gives the differential capacity:

$$q = (1-\theta) q_w + \theta Q \quad (15)$$

$$C = (1-\theta) C_w + \theta C_{org} + (Q - q_w) \frac{d\theta}{dV} \quad (44)$$

Using experimental charges and capacities for the background electrolyte, and C_{org} and Q as calculated earlier, the differential capacity can be calculated. Values for $d\theta/dV$ are taken from the slopes of θ vs. V curves; these were simply fit by a polynomial and analytically differentiated.

Comparisons between experimental capacities and those calculated from equation 44 are given in Figures 30-33 for iso-pentanol and pentanoic acid in $HClO_4$ at low and high solute concentrations; all data are given in Appendix C. For the low concentrations, agreement is good over the entire potential region, and for high concentrations it is excellent in the region of maximum adsorption. The calculated desorption peaks are consistently lower than the experimental values. The use of a polynomial to calculate $d\theta/dV$ tends to smooth out rapid changes in θ which might occur in the capacity peak potential region. However, the agreement shown over the large potential and concentration range studied is superior to all previous attempts to fit capacity curves.

The method described here has an advantage over a Frumkin fit (47) to calculate capacity; in the latter case, agreement with experimental data is good only for moderate concentrations of organic material. Russian electrochemists,

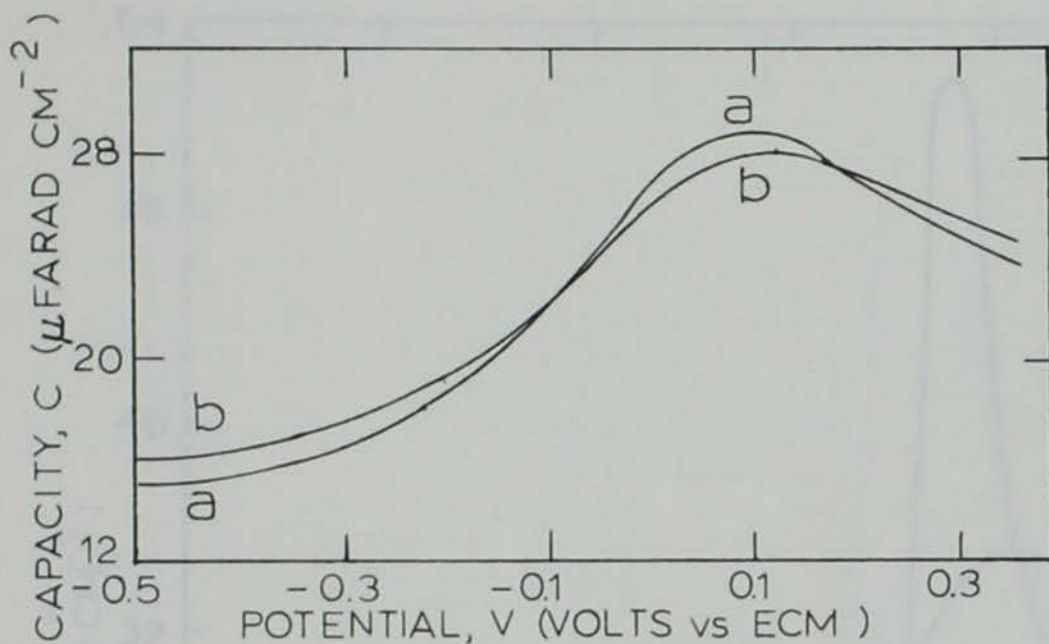


Figure 30. Capacity vs. potential curves for iso-pentanol in 0.1 N HClO_4 , reduced concentration = 0.0123. (a) Experimental, (b) Equation 44

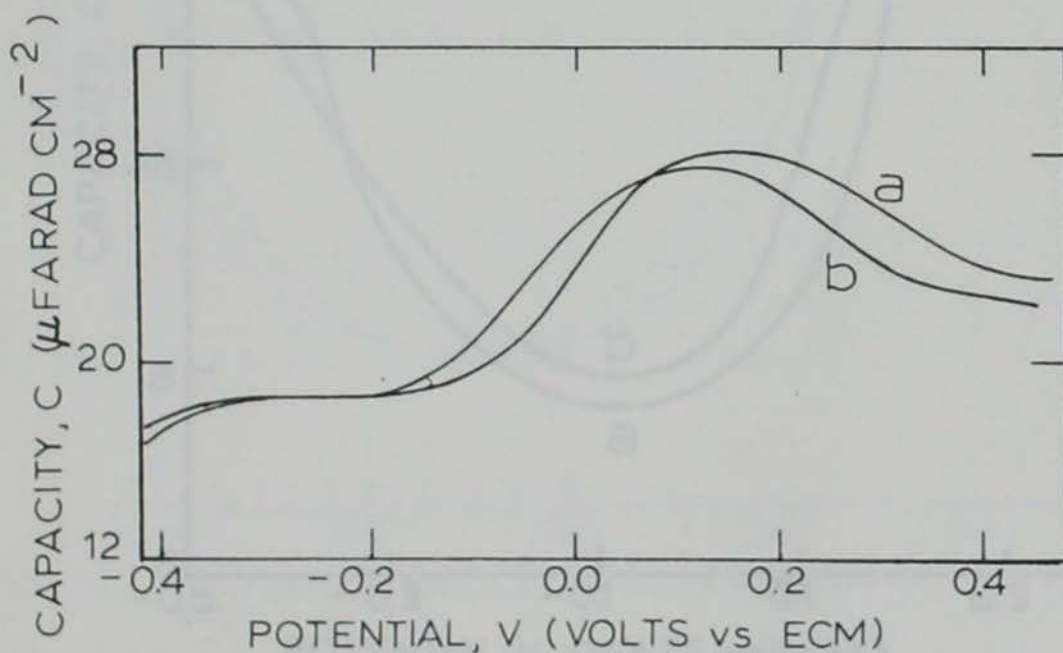


Figure 31. Capacity vs. potential curves for pentanoic acid in 0.1 N HClO_4 , reduced concentration = 0.0123. (a) Experimental, (b) Equation 44

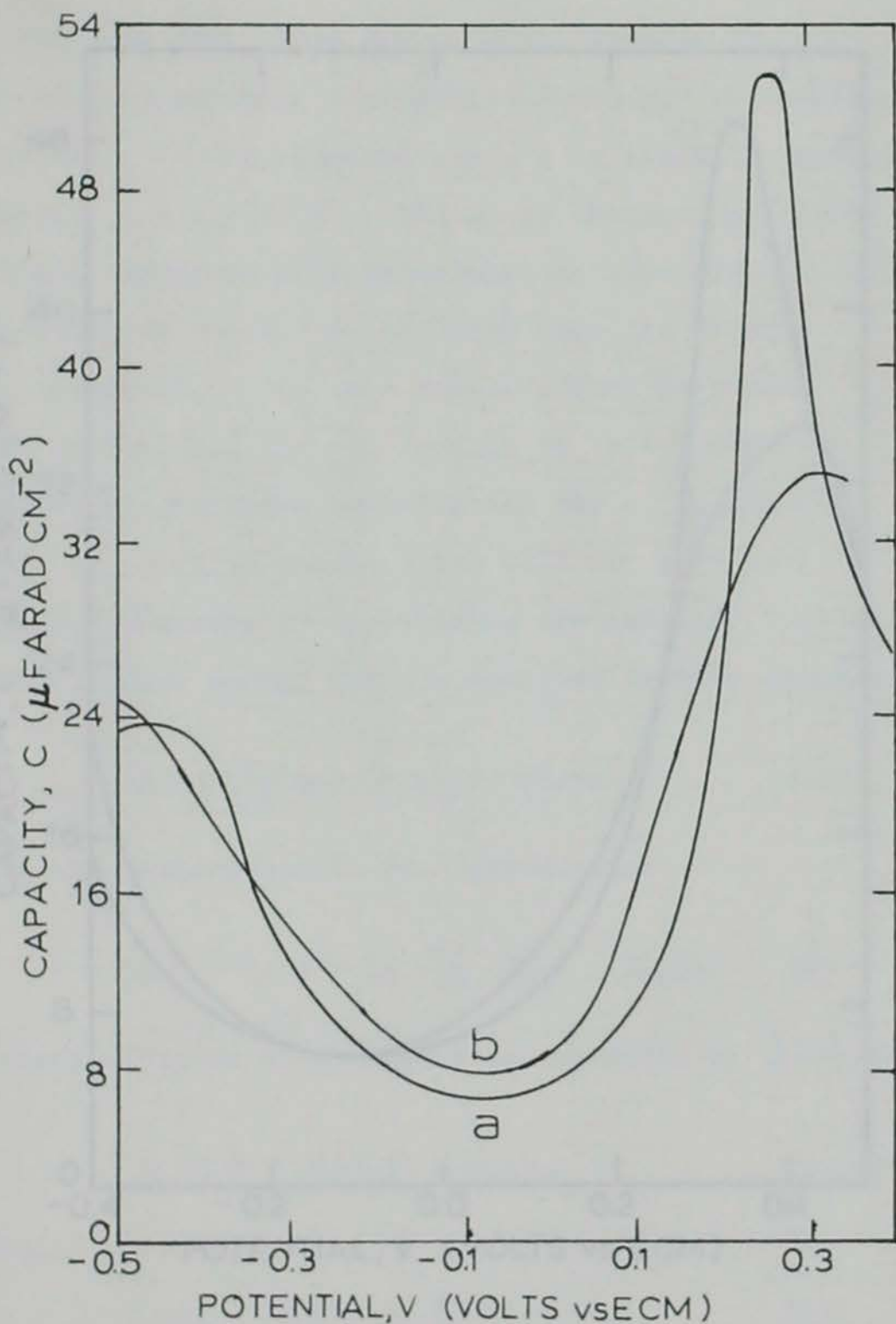


Figure 32. Capacity vs. potential curves for iso-pentanol in 0.1 N HClO₄, reduced concentration = 0.0909. (a) Experimental, (b) Equation 44

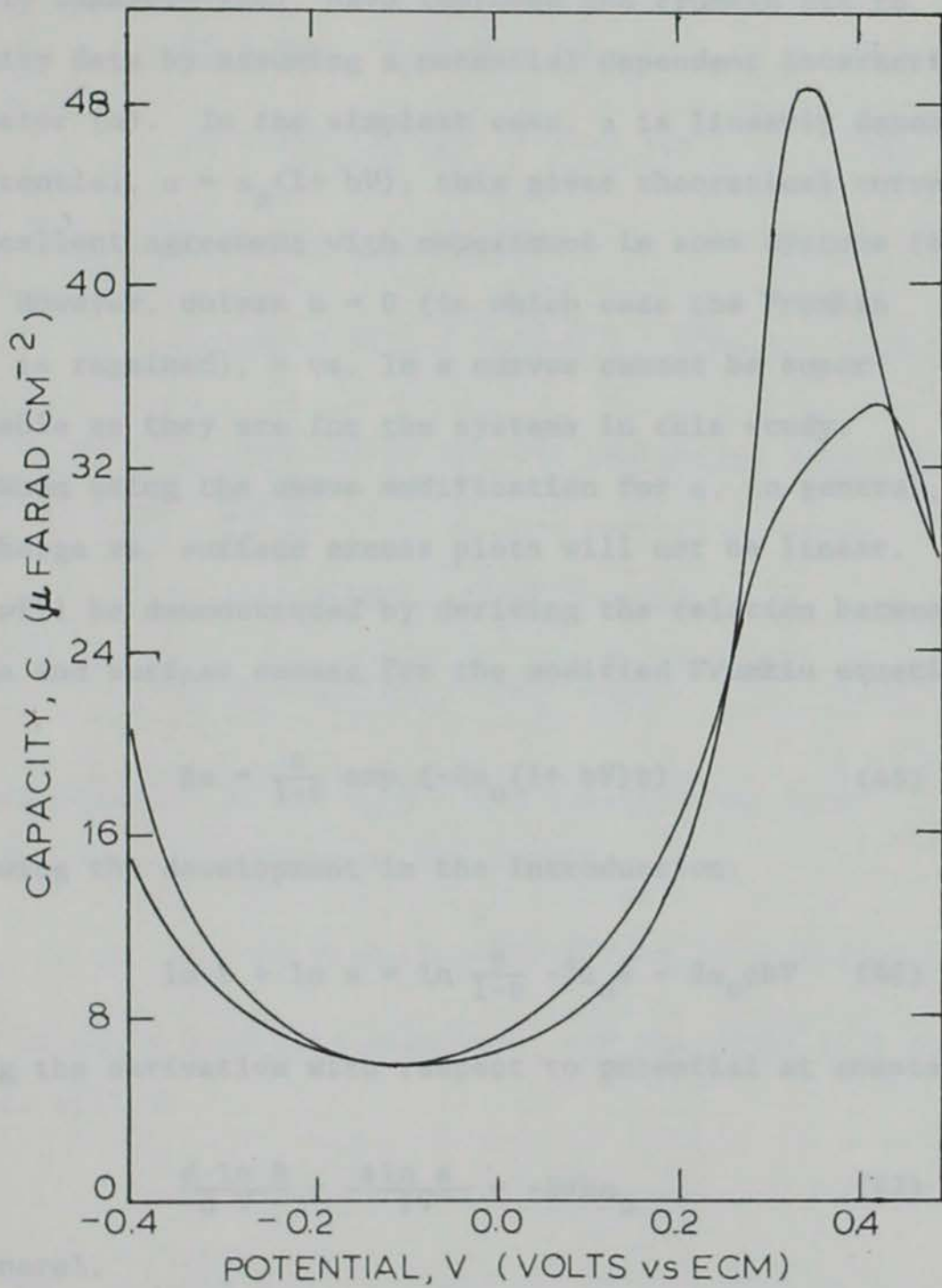


Figure 33. Capacity vs. potential curves for pentanoic acid in 0.1 N HClO_4 , reduced concentration = 0.1304.
 (a) Experimental, (b) Equation 44

notably Damaskin (66), have improved the Frumkin fit to capacity data by assuming a potential dependent interaction parameter (α). In the simplest case, α is linearly dependent on potential, $\alpha = \alpha_0(1 + bV)$; this gives theoretical curves in excellent agreement with experiment in some systems (66, 67). However, unless $b = 0$ (in which case the Frumkin model is regained), π vs. $\ln a$ curves cannot be superimposable as they are for the systems in this study.

When using the above modification for α , in general, the charge vs. surface excess plots will not be linear. This will be demonstrated by deriving the relation between charge and surface excess for the modified Frumkin equation:

$$Ba = \frac{\theta}{1-\theta} \exp(-2\alpha_0(1+bV)\theta) \quad (45)$$

Following the development in the Introduction:

$$\ln B + \ln a = \ln \frac{\theta}{1-\theta} - 2\alpha_0\theta - 2\alpha_0\theta bV \quad (46)$$

Taking the derivative with respect to potential at constant θ

$$\frac{d \ln B}{dV} + \frac{\partial \ln a}{\partial V} = -2\theta b\alpha_0 \quad (47)$$

In general,

$$-RT\Gamma_m \frac{\partial \ln a}{\partial V} = \frac{\partial q}{\partial \theta} \quad (11)$$

so, substituting equation 11 into equation 47:

$$\frac{\partial q}{\partial \theta} = RT\Gamma_m \left(\frac{d \ln B}{d V} + 2\theta b\alpha_o \right) \quad (48)$$

$$dq = RT\Gamma_m \left(\frac{d \ln B}{d V} + 2\theta b\alpha_o \right) d\theta \quad (49)$$

Integrating equation 49 indefinitely:

$$q = q' + RT\Gamma_m \left(\frac{d \ln B}{d V} \theta + \theta^2 b\alpha_o \right) \quad (50)$$

at $\theta = 0$, $q' = q_w$, the charge for the background electrolyte, and at $\theta = 1$, $q = Q$ and:

$$Q = q_w + RT\Gamma_m \left(\frac{d \ln B}{d V} + b\alpha_o \right), \text{ or} \quad (51)$$

$$Q - q_w - RT\Gamma_m b\alpha_o = RT\Gamma_m \frac{d \ln B}{d V} \quad (52)$$

Solving equation 52 for $\frac{d \ln B}{d V}$ and substituting into equation 50, one arrives at the result:

$$q = (1-\theta) q_w + \theta Q + RT\Gamma_m b\alpha_o (\theta^2 - \theta) \quad (53)$$

There is now a quadratic term in θ , and the slope of q vs. θ plots will be

$$\frac{dq}{d\theta} = (Q - q_w) + 2RT\Gamma_m b\alpha_o \left(\theta - \frac{1}{2} \right) \quad (54)$$

Since $\frac{dq}{d\theta}$ is independent of θ for the systems studied here, $\frac{d^2 q}{d\theta^2} = 0$, and $b = 0$. Therefore, the Damaskin modification is not relevant to the present data.

Benzyl Alcohol

Analysis of the benzyl alcohol data was much more difficult than for the aliphatic compounds studied. The π vs. $\ln a$ plots were superimposable over only part of the potential region; outside this region, the limiting slopes of the π vs. $\ln a$ plots varied with potential, indicating a changing orientation of adsorbate. The non-linearity of the charge vs. surface excess plots at negative potentials also indicates that the Frumkin isotherm can be applied only to a portion of the potential region.

For the potential region for which the charge vs. surface excess plots were linear, an analysis similar to that for the aliphatic compounds was carried out. Using the slopes of these lines (Tables 5-6), and the experimental q_w 's, Q was calculated for benzyl alcohol in both 0.1 N $HClO_4$ and 1.0 N $NaNO_3$ from equation 39. Q was plotted against potential; these plots are shown in Figure 34 for both systems.

The $HClO_4$ plot shows a slight curvature at most negative potentials, then a linear portion from 0.278 to 0.478 volts vs. ECM. For $NaNO_3$, the plot is linear except for the most positive point at 0.530 volts vs. ECM. As for the aliphatic compounds, the slopes and intercepts of these lines give C_{org} and V_n . A comparison of the values obtained

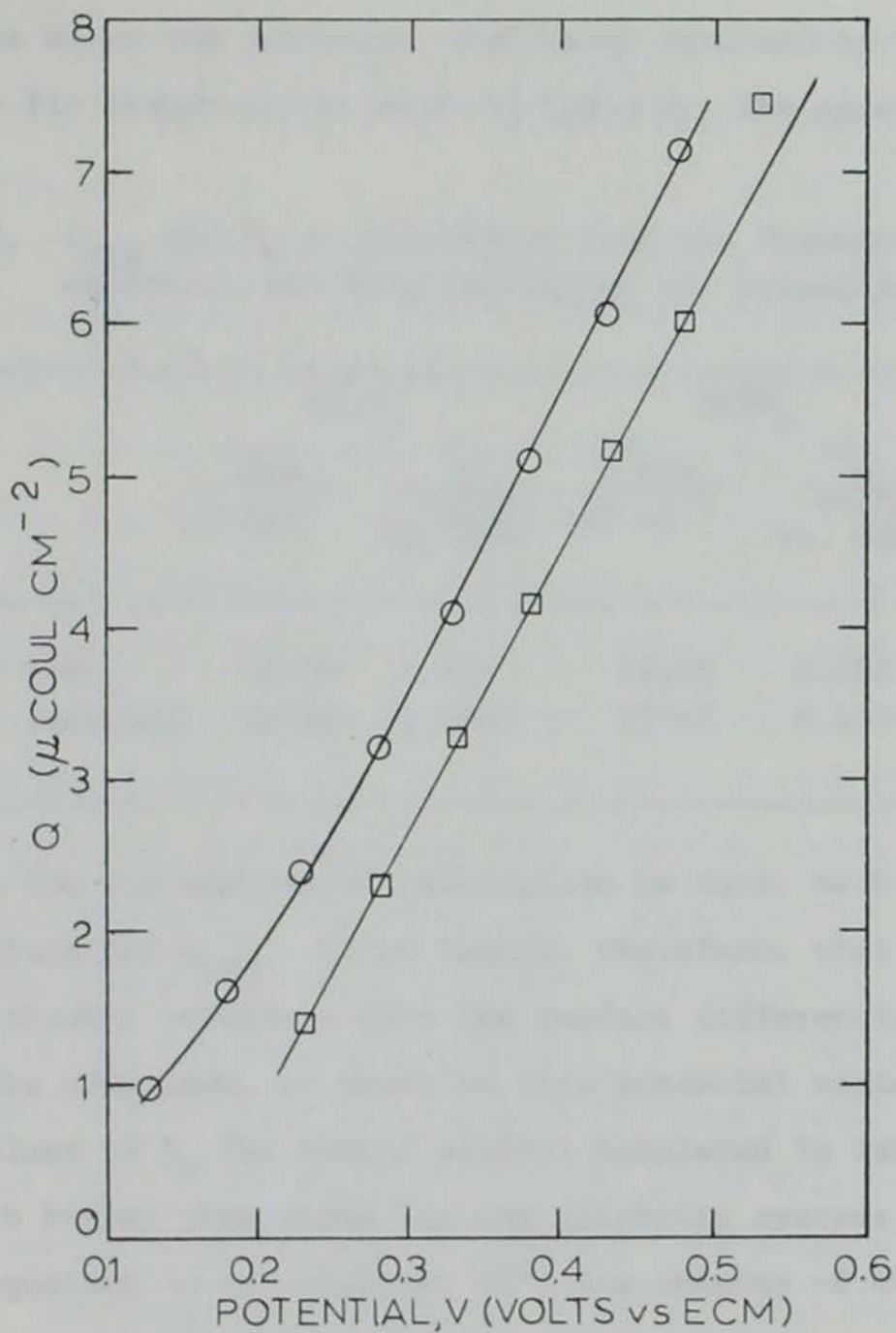


Figure 34. Charge vs. potential plots for benzyl alcohol.

○ 0.1 N HClO₄ □ 1.0 N NaNO₃

from the slope and intercept with those obtained by the Frumkin fit (Table 1) is shown in Table 8. The agreement

Table 8. C_{org} and V_n as calculated from the Frumkin equation, and from the charge vs. potential plots

| | HClO ₄ | | NaNO ₃ | |
|------------------|---|------------------------------------|---|------------------------------------|
| | $\frac{C_{org}}{\mu F \text{ cm}^{-2}}$ | $\frac{V_n}{\text{volts vs. ECM}}$ | $\frac{C_{org}}{\mu F \text{ cm}^{-2}}$ | $\frac{V_n}{\text{volts vs. ECM}}$ |
| Q vs. V plot | 19.52 | 0.115 | 18.66 | 0.153 |
| Frumkin isotherm | 16.28 | 0.163 | 19.65 | 0.185 |

between the two methods of calculation is fair; both give high values for C_{org} . It is likely, therefore, that the benzyl alcohol interacts with the surface differently from aliphatic compounds, at least in this potential region.

Values of B_o for benzyl alcohol tabulated in Table 1 are much higher than those for the aliphatic systems. Using equation 43 to calculate ΔG^o , one obtains -6.01 and -6.17 kcal mole⁻¹ for 0.1 N HClO₄ and 1.0 N NaNO₃ respectively. This stronger interaction may indicate that the benzyl alcohol can replace even the first layer of water, leading to a different structure for the interface. Following the analysis for aliphatic compounds, the linear

plots in Figure 34 indicate that no specific adsorption is present for these systems. The higher value of C_{org} is consistent with a more compact interfacial region; in the equation $C = \epsilon/4\pi d$, as d gets smaller, C gets larger.

A strong interaction with the mercury surface is also indicated by the capacity curves shown in Figures 35-37. For the aliphatic compounds, there are two well-defined desorption peaks, one on either side of the ECM. The benzyl alcohol capacity curves show well-defined peaks at cathodic polarizations, however, there are only small, ill-defined peaks for anodic polarization. The effect is due to the benzyl alcohol, not the electrolyte, as the electrolytes chosen for this study run from fluoride, believed to be not specifically adsorbed (68), to perchlorate, known to be specifically adsorbed. Nitrate adsorption is intermediate to the two above electrolytes (69), and was chosen to compare curves taken here with those taken previously by Miller (70). The two sets of curves agree well with each other; the lack of anodic peaks is also observed by Miller. The peaks result from a change in θ with potential over a small potential region. The lack of anodic peaks suggests that the rapid change in $d\theta/dV$ does not occur for benzyl alcohol, and that desorption occurs over a wider potential region than for aliphatic compounds.

Equation 44 can be used to calculate the capacity for

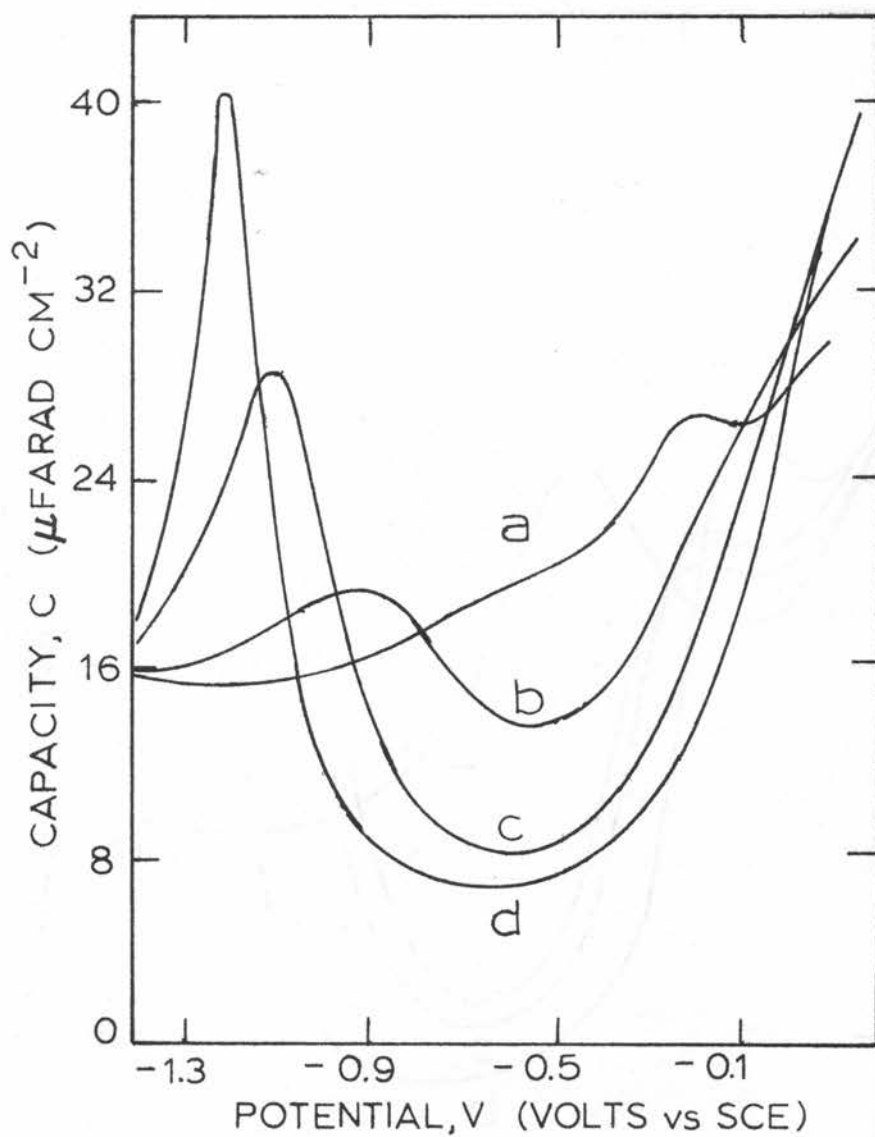


Figure 35. Capacity vs. potential plots for benzyl alcohol in 0.90 N NaF, reduced concentrations of benzyl alcohol (a) 0.0, (b) 0.005, (c) 0.035, (d) 0.106

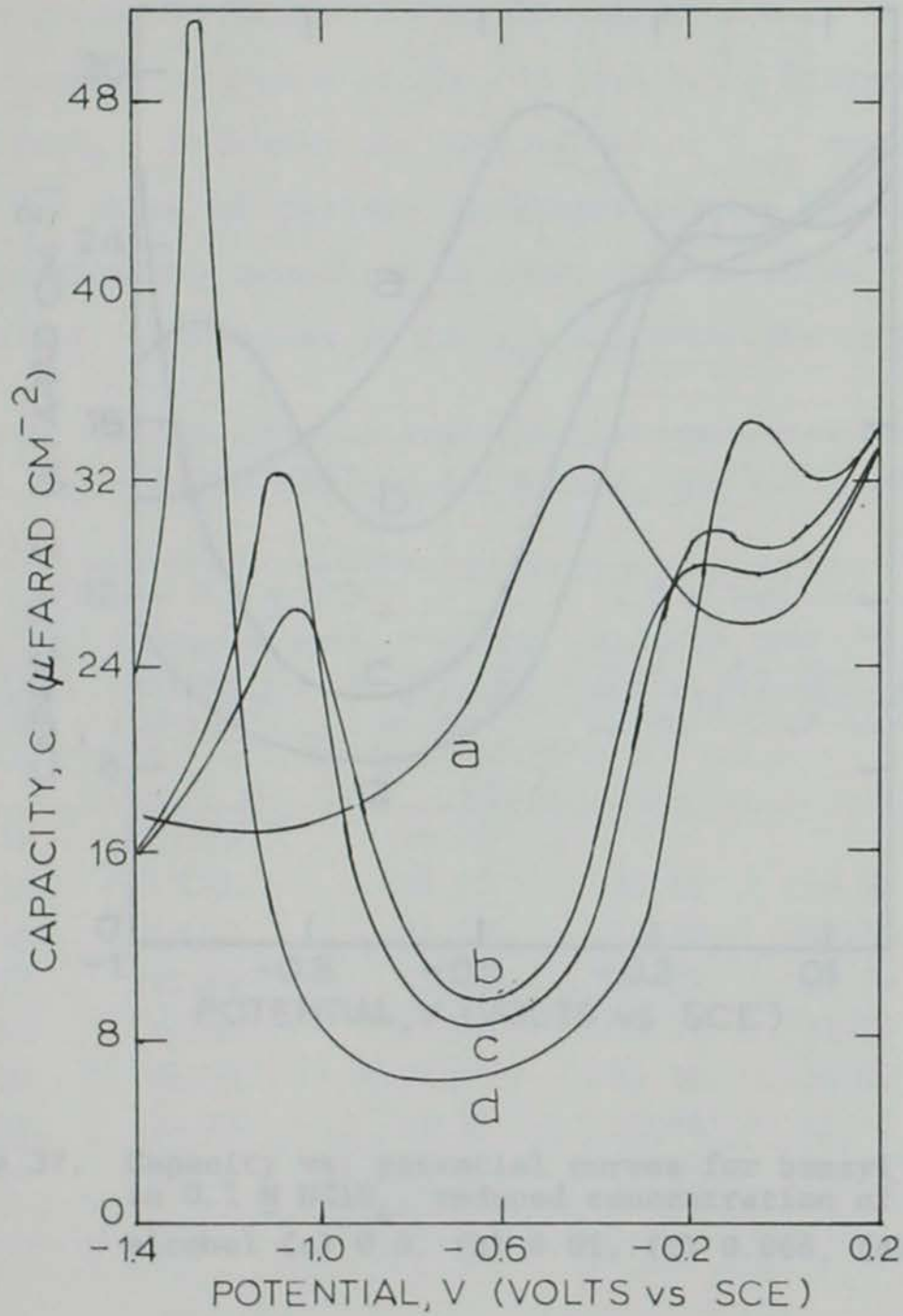


Figure 36. Capacity vs. potential plots for benzyl alcohol in 0.2 N NaNO₃, reduced concentrations of benzyl alcohol (a) 0.0, (b) 0.025, (c) 0.051, (d) 0.200

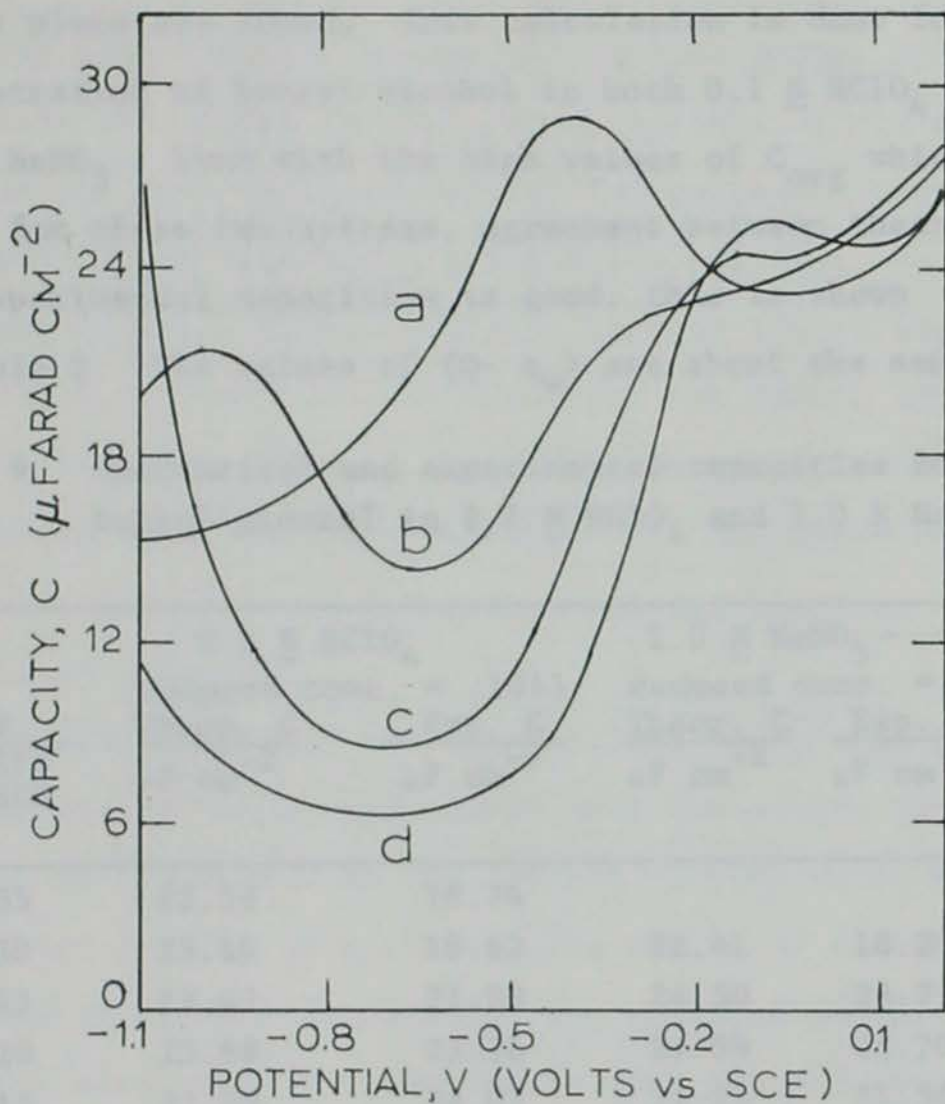


Figure 37. Capacity vs. potential curves for benzyl alcohol in 0.1 N HClO₄, reduced concentration of benzyl alcohol (a) 0.0, (b) 0.01, (c) 0.066, (d) 0.262

the potential region for which linear charge vs. surface excess plots are found. This calculation is done for one concentration of benzyl alcohol in both 0.1 N HClO₄ and 1.0 N NaNO₃. Even with the high values of C_{org} which were found for these two systems, agreement between theoretical and experimental capacities is good; this is shown in Table 9. The values of (Q- q_w) are about the same as

Table 9. Theoretical and experimental capacities for benzyl alcohol in 0.1 N HClO₄ and 1.0 N NaNO₃

| V volts vs. SCE | 0.1 <u>N</u> HClO ₄ reduced conc. = .1013 | | 1.0 <u>N</u> NaNO ₃ reduced conc. = .1063 | |
|-----------------------|---|-------------------------------|---|-------------------------------|
| | Theor. C μF cm ⁻² | Exp. C μF cm ⁻² | Theor. C μF cm ⁻² | Exp. C μF cm ⁻² |
| -0.35 | 22.58 | 16.74 | | |
| -0.30 | 23.10 | 19.62 | 22.41 | 18.26 |
| -0.25 | 23.47 | 21.98 | 24.50 | 23.79 |
| -0.20 | 23.68 | 23.36 | 27.50 | 28.70 |
| -0.15 | 23.88 | 24.03 | 31.21 | 31.54 |
| -0.10 | 23.91 | 24.17 | 33.33 | 32.07 |
| -0.05 | 24.14 | 24.19 | 32.98 | 31.46 |
| 0.00 | 24.37 | 24.31 | 26.16 | 30.77 |

for iso-pentanol and pentanoic acid, however, dθ/dV is about one fourth that for the aliphatic compounds, indicating that benzyl alcohol is desorbed over a wider potential region.

Summary and Suggestions for Future Work

The use of linear charge vs. surface excess plots to calculate the charge on the covered portion of the mercury surface has been demonstrated for iso-pentanol, pentanoic acid and benzyl alcohol in 0.1 N HClO_4 solution, for iso-pentanol in 0.1 N H_2SO_4 solution, and for benzyl alcohol in 1.0 N NaNO_3 solution. A model for the double layer has been developed which uses the charge on the covered surface to calculate the amount of specifically adsorbed charge on the covered surface, a quantity which has not been calculated previously.

For the aliphatic systems studied, the charge vs. surface excess plots were linear over the entire potential region, so the charge on the covered surface could be calculated for all potentials. The amount of specifically adsorbed charge was calculated; the relative amounts of specific adsorption are consistent with the free energies of adsorption of the organic compounds. Iso-pentanol is held more strongly to the electrode than pentanoic acid, and therefore, shows less specific adsorption. For iso-pentanol in H_2SO_4 , the sulfate ion is less strongly adsorbed near the potential of zero charge than is perchlorate, and less specific adsorption is seen here also. The electrocapillary data were also used to calculate capacity curves for the perchloric acid solutions; the agreement with

experimental curves is excellent over a wide potential and concentration range.

In the case of benzyl alcohol, the results are somewhat more ambiguous. Linear charge vs. surface excess plots were obtained only for a small potential region. Analysis of the results for this region gave values of C_{org} which were much higher than experimental ones. Based on the theory presented here, it appears that benzyl alcohol is held more strongly to the surface than the aliphatic compounds; no specific adsorption of anions is indicated. This strong adsorption is also seen in the capacity curves for these systems. The anodic desorption peaks are not present, indicating a slow change in coverage with potential. This is shown in the calculation of the capacity; small peaks are calculated due to a lower value of $d\theta/dV$ than for aliphatic compounds.

Future work might include the following areas. Adsorption of organic compounds from electrolyte solutions which contain anions that are more strongly specifically adsorbed to the electrode (i.e. chloride) should be studied. The amount of specifically adsorbed charge calculated using the theory proposed should be larger for the more strongly held species. Also, an attempt should be made to directly calculate the amount of specific adsorption. In principal, this can be done in the same way that organic adsorption is

calculated, by varying the concentration. In these experiments, the concentration of organic material would be held constant, and a family of electrocapillary curves would be taken for different concentrations of electrolyte. This procedure would then be repeated for another concentration of organic substance. The specifically adsorbed charge calculated by this method could then be compared with that calculated by the theory; differences in these values could then be used to modify the model as necessary.

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APPENDIX A

Polynomial Coefficients

DEPENDENCE OF MERCURY INTERFACIAL TENSION ON CONCENTRATION AND POLARIZATION

POLYNOMIAL COEFFICIENTS FOR ISO PENTANOL IN 0.1 N HClO₄

| DEGREE | 0.0 | 0.01230 | 0.02440 | 0.03610 | 0.04760 | 0.06580 |
|--------|----------|----------|----------|----------|----------|-----------|
| 0 | 395.763 | 395.664 | 395.596 | 395.433 | 395.512 | 395.253 |
| 1 | -120.751 | -120.469 | -119.066 | -119.066 | -118.402 | -117.797 |
| 2 | -118.402 | -117.837 | -121.127 | -118.658 | -118.647 | -122.564 |
| 3 | -28.176 | 2.197 | -28.281 | -26.877 | -27.222 | 36.102 |
| 4 | -86.112 | -78.278 | -150.135 | -284.875 | -380.335 | -474.775 |
| 5 | 171.693 | -196.944 | 184.853 | 121.480 | 157.921 | -615.798 |
| 6 | 732.049 | -327.338 | 1639.006 | 3099.449 | 4172.320 | 3801.604 |
| 7 | 905.253 | -454.517 | 3019.564 | 6964.605 | 9008.977 | 11256.656 |
| 8 | 566.299 | -347.013 | 2630.070 | 7051.738 | 8526.027 | 12560.352 |
| 9 | 201.970 | -100.690 | 1139.029 | 3505.028 | 3859.111 | 6531.188 |
| 10 | 36.290 | 0.0 | 197.602 | 697.188 | 680.380 | 1324.756 |

REDUCED CONCENTRATION

| DEGREE | 0.09090 | 0.13040 |
|--------|-----------|-----------|
| 0 | 395.094 | 394.960 |
| 1 | -117.332 | -115.562 |
| 2 | -131.233 | -160.552 |
| 3 | 135.772 | 281.549 |
| 4 | -319.003 | 210.165 |
| 5 | -1694.814 | -2933.087 |
| 6 | -277.092 | -7665.117 |
| 7 | 5188.313 | -7716.742 |
| 8 | 7966.020 | -2935.998 |
| 9 | 4801.719 | 274.911 |
| 10 | 1073.473 | 339.992 |

REDUCED CONCENTRATION

DEPENDENCE OF MERCURY INTERFACIAL TENSION ON CONCENTRATION AND POLARIZATION

POLYNOMIAL COEFFICIENTS FOR ISO PENTANOL IN 0.1 N H2SO4

| DEGREE | 0.0 | 0.01235 | 0.02439 | 0.03614 | 0.04762 | 0.06977 |
|--------|-----------|-----------|-----------|-----------|-----------|-----------|
| 0 | 294.309 | 291.788 | 296.853 | 287.666 | 287.143 | 289.838 |
| 1 | -395.636 | -433.869 | -363.158 | -489.185 | -501.379 | -461.979 |
| 2 | -653.979 | -894.390 | -511.842 | -1175.911 | -1336.652 | -1118.213 |
| 3 | -1200.815 | -1981.768 | -928.763 | -2600.022 | -3450.719 | -2843.763 |
| 4 | -1936.990 | -3342.082 | -1653.018 | -3513.170 | -5930.805 | -5076.254 |
| 5 | -2095.143 | -3522.713 | -1812.630 | -1496.780 | -5632.672 | -5352.426 |
| 6 | -1479.823 | -2270.896 | -1141.212 | 2319.243 | -2164.386 | -3231.527 |
| 7 | -660.152 | -860.224 | -380.952 | 3956.235 | 849.577 | -1035.189 |
| 8 | -169.139 | -171.766 | -52.315 | 2601.618 | 1271.389 | -136.563 |
| 9 | -18.558 | -13.302 | 1139.029 | 833.286 | 513.744 | 6531.188 |
| 10 | 36.290 | 0.0 | 197.602 | 107.417 | 74.659 | 1324.756 |

REDUCED CONCENTRATION

| DEGREE | 0.09091 | 0.13043 | 0.20000 | 0.35484 | 0.50000 |
|--------|------------|------------|------------|----------|----------|
| 0 | 281.612 | 280.681 | 288.508 | 317.164 | 308.379 |
| 1 | -590.046 | -610.962 | -519.904 | -70.699 | -160.203 |
| 2 | -1887.604 | -2055.306 | -1709.227 | 1083.751 | 794.054 |
| 3 | -5272.090 | -5990.680 | -5735.781 | 3296.949 | 3028.997 |
| 4 | -9477.391 | -11135.227 | -12673.879 | 4143.738 | 4370.531 |
| 5 | -10037.438 | -12091.518 | -16568.949 | 2626.008 | 3295.744 |
| 6 | -6118.152 | -7501.586 | -12937.477 | 777.141 | 1338.572 |
| 7 | -1987.990 | -2467.887 | -5955.344 | 51.128 | 264.141 |
| 8 | -267.019 | -334.464 | -1495.236 | -14.231 | 17.047 |
| 9 | 4801.719 | 274.911 | -158.212 | 0.0 | 0.0 |
| 10 | 1073.473 | 339.992 | 0.0 | 0.0 | 0.0 |

DEPENDENCE OF MERCURY INTERFACIAL TENSION ON CONCENTRATION AND POLARIZATION

POLYNOMIAL COEFFICIENTS FOR PENTANOIC ACID IN 0.1 N HClO₄

| DEGREE | 0.0 | 0.01230 | 0.02440 | 0.04760 | 0.09090 | 0.13040 |
|--------|-----------|----------|----------|----------|-----------|-----------|
| 0 | 395.004 | 394.856 | 394.891 | 394.293 | 393.564 | 393.043 |
| 1 | -122.974 | -122.021 | -120.723 | -119.197 | -117.119 | -111.984 |
| 2 | -118.692 | -119.996 | -121.487 | -133.472 | -146.668 | -178.918 |
| 3 | 14.102 | 17.691 | 9.094 | 32.684 | 157.004 | 179.632 |
| 4 | 1.229 | -50.558 | -176.215 | -130.406 | -43.624 | 438.474 |
| 5 | -196.610 | -306.260 | -216.918 | -296.393 | -1495.540 | -1490.020 |
| 6 | -886.774 | -687.461 | 1325.745 | 1185.141 | -1473.431 | -5901.613 |
| 7 | -1581.487 | -886.418 | 3954.568 | 3769.211 | 2272.780 | -8404.016 |
| 8 | -1292.123 | -597.304 | 4493.816 | 4135.547 | 5209.887 | -6000.945 |
| 9 | -459.662 | -159.837 | 2391.178 | 2072.476 | 3610.694 | -2070.859 |
| 10 | -48.313 | 0.0 | 456.879 | 403.196 | 882.578 | -254.330 |

REDUCED CONCENTRATION

| DEGREE | 0.16660 |
|--------|------------|
| 0 | 392.711 |
| 1 | -108.076 |
| 2 | -208.729 |
| 3 | 223.493 |
| 4 | 1078.624 |
| 5 | -1190.809 |
| 6 | -11329.438 |
| 7 | -23727.043 |
| 8 | -24235.629 |
| 9 | -12494.469 |
| 10 | -2603.177 |

REDUCED CONCENTRATION

DEPENDENCE OF MERCURY INTERFACIAL TENSION ON CONCENTRATION AND POLARIZATION

POLYNOMIAL COEFFICIENTS FOR BENZYL ALCOHOL IN 0.1 N HClO₄

| DEGREE | 0.0 | 0.00242 | 0.00483 | 0.01013 | 0.02538 | 0.03543 |
|--------|------------|-----------|-----------|-----------|----------|-----------|
| 0 | 394.635 | 394.549 | 393.830 | 391.437 | 388.420 | 386.832 |
| 1 | -123.483 | -117.507 | -114.321 | -109.901 | -103.243 | -101.229 |
| 2 | -126.414 | -126.511 | -125.628 | -127.835 | -124.124 | -96.308 |
| 3 | 17.089 | 3.446 | 15.769 | -36.455 | -45.318 | 72.697 |
| 4 | 242.027 | 157.579 | 65.956 | 37.788 | -58.992 | -289.277 |
| 5 | 48.027 | 156.153 | -348.577 | 71.389 | 166.899 | -2202.421 |
| 6 | -3315.742 | -1904.803 | -1561.894 | -919.073 | 950.581 | -4902.053 |
| 7 | -9575.672 | -6857.949 | -2555.257 | -3483.692 | 1414.874 | -5406.648 |
| 8 | -11537.297 | -9681.859 | -2103.608 | -4970.324 | 777.617 | -3070.233 |
| 9 | -6551.828 | -6338.441 | -865.358 | -3218.438 | 37.224 | -760.322 |
| 10 | -1445.232 | -1596.692 | -139.592 | -792.171 | -68.296 | -33.448 |

| DEGREE | 0.06771 | 0.10630 | 0.15170 | 0.26246 | 0.38845 |
|--------|----------|-----------|----------|-----------|----------|
| 0 | 383.083 | 380.468 | 378.792 | 374.178 | 371.020 |
| 1 | -96.667 | -93.133 | -89.624 | -85.639 | -81.238 |
| 2 | -117.586 | -128.041 | -125.843 | -133.558 | -133.092 |
| 3 | 14.630 | -24.558 | -27.165 | -16.020 | -31.471 |
| 4 | -143.040 | 54.825 | -39.558 | 186.827 | 62.891 |
| 5 | -746.649 | 13.215 | -56.266 | 41.911 | 82.587 |
| 6 | -649.437 | -390.224 | 786.938 | -1630.514 | 417.885 |
| 7 | 578.266 | -1215.595 | 2481.608 | -4692.891 | 1130.655 |
| 8 | 1068.339 | -1616.963 | 3044.688 | -5868.500 | 1308.124 |
| 9 | 403.849 | -1008.540 | 1734.773 | -3528.505 | 691.177 |
| 10 | -360.939 | -242.769 | 381.258 | -832.453 | 137.192 |

DEPENDENCE OF MERCURY INTERFACIAL TENSION ON CONCENTRATION AND POLARIZATION

POLYNOMIAL COEFFICIENTS FOR BENZYL ALCOHOL IN 1.0 N NaNO₃

| DEGREE | 0.0 | 0.00506 | 0.01010 | 0.01771 | 0.03097 | 0.05065 |
|--------|----------|-----------|----------|-----------|-----------|-----------|
| 0 | 383.956 | 382.425 | 381.500 | 380.646 | 379.413 | 378.511 |
| 1 | -141.509 | -135.738 | -131.346 | -128.625 | -123.170 | -120.004 |
| 2 | -135.488 | -132.949 | -147.636 | -139.280 | -144.628 | -143.282 |
| 3 | -60.761 | -49.373 | -99.546 | -133.308 | -118.938 | 3.843 |
| 4 | -91.191 | -344.716 | -351.808 | -861.851 | -823.622 | -176.858 |
| 5 | -15.042 | -1126.036 | -649.744 | -2381.399 | -2395.276 | -1058.126 |
| 6 | -287.293 | -1953.912 | -351.766 | -3180.422 | -3168.952 | -2238.767 |
| 7 | -896.484 | -1971.785 | 384.396 | -2226.694 | -2121.262 | -2794.275 |
| 8 | -965.124 | -1168.253 | 616.157 | -790.915 | -701.809 | -2154.625 |
| 9 | -456.089 | -379.330 | 303.540 | -112.835 | -90.940 | -914.651 |
| 10 | -81.089 | -52.335 | 52.606 | 0.0 | 0.0 | -160.055 |

REDUCED CONCENTRATION

| DEGREE | 0.10131 | 0.20236 | 0.35433 |
|--------|------------|------------|----------|
| 0 | 374.966 | 371.463 | 367.396 |
| 1 | -110.868 | -104.512 | -95.163 |
| 2 | -148.768 | -150.994 | -206.063 |
| 3 | -125.818 | -12.386 | -251.496 |
| 4 | -1203.528 | -925.872 | -324.321 |
| 5 | -4876.223 | -5279.910 | -329.690 |
| 6 | -9630.008 | -11748.816 | -181.688 |
| 7 | -10798.547 | -13772.777 | -36.835 |
| 8 | -7030.285 | -9000.262 | 0.0 |
| 9 | -2469.360 | -3097.405 | 0.0 |
| 10 | -360.939 | -437.410 | 0.0 |

APPENDIX B

Charge and Surface Excess

CHARGE ON THE ELECTRODE FOR ISC PENTANOL IN 0.1 N HClO₄ (MICROCOUL./CM²)

| VOLTS VS ECM | REDUCED CONCENTRATION | | | | | | | | | |
|-----------------|-----------------------|--------|--------|--------|--------|--------|--------|--------|--|--|
| | 0.0 | 0.0123 | 0.0244 | 0.0361 | 0.0476 | 0.0698 | 0.0909 | 0.1304 | | |
| -9.97 | -9.87 | -9.70 | -9.55 | -9.32 | -8.81 | -8.21 | -7.34 | | | |
| -9.16 | -9.03 | -8.87 | -8.66 | -8.44 | -7.76 | -7.07 | -6.07 | | | |
| -8.35 | -8.19 | -8.04 | -7.76 | -7.48 | -6.71 | -6.02 | -5.06 | | | |
| -7.52 | -7.35 | -7.18 | -6.85 | -6.49 | -5.68 | -5.06 | -4.27 | | | |
| -6.66 | -6.50 | -6.31 | -5.94 | -5.51 | -4.72 | -4.20 | -3.62 | | | |
| -5.74 | -5.60 | -5.42 | -5.04 | -4.59 | -3.86 | -3.45 | -3.06 | | | |
| -4.76 | -4.64 | -4.49 | -4.15 | -3.77 | -3.14 | -2.84 | -2.58 | | | |
| -3.69 | -3.60 | -3.54 | -3.28 | -3.03 | -2.56 | -2.37 | -2.17 | | | |
| -2.53 | -2.49 | -2.53 | -2.39 | -2.34 | -2.09 | -2.00 | -1.83 | | | |
| -1.29 | -1.31 | -1.45 | -1.46 | -1.61 | -1.65 | -1.68 | -1.56 | | | |
| 0.01 | 0.06 | 0.31 | 0.46 | 0.80 | 1.14 | 1.32 | 1.50 | | | |
| 1.35 | 1.22 | 0.91 | 0.64 | 0.18 | 0.46 | 0.81 | 0.99 | | | |
| 2.72 | 2.53 | 2.20 | 1.86 | 1.34 | 1.69 | 2.06 | 2.53 | | | |
| 4.08 | 3.86 | 3.54 | 3.20 | 2.68 | 3.16 | 3.36 | 4.18 | | | |
| 5.41 | 5.17 | 4.91 | 4.61 | 4.17 | 4.82 | 4.01 | 5.68 | | | |
| 6.70 | 6.48 | 6.26 | 6.05 | 5.72 | 6.55 | 5.83 | 7.49 | | | |
| 7.93 | 7.75 | 7.58 | 7.47 | 7.25 | 8.23 | 7.68 | 9.54 | | | |
| 9.12 | 9.00 | 8.84 | 8.82 | 8.69 | 9.76 | 9.44 | | | | |
| 10.28 | 10.22 | 10.06 | 10.08 | 9.99 | | | | | | |

CHARGE ON THE ELECTRODE FOR ISO PENTANOL IN 0.1 N H2SO4 (MICROCCUL./CM2)

REDUCED CONCENTRATION

| VOLTS VS ECM | 0.0 | 0.0123 | 0.0244 | 0.0361 | 0.0476 | 0.0698 | 0.0909 | 0.1304 | 0.2000 | 0.3548 | 0.5000 |
|--------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| -11.11 | -11.00 | -10.91 | -10.87 | -10.82 | -10.62 | -10.37 | -9.95 | -9.21 | -8.71 | -7.60 | -6.71 |
| -10.36 | -10.28 | -10.21 | -10.09 | -10.01 | -9.84 | -9.55 | -9.02 | -8.10 | -7.60 | -6.53 | -5.78 |
| -9.59 | -9.53 | -9.47 | -9.31 | -9.16 | -8.99 | -8.69 | -8.07 | -7.05 | -6.53 | -5.64 | -5.01 |
| -8.81 | -8.74 | -8.68 | -8.52 | -8.32 | -8.08 | -7.77 | -7.07 | -6.05 | -5.53 | -4.85 | -4.35 |
| -7.98 | -7.91 | -7.84 | -7.70 | -7.48 | -7.16 | -6.81 | -6.06 | -5.12 | -4.60 | -4.15 | -3.77 |
| -7.14 | -7.04 | -6.96 | -6.85 | -6.64 | -6.24 | -5.85 | -5.08 | -4.27 | -3.75 | -3.53 | -3.26 |
| -6.25 | -6.14 | -6.05 | -5.98 | -5.78 | -5.35 | -4.94 | -4.19 | -3.53 | -3.01 | -2.99 | -2.81 |
| -5.32 | -5.21 | -5.13 | -5.06 | -4.90 | -4.50 | -4.10 | -3.42 | -2.91 | -2.41 | -2.53 | -2.43 |
| -4.34 | -4.26 | -4.18 | -4.13 | -4.01 | -3.69 | -3.35 | -2.80 | -2.41 | -2.04 | -2.16 | -2.11 |
| -3.32 | -3.28 | -3.22 | -3.17 | -3.11 | -2.91 | -2.67 | -2.31 | -2.04 | -1.74 | -1.88 | -1.85 |
| -2.25 | -2.20 | -2.25 | -2.20 | -2.18 | -2.14 | -2.04 | -1.89 | -1.74 | -1.49 | -1.65 | -1.65 |
| -1.13 | -1.20 | -1.21 | -1.20 | -1.22 | -1.34 | -1.41 | -1.51 | -1.49 | -1.21 | -1.47 | -1.48 |
| 0.05 | 0.08 | 0.14 | 0.16 | 0.22 | 0.48 | 0.72 | 1.07 | 1.21 | 1.04 | 1.28 | 1.31 |
| 1.27 | 1.09 | 0.99 | 0.93 | 0.85 | 0.47 | 0.08 | 0.51 | 0.83 | 1.11 | 1.04 | 1.11 |
| 2.55 | 2.34 | 2.19 | 2.10 | 2.00 | 1.55 | 1.05 | 0.26 | 0.28 | 0.68 | 0.68 | 0.82 |
| 3.89 | 3.67 | 3.47 | 3.37 | 3.25 | 2.78 | 2.21 | 1.29 | 0.52 | 0.15 | 0.15 | 0.38 |
| 5.27 | 5.08 | 4.84 | 4.74 | 4.62 | 4.16 | 3.59 | 2.60 | 1.61 | 0.64 | 0.64 | 0.26 |
| 6.71 | 6.56 | 6.31 | 6.23 | 6.11 | 5.70 | 5.19 | 4.19 | 3.03 | 1.73 | 1.73 | 1.18 |
| 8.20 | 8.10 | 7.86 | 7.81 | 7.71 | 7.37 | 6.96 | 6.04 | 4.78 | 3.18 | 3.18 | 2.43 |
| 9.74 | 9.71 | 9.51 | 9.48 | 9.41 | 9.14 | 8.85 | 8.08 | 6.83 | 5.01 | 5.01 | 4.06 |

CHARGE ON THE ELECTRODE FOR PENTANOIC ACID IN 0.1 N HClO₄ (MICROCOUL./CM²)

| VOLTS VS ECM | REDUCED CONCENTRATION | | | | | | | | | | |
|-----------------|-----------------------|--------|--------|--------|--------|--------|--------|--|--|--|--|
| | 0.0 | 0.0123 | 0.0244 | 0.0476 | 0.0909 | 0.1304 | 0.1666 | | | | |
| -8.54 | -8.40 | -8.05 | -7.43 | -5.90 | -4.96 | -4.56 | | | | | |
| -7.72 | -7.50 | -7.14 | -6.37 | -4.85 | -4.05 | -3.75 | | | | | |
| -6.89 | -6.60 | -6.22 | -5.35 | -3.96 | -3.36 | -3.10 | | | | | |
| -6.00 | -5.69 | -5.28 | -4.41 | -3.20 | -2.84 | -2.63 | | | | | |
| -5.03 | -4.75 | -4.34 | -3.57 | -2.58 | -2.43 | -2.30 | | | | | |
| -3.97 | -3.76 | -3.59 | -2.82 | -2.08 | -2.08 | -2.05 | | | | | |
| -2.82 | -2.72 | -2.46 | -2.14 | -1.69 | -1.76 | -1.81 | | | | | |
| -1.59 | -1.61 | -1.51 | -1.48 | -1.37 | -1.46 | -1.55 | | | | | |
| -0.31 | -0.45 | -0.54 | -0.79 | -1.07 | -1.14 | -1.23 | | | | | |
| 1.01 | 0.76 | 0.49 | -0.01 | -0.17 | -0.77 | -0.85 | | | | | |
| 0.037 | 0.01 | 0.60 | 0.91 | 0.60 | 0.31 | 0.42 | | | | | |
| 0.137 | 3.28 | 2.80 | 1.99 | 0.60 | 0.30 | 0.10 | | | | | |
| 0.187 | 4.57 | 4.08 | 3.23 | 1.67 | 1.13 | 0.76 | | | | | |
| 0.237 | 5.87 | 5.44 | 4.62 | 3.04 | 2.25 | 1.64 | | | | | |
| 0.287 | 7.18 | 6.83 | 6.10 | 4.68 | 3.67 | 2.85 | | | | | |
| 0.337 | 8.47 | 8.22 | 7.62 | 6.49 | 5.38 | 4.44 | | | | | |
| 0.387 | 9.74 | 9.56 | 9.12 | 8.35 | 7.30 | 6.40 | | | | | |
| 0.437 | 11.10 | 10.99 | 10.56 | 10.13 | 9.30 | 8.61 | | | | | |
| 0.487 | 12.30 | 12.20 | 11.92 | 11.71 | 11.20 | 10.81 | | | | | |

CHARGE ON THE ELECTRODE FOR BENZYL ALCOHOL IN 1.0 N NaNO_3 (MICROCOUL./CM²)

REDUCED CONCENTRATION

| VOLTS VS ECM | 0.0 | 0.0051 | 0.0101 | 0.0177 | 0.0310 | 0.0506 | 0.1013 | 0.2024 | 0.3543 |
|-----------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| -12.59 | -12.59 | -12.32 | -12.01 | -11.75 | -11.09 | -9.82 | -7.97 | -5.98 | -5.40 |
| -10.87 | -10.87 | -10.29 | -9.69 | -9.29 | -8.26 | -6.78 | -5.59 | -4.51 | -4.16 |
| -9.04 | -9.04 | -8.11 | -7.29 | -6.80 | -5.64 | -4.60 | -4.08 | -3.74 | -3.43 |
| -6.92 | -6.92 | -5.82 | -5.01 | -4.55 | -3.54 | -3.22 | -3.08 | -3.09 | -2.94 |
| -4.39 | -4.39 | -3.48 | -2.92 | -2.64 | -2.02 | -2.29 | -2.24 | -2.33 | -2.47 |
| -1.52 | -1.52 | -1.11 | -0.96 | -0.94 | -0.82 | -1.35 | -1.38 | -1.52 | -1.84 |
| -0.020 | -0.020 | -0.40 | -0.37 | -0.44 | -0.47 | -1.01 | -1.09 | -1.28 | -1.60 |
| 0.030 | 0.030 | 0.79 | 0.64 | 0.43 | 0.16 | -0.37 | -0.56 | -0.88 | -1.14 |
| 0.080 | 0.080 | 2.00 | 1.69 | 1.37 | 0.90 | 0.40 | 0.05 | -0.45 | -0.61 |
| 0.130 | 0.130 | 3.22 | 2.79 | 2.41 | 1.78 | 1.30 | 0.77 | 0.07 | 0.01 |
| 0.180 | 0.180 | 4.47 | 3.96 | 3.56 | 2.81 | 2.34 | 1.64 | 0.73 | 0.72 |
| 0.230 | 0.230 | 5.74 | 5.18 | 4.81 | 4.00 | 3.51 | 2.69 | 1.61 | 1.53 |
| 0.280 | 0.280 | 7.04 | 6.44 | 6.14 | 5.32 | 4.80 | 3.90 | 2.73 | 2.45 |
| 0.330 | 0.330 | 8.35 | 7.74 | 7.52 | 6.72 | 6.18 | 5.26 | 4.10 | 3.48 |
| 0.380 | 0.380 | 9.66 | 9.05 | 8.89 | 8.15 | 7.62 | 6.72 | 5.65 | 4.67 |
| 0.430 | 0.430 | 10.97 | 10.37 | 10.23 | 9.55 | 9.09 | 8.20 | 7.30 | 6.04 |
| 0.480 | 0.480 | 12.27 | 11.72 | 11.53 | 10.93 | 10.56 | 9.65 | 8.92 | 7.63 |
| 0.530 | 0.530 | 13.57 | 13.13 | 12.86 | 12.32 | 12.00 | 11.09 | 10.45 | 9.52 |
| 0.580 | 0.580 | 14.96 | 14.71 | 14.41 | 13.90 | 13.44 | 12.75 | 12.04 | 11.78 |

CHARGE ON THE ELECTRODE FOR BENZYL ALCOHOL IN 0.1 N HClO₄ (MICROCOUL./CM²)

| VOLTS VS ECM | REDUCED CONCENTRATION | | | | | | | | | |
|-----------------|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| | 0.0 | 0.0024 | 0.0048 | 0.0101 | 0.0254 | 0.0354 | 0.0677 | 0.1063 | 0.1517 | 0.2625 |
| -9.16 | -8.85 | -8.69 | -7.79 | -6.51 | -6.03 | -4.90 | -4.63 | -4.24 | -4.00 | -3.82 |
| -7.21 | -7.27 | -6.72 | -5.77 | -4.77 | -4.39 | -4.25 | -3.53 | -3.42 | -3.27 | -3.20 |
| -5.36 | -5.13 | -4.72 | -3.82 | -3.18 | -3.06 | -3.10 | -2.62 | -2.67 | -2.53 | -2.54 |
| -3.51 | -3.05 | -2.68 | -2.12 | -1.77 | -1.78 | -1.81 | -1.77 | -1.84 | -1.86 | -1.84 |
| -1.26 | -1.01 | -0.61 | -0.48 | -0.43 | -0.46 | -0.66 | -0.80 | -0.90 | -1.06 | -1.08 |
| -0.013 | -0.21 | 0.16 | 0.17 | 0.09 | 0.04 | -0.25 | -0.38 | -0.52 | -0.70 | -0.78 |
| 0.037 | 0.91 | 1.19 | 1.10 | 0.85 | 0.75 | 0.32 | 0.26 | 0.05 | 0.14 | 0.32 |
| 0.087 | 2.09 | 2.22 | 2.08 | 1.69 | 1.51 | 0.97 | 0.98 | 0.69 | 0.50 | 0.21 |
| 0.137 | 3.30 | 3.25 | 3.11 | 2.60 | 2.35 | 1.72 | 1.78 | 1.43 | 1.22 | 0.83 |
| 0.187 | 4.51 | 4.30 | 4.17 | 3.58 | 3.30 | 2.62 | 2.66 | 2.26 | 2.01 | 1.56 |
| 0.237 | 5.70 | 5.38 | 5.23 | 4.63 | 4.35 | 3.64 | 3.60 | 3.21 | 2.88 | 2.40 |
| 0.287 | 6.88 | 6.50 | 6.31 | 5.71 | 5.51 | 4.79 | 4.62 | 4.24 | 3.82 | 3.35 |
| 0.337 | 8.06 | 7.68 | 7.41 | 6.82 | 6.73 | 6.00 | 5.70 | 5.35 | 4.86 | 4.42 |
| 0.387 | 9.26 | 8.91 | 8.55 | 7.95 | 7.95 | 7.25 | 6.85 | 6.52 | 6.01 | 5.58 |
| 0.437 | 10.49 | 10.17 | 9.74 | 9.11 | 9.10 | 8.47 | 8.05 | 7.72 | 7.25 | 6.82 |
| 0.487 | 11.75 | 11.43 | 10.99 | 10.32 | 10.12 | 9.67 | 9.31 | 8.96 | 8.56 | 8.12 |

SURFACE EXCESS ($\times 10^{10}$ MOLES/CM²) FOR PENTANOIC ACID IN 0.1 N HClO₄

REDUCED CONCENTRATION

| VOLTS VS ECM | 0.0123 | 0.0244 | 0.0476 | 0.0909 | 0.1304 | 0.1666 |
|-----------------|--------|--------|--------|--------|--------|--------|
| -0.413 | 0.29 | 0.34 | 1.01 | 2.25 | 2.92 | 3.69 |
| -0.363 | 0.29 | 0.38 | 1.44 | 2.63 | 3.50 | 4.22 |
| -0.313 | 0.29 | 0.53 | 1.87 | 3.02 | 4.07 | 4.45 |
| -0.263 | 0.34 | 0.72 | 2.20 | 3.50 | 4.36 | 4.55 |
| -0.213 | 0.38 | 0.96 | 2.44 | 4.02 | 4.45 | 4.60 |
| -0.163 | 0.43 | 1.15 | 2.59 | 4.22 | 4.55 | 4.65 |
| -0.113 | 0.43 | 1.25 | 2.73 | 4.36 | 4.55 | 4.65 |
| -0.063 | 0.48 | 1.39 | 2.78 | 4.36 | 4.60 | 4.69 |
| -0.013 | 0.43 | 1.39 | 2.78 | 4.36 | 4.60 | 4.69 |
| 0.037 | 0.43 | 1.25 | 2.68 | 4.26 | 4.55 | 4.65 |
| 0.087 | 0.38 | 1.05 | 2.49 | 4.02 | 4.50 | 4.65 |
| 0.137 | 0.34 | 0.77 | 2.25 | 3.59 | 4.36 | 4.55 |
| 0.187 | 0.29 | 0.53 | 1.92 | 3.07 | 4.07 | 4.41 |
| 0.237 | 0.24 | 0.38 | 1.48 | 2.68 | 3.50 | 4.17 |
| 0.287 | 0.24 | 0.29 | 1.01 | 2.25 | 2.92 | 3.50 |
| 0.337 | 0.24 | 0.24 | 0.62 | 1.68 | 2.44 | 2.83 |
| 0.387 | 0.24 | 0.24 | 0.43 | 1.10 | 1.87 | 2.30 |
| 0.437 | 0.19 | 0.24 | 0.34 | 0.67 | 1.25 | 1.63 |
| 0.487 | 0.19 | 0.19 | 0.29 | 0.53 | 0.77 | 0.96 |

SURFACE EXCESS (X10**10 MOLES/CM2) FOR ISO PENTANOL IN 0.1 N H2SO4

REDUCED CONCENTRATION

| VOLTS VS ECM | 0.0123 | 0.0244 | 0.0361 | 0.0476 | 0.0698 | 0.0909 | 0.1304 | 0.2000 | 0.3548 | 0.5000 |
|-----------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| -0.600 | 0.02 | 0.07 | 0.13 | 0.19 | 0.32 | 0.47 | 0.79 | 1.43 | 2.77 | 3.68 |
| -0.550 | 0.03 | 0.10 | 0.18 | 0.26 | 0.46 | 0.67 | 1.13 | 1.95 | 3.45 | 4.20 |
| -0.500 | 0.05 | 0.14 | 0.24 | 0.35 | 0.60 | 0.89 | 1.46 | 2.41 | 3.90 | 4.48 |
| -0.450 | 0.06 | 0.17 | 0.30 | 0.44 | 0.77 | 1.13 | 1.80 | 2.87 | 4.23 | 4.66 |
| -0.400 | 0.09 | 0.22 | 0.39 | 0.58 | 1.01 | 1.45 | 2.24 | 3.39 | 4.50 | 4.81 |
| -0.350 | 0.11 | 0.29 | 0.51 | 0.76 | 1.31 | 1.83 | 2.72 | 3.84 | 4.69 | 4.91 |
| -0.300 | 0.13 | 0.35 | 0.61 | 0.92 | 1.54 | 2.12 | 3.07 | 4.10 | 4.78 | 4.96 |
| -0.250 | 0.17 | 0.43 | 0.76 | 1.13 | 1.85 | 2.49 | 3.47 | 4.35 | 4.87 | 5.01 |
| -0.200 | 0.19 | 0.50 | 0.88 | 1.30 | 2.08 | 2.76 | 3.72 | 4.48 | 4.92 | 5.04 |
| -0.150 | 0.20 | 0.53 | 0.95 | 1.39 | 2.20 | 2.90 | 3.83 | 4.54 | 4.94 | 5.04 |
| -0.100 | 0.21 | 0.56 | 0.99 | 1.44 | 2.28 | 2.98 | 3.90 | 4.57 | 4.96 | 5.05 |
| -0.050 | 0.22 | 0.59 | 1.05 | 1.52 | 2.38 | 3.09 | 3.98 | 4.62 | 4.97 | 5.07 |
| 0.0 | 0.20 | 0.53 | 0.95 | 1.39 | 2.20 | 2.90 | 3.83 | 4.54 | 4.94 | 5.06 |
| 0.050 | 0.19 | 0.49 | 0.87 | 1.28 | 2.06 | 2.74 | 3.69 | 4.47 | 4.92 | 5.05 |
| 0.100 | 0.17 | 0.43 | 0.76 | 1.13 | 1.85 | 2.49 | 3.47 | 4.35 | 4.87 | 5.01 |
| 0.150 | 0.13 | 0.33 | 0.59 | 0.88 | 1.49 | 2.06 | 3.00 | 4.05 | 4.77 | 4.97 |
| 0.200 | 0.10 | 0.26 | 0.46 | 0.68 | 1.18 | 1.67 | 2.52 | 3.67 | 4.62 | 4.87 |
| 0.250 | 0.05 | 0.10 | 0.23 | 0.34 | 0.98 | 1.17 | 1.92 | 3.32 | 4.41 | 4.73 |
| 0.300 | 0.05 | 0.14 | 0.23 | 0.34 | 0.60 | 0.88 | 1.45 | 2.40 | 3.89 | 4.47 |
| 0.350 | 0.03 | 0.09 | 0.16 | 0.24 | 0.41 | 0.61 | 1.02 | 1.80 | 3.26 | 4.07 |

SURFACE EXCESS (X10**10 MOLES/CM2) FOR ISO PENTANOL IN 0.1 N HCL04

REDUCED CONCENTRATION

| VDLTS VS ECM | 0.0123 | 0.0244 | 0.0367 | 0.0476 | 0.0690 | 0.0909 | 0.1304 |
|--------------|--------|--------|--------|--------|--------|--------|--------|
| -0.500 | 0.10 | 0.29 | 0.43 | 0.62 | 1.09 | 1.57 | 2.19 |
| -0.450 | 0.14 | 0.38 | 0.62 | 0.90 | 1.43 | 1.95 | 2.90 |
| -0.400 | 0.24 | 0.48 | 0.76 | 1.14 | 1.86 | 2.48 | 3.43 |
| -0.350 | 0.24 | 0.62 | 1.00 | 1.48 | 2.24 | 2.90 | 3.90 |
| -0.300 | 0.33 | 0.76 | 1.19 | 1.71 | 2.57 | 3.43 | 4.24 |
| -0.250 | 0.33 | 0.86 | 1.43 | 1.95 | 3.00 | 3.81 | 4.33 |
| -0.200 | 0.38 | 1.00 | 1.62 | 2.09 | 3.33 | 4.09 | 4.47 |
| -0.150 | 0.38 | 1.05 | 1.71 | 2.33 | 3.67 | 4.19 | 4.52 |
| -0.100 | 0.38 | 1.09 | 1.81 | 2.43 | 3.76 | 4.28 | 4.52 |
| -0.050 | 0.43 | 1.09 | 1.76 | 2.43 | 3.71 | 4.28 | 4.52 |
| 0.0 | 0.38 | 1.05 | 1.71 | 2.33 | 3.62 | 4.24 | 4.52 |
| 0.050 | 0.33 | 0.95 | 1.57 | 2.09 | 3.33 | 4.09 | 4.47 |
| 0.100 | 0.33 | 0.76 | 1.33 | 1.86 | 2.90 | 3.81 | 4.38 |
| 0.150 | 0.24 | 0.62 | 1.09 | 1.48 | 2.43 | 3.24 | 4.24 |
| 0.200 | 0.19 | 0.48 | 0.81 | 1.09 | 2.00 | 2.62 | 3.76 |
| 0.250 | 0.10 | 0.33 | 0.57 | 0.71 | 1.48 | 2.05 | 2.95 |
| 0.300 | 0.05 | 0.19 | 0.38 | 0.43 | 1.00 | 1.48 | 2.24 |
| 0.350 | 0.05 | 0.14 | 0.24 | 0.25 | 0.62 | 0.95 | 1.57 |
| 0.400 | 0.05 | 0.05 | 0.10 | 0.14 | 0.24 | 0.52 | 0.81 |

SURFACE EXCESS ($\times 10^{10}$ MOLES/CM²) FOR BENZYL ALCOHOL IN 1.0 N NAN03

| VOLTS VS ECM | REDUCED CONCENTRATION | | | | | | | | | |
|-----------------|-----------------------|--------|--------|--------|--------|--------|--------|--------|--|--|
| | 0.0051 | 0.0101 | 0.0177 | 0.0310 | 0.0506 | 0.1013 | 0.2024 | 0.3543 | | |
| -0.550 | 0.15 | 0.15 | 0.34 | 0.54 | 1.86 | 3.33 | 4.22 | 5.11 | | |
| -0.450 | 0.50 | 0.61 | 0.81 | 1.16 | 2.89 | 3.73 | 4.94 | 5.35 | | |
| -0.350 | 0.75 | 1.08 | 1.44 | 2.22 | 3.79 | 4.28 | 4.61 | 4.61 | | |
| -0.250 | 0.97 | 1.58 | 2.30 | 3.11 | 3.71 | 4.65 | 5.04 | 5.65 | | |
| -0.150 | 1.92 | 2.12 | 2.24 | 2.99 | 3.65 | 4.44 | 5.40 | 5.45 | | |
| -0.050 | 1.79 | 1.98 | 2.31 | 3.60 | 4.13 | 4.84 | 5.11 | 5.11 | | |
| -0.020 | 1.09 | 2.08 | 2.49 | 2.93 | 3.40 | 4.59 | 4.72 | 4.76 | | |
| 0.030 | 1.03 | 2.08 | 2.49 | 2.94 | 3.32 | 4.58 | 4.72 | 4.75 | | |
| 0.080 | 1.09 | 2.09 | 2.44 | 2.86 | 3.18 | 4.53 | 4.71 | 4.75 | | |
| 0.130 | 0.93 | 1.88 | 2.30 | 2.81 | 3.03 | 4.43 | 4.70 | 4.74 | | |
| 0.180 | 0.89 | 1.71 | 2.18 | 2.65 | 2.93 | 3.19 | 4.67 | 4.73 | | |
| 0.230 | 0.75 | 1.49 | 1.93 | 2.57 | 2.80 | 3.77 | 4.61 | 4.71 | | |
| 0.280 | 0.72 | 1.29 | 1.73 | 2.36 | 2.67 | 3.18 | 4.50 | 4.68 | | |
| 0.330 | 0.64 | 1.03 | 1.37 | 2.13 | 2.48 | 2.97 | 4.07 | 4.63 | | |
| 0.380 | 0.64 | 0.88 | 1.17 | 1.84 | 2.23 | 2.84 | 3.38 | 4.51 | | |
| 0.430 | 0.56 | 0.74 | 0.97 | 1.52 | 1.90 | 2.67 | 3.04 | 4.11 | | |
| 0.480 | 0.56 | 0.66 | 0.81 | 1.18 | 1.58 | 2.48 | 2.86 | 3.40 | | |
| 0.530 | 0.54 | 0.60 | 0.71 | 0.96 | 1.21 | 2.21 | 2.69 | 2.97 | | |
| 0.580 | 0.53 | 0.57 | 0.64 | 0.77 | 0.91 | 1.85 | 2.48 | 2.88 | | |

SURFACE EXCESS ($\times 10^{10}$ MOLES/CM²) FOR BENZYL ALCOHOL IN 0.1 N HCL04

| VOLTS VS ECM | REDUCED CONCENTRATION | | | | | | | | | |
|-----------------|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| | 0.0024 | 0.0048 | 0.0101 | 0.0254 | 0.0354 | 0.0677 | 0.1063 | 0.1517 | 0.2625 | 0.3884 |
| -0.450 | 1.08 | 1.01 | 1.11 | 1.37 | 1.61 | 2.66 | 2.90 | 3.23 | 3.84 | 4.25 |
| -0.350 | 1.09 | 1.11 | 1.23 | 1.78 | 2.21 | 3.03 | 3.32 | 3.67 | 4.24 | 4.54 |
| -0.250 | 1.10 | 1.17 | 1.36 | 2.23 | 2.57 | 3.29 | 3.63 | 3.99 | 4.46 | 4.69 |
| -0.150 | 1.14 | 1.22 | 1.58 | 2.53 | 2.80 | 3.50 | 3.91 | 4.17 | 4.57 | 4.80 |
| -0.050 | 1.18 | 1.29 | 1.78 | 2.69 | 2.94 | 3.62 | 3.96 | 4.24 | 4.61 | 4.83 |
| -0.013 | 1.18 | 1.29 | 1.82 | 2.71 | 2.97 | 3.63 | 3.97 | 4.24 | 4.60 | 4.76 |
| 0.037 | 1.20 | 1.34 | 1.92 | 2.76 | 2.98 | 3.63 | 3.97 | 4.24 | 4.60 | 4.76 |
| 0.087 | 1.15 | 1.33 | 1.80 | 2.68 | 2.94 | 3.55 | 3.90 | 4.16 | 4.51 | 4.74 |
| 0.137 | 1.16 | 1.29 | 1.84 | 2.65 | 2.87 | 3.46 | 3.82 | 4.08 | 4.48 | 4.70 |
| 0.187 | 1.10 | 1.26 | 1.67 | 2.53 | 2.76 | 3.33 | 3.70 | 3.95 | 4.39 | 4.64 |
| 0.237 | 1.11 | 1.23 | 1.65 | 2.48 | 2.71 | 3.23 | 3.59 | 3.86 | 4.32 | 4.56 |
| 0.287 | 0.97 | 1.19 | 1.51 | 2.30 | 2.57 | 3.07 | 3.43 | 3.68 | 4.17 | 4.46 |
| 0.337 | 0.97 | 1.15 | 1.44 | 2.19 | 2.44 | 2.96 | 3.29 | 3.52 | 4.04 | 4.32 |
| 0.387 | 0.69 | 1.09 | 1.34 | 1.95 | 2.26 | 2.81 | 3.13 | 3.28 | 3.86 | 4.16 |
| 0.437 | 0.69 | 1.00 | 1.30 | 1.80 | 2.07 | 2.68 | 2.99 | 3.18 | 3.59 | 3.99 |
| 0.487 | 0.46 | 0.87 | 1.22 | 1.57 | 2.01 | 2.49 | 2.82 | 2.99 | 3.46 | 3.77 |

EXPERIMENTAL AND THEORETICAL CAPACITY VALUES FOR
PENTANDIC ACID IN 0.1 N HClO₄ (CAPACITY IN MICROFARAD/CM²)

| VOLTS VS ECM | REDUCED CONCENTRATION 0.0123 | | REDUCED CONCENTRATION 0.0244 | |
|-----------------|------------------------------------|-------|------------------------------------|-------|
| | THEOR | EXPTL | THEOR | EXPTL |
| -0.413 | 16.96 | 17.31 | 18.81 | 17.92 |
| -0.363 | 17.34 | 17.87 | 19.23 | 18.26 |
| -0.313 | 17.89 | 18.12 | 18.94 | 18.66 |
| -0.263 | 18.16 | 18.19 | 18.25 | 18.28 |
| -0.213 | 18.40 | 18.38 | 17.90 | 17.85 |
| -0.163 | 18.72 | 19.01 | 17.57 | 16.71 |
| -0.113 | 20.20 | 19.25 | 17.69 | 16.20 |
| -0.063 | 22.80 | 20.81 | 18.27 | 16.64 |
| -0.013 | 24.72 | 23.15 | 20.00 | 17.91 |
| 0.037 | 26.71 | 25.24 | 23.05 | 20.72 |
| 0.087 | 27.48 | 27.55 | 25.95 | 24.20 |
| 0.137 | 27.25 | 28.28 | 27.61 | 27.55 |
| 0.187 | 26.41 | 28.09 | 28.44 | 28.93 |
| 0.237 | 25.19 | 27.15 | 28.18 | 28.53 |
| 0.287 | 23.92 | 25.96 | 27.20 | 27.37 |
| 0.337 | 23.04 | 25.06 | 25.32 | 26.02 |
| 0.387 | 22.25 | 23.91 | 23.88 | 24.91 |
| 0.437 | 22.07 | 23.23 | 23.04 | 24.17 |
| 0.487 | 21.95 | 23.08 | 22.05 | 24.06 |

| VOLTS VS ECM | REDUCED CONCENTRATION 0.0698 | | REDUCED CONCENTRATION 0.0909 | |
|-----------------|------------------------------------|-------|------------------------------------|-------|
| | THEOR | EXPTL | THEOR | EXPTL |
| -0.413 | 24.80 | 20.05 | 26.61 | 24.36 |
| -0.363 | 22.37 | 21.16 | 23.58 | 17.12 |
| -0.313 | 19.03 | 20.42 | 18.13 | 12.93 |
| -0.263 | 15.55 | 17.57 | 14.66 | 9.72 |
| -0.213 | 13.54 | 14.21 | 10.58 | 8.13 |
| -0.163 | 12.73 | 11.49 | 8.24 | 7.16 |
| -0.113 | 12.43 | 10.16 | 7.19 | 6.93 |
| -0.063 | 13.16 | 10.01 | 6.91 | 6.47 |
| -0.013 | 14.42 | 10.17 | 7.56 | 6.98 |
| 0.037 | 17.03 | 12.35 | 9.83 | 8.02 |
| 0.087 | 19.56 | 16.10 | 12.14 | 9.86 |
| 0.137 | 22.53 | 23.09 | 17.11 | 13.18 |
| 0.187 | 24.80 | 30.17 | 21.80 | 19.00 |
| 0.237 | 27.49 | 33.86 | 25.52 | 28.13 |
| 0.287 | 29.75 | 32.52 | 30.61 | 42.23 |
| 0.337 | 30.11 | 29.41 | 32.50 | 41.26 |
| 0.387 | 27.34 | 27.06 | 33.27 | 34.18 |
| 0.437 | 24.99 | 25.71 | 30.42 | 29.77 |
| 0.487 | 23.26 | 25.23 | 28.55 | 27.94 |

EXPERIMENTAL AND THEORETICAL CAPACITY VALUES FOR
 PENTANOIC ACID IN 0.1 N HClO₄ (CAPACITY IN MICROFARAD/CM²)

| VOLTS VS ECM | REDUCED CONCENTRATION 0.1304 | | REDUCED CONCENTRATION 0.0 |
|-----------------|------------------------------------|-------|---------------------------------|
| | THEOR | EXPTL | EXPTL |
| -0.413 | 23.58 | 18.42 | 16.13 |
| -0.363 | 15.01 | 12.11 | 16.56 |
| -0.313 | 9.26 | 7.53 | 17.28 |
| -0.263 | 8.81 | 7.96 | 18.04 |
| -0.213 | 7.15 | 6.81 | 19.03 |
| -0.163 | 6.31 | 6.30 | 20.28 |
| -0.113 | 5.95 | 5.77 | 22.01 |
| -0.063 | 6.03 | 5.98 | 24.01 |
| -0.013 | 6.24 | 6.07 | 26.39 |
| 0.037 | 7.31 | 6.63 | 28.05 |
| 0.087 | 8.79 | 7.94 | 28.76 |
| 0.137 | 10.82 | 9.78 | 28.28 |
| 0.187 | 14.78 | 13.00 | 27.09 |
| 0.237 | 20.42 | 19.58 | 25.73 |
| 0.287 | 27.36 | 34.61 | 24.44 |
| 0.337 | 32.14 | 48.29 | 23.52 |
| 0.387 | 34.80 | 44.18 | 22.95 |
| 0.437 | 34.53 | 35.82 | 22.75 |
| 0.487 | 29.48 | 30.61 | 22.92 |

EXPERIMENTAL AND THEORETICAL CAPACITY VALUES FOR
ISO PENTANOL IN 0.1 N HClO₄ (CAPACITY IN MICROFARAD/CM²)

| VOLTS VS ECM | REDUCED CONCENTRATION 0.0123 | | REDUCED CONCENTRATION 0.0244 | |
|-----------------|------------------------------------|-------|------------------------------------|-------|
| | THEOR | EXPTL | THEOR | EXPTL |
| -0.500 | 15.73 | 15.95 | 17.61 | 16.75 |
| -0.450 | 16.04 | 16.17 | 17.63 | 16.81 |
| -0.400 | 16.51 | 16.38 | 17.69 | 16.92 |
| -0.350 | 17.02 | 16.64 | 17.73 | 17.08 |
| -0.300 | 17.57 | 17.26 | 17.81 | 17.19 |
| -0.250 | 18.11 | 17.60 | 17.94 | 17.32 |
| -0.200 | 19.02 | 18.59 | 18.03 | 17.41 |
| -0.150 | 20.15 | 19.86 | 18.20 | 17.61 |
| -0.100 | 21.69 | 21.53 | 19.19 | 18.54 |
| -0.050 | 23.47 | 23.74 | 20.45 | 20.32 |
| -0.000 | 25.56 | 26.12 | 23.50 | 24.16 |
| 0.050 | 26.80 | 28.00 | 25.63 | 27.48 |
| 0.100 | 27.93 | 29.14 | 27.26 | 28.17 |
| 0.150 | 27.61 | 28.32 | 27.97 | 29.41 |
| 0.200 | 27.16 | 27.29 | 27.72 | 28.17 |
| 0.250 | 26.35 | 25.71 | 27.21 | 26.88 |
| 0.300 | 25.47 | 24.84 | 26.00 | 25.29 |
| 0.350 | 24.39 | 23.90 | 25.08 | 24.13 |
| 0.400 | 23.52 | 23.07 | 24.16 | 23.42 |

| VOLTS VS ECM | REDUCED CONCENTRATION 0.0361 | | REDUCED CONCENTRATION 0.0476 | |
|-----------------|------------------------------------|-------|------------------------------------|-------|
| | THEOR | EXPTL | THEOR | EXPTL |
| -0.500 | 17.25 | 17.00 | 18.42 | 17.93 |
| -0.450 | 18.41 | 17.43 | 19.35 | 18.80 |
| -0.400 | 18.74 | 17.86 | 19.54 | 19.31 |
| -0.350 | 18.31 | 17.98 | 19.03 | 19.15 |
| -0.300 | 17.79 | 17.62 | 18.00 | 18.04 |
| -0.250 | 17.14 | 17.01 | 16.20 | 15.95 |
| -0.200 | 16.45 | 15.51 | 14.81 | 13.23 |
| -0.150 | 16.18 | 13.87 | 14.09 | 11.34 |
| -0.100 | 16.73 | 14.06 | 14.22 | 10.66 |
| -0.050 | 17.80 | 14.94 | 15.37 | 10.84 |
| -0.000 | 20.21 | 17.28 | 17.26 | 12.08 |
| 0.050 | 23.24 | 24.00 | 20.00 | 15.81 |
| 0.100 | 25.68 | 29.33 | 23.76 | 26.83 |
| 0.150 | 27.59 | 32.25 | 27.06 | 35.48 |
| 0.200 | 28.88 | 29.62 | 29.71 | 32.23 |
| 0.250 | 29.15 | 27.70 | 31.18 | 29.54 |
| 0.300 | 27.06 | 25.51 | 30.31 | 27.20 |
| 0.350 | 24.93 | 24.31 | 27.23 | 25.58 |
| 0.400 | 23.85 | 23.17 | 25.91 | 24.83 |

EXPERIMENTAL AND THEORETICAL CAPACITY VALUES FOR
ISO PENTANOL IN 0.1 N HClO₄ (CAPACITY IN MICROFARAD/CM²)

| VOLTS VS ECM | REDUCED CONCENTRATION 0.0698 | | REDUCED CONCENTRATION 0.0909 | |
|-----------------|------------------------------------|-------|------------------------------------|-------|
| | THEOR | EXPTL | THEOR | EXPTL |
| -0.500 | 20.00 | 21.23 | 25.33 | 24.16 |
| -0.450 | 20.51 | 22.08 | 22.98 | 24.10 |
| -0.400 | 20.49 | 21.72 | 20.21 | 22.39 |
| -0.350 | 19.56 | 19.87 | 17.83 | 16.77 |
| -0.300 | 17.01 | 16.03 | 15.18 | 13.04 |
| -0.250 | 14.32 | 12.28 | 12.36 | 10.43 |
| -0.200 | 11.47 | 10.11 | 9.54 | 8.61 |
| -0.150 | 9.82 | 6.74 | 7.93 | 7.33 |
| -0.100 | 9.60 | 7.81 | 7.57 | 6.80 |
| -0.050 | 10.23 | 7.99 | 7.98 | 6.83 |
| -0.000 | 11.87 | 8.83 | 8.64 | 7.49 |
| 0.050 | 15.92 | 11.21 | 11.68 | 8.75 |
| 0.100 | 20.80 | 15.55 | 16.30 | 11.03 |
| 0.150 | 24.73 | 24.91 | 22.44 | 16.61 |
| 0.200 | 28.78 | 46.02 | 29.03 | 32.94 |
| 0.250 | 32.66 | 39.41 | 33.36 | 54.13 |
| 0.300 | 32.47 | 30.51 | 35.49 | 37.78 |
| 0.350 | 29.36 | 27.73 | 35.01 | 30.16 |
| 0.400 | 27.49 | 26.71 | 31.92 | 27.28 |

| VOLTS VS ECM | REDUCED CONCENTRATION 0.1304 | | REDUCED CONCENTRATION 0.0 |
|-----------------|------------------------------------|-------|---------------------------------|
| | THEOR | EXPTL | EXPTL |
| -0.500 | 23.82 | 26.81 | 15.63 |
| -0.450 | 21.97 | 22.13 | 15.72 |
| -0.400 | 16.63 | 15.86 | 16.33 |
| -0.350 | 13.71 | 12.02 | 16.79 |
| -0.300 | 11.21 | 9.68 | 17.70 |
| -0.250 | 9.55 | 8.24 | 18.48 |
| -0.200 | 8.06 | 7.35 | 19.68 |
| -0.150 | 7.20 | 6.57 | 21.04 |
| -0.100 | 6.83 | 6.19 | 23.00 |
| -0.050 | 7.01 | 6.15 | 24.97 |
| -0.000 | 7.79 | 6.44 | 27.23 |
| 0.050 | 8.95 | 7.18 | 28.40 |
| 0.100 | 10.80 | 8.13 | 28.52 |
| 0.150 | 13.91 | 9.87 | 27.71 |
| 0.200 | 19.32 | 12.66 | 26.37 |
| 0.250 | 27.60 | 17.94 | 25.09 |
| 0.300 | 36.16 | 63.81 | 23.96 |
| 0.350 | 43.48 | 42.19 | 23.24 |
| 0.400 | 45.92 | 31.23 | |