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The inference of adsorption from double layer capacity studies

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THE INFERENCE OF ADSORPTION FROM
DOUBLE LAYER CAPACITY STUDIES

45 by

Robert Edward Minturn

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

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Iowa State College

1955

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DEDICATION

To Virginia

I. INTRODUCTION

A. Adsorption from Solution

Adsorption from solution may be defined as the concentration of one or more of the components of the solution at an interface between the solution phase and some external phase. A substance is consequently said to be adsorbed at an interface if its equilibrium concentration in the neighborhood of the interface is greater than that in the bulk solution. This investigation is concerned with the adsorption of a number of organic compounds at the interface between mercury and aqueous solutions of these compounds.

The adsorption of various organic compounds from aqueous solutions is a phenomena of quite widespread interest, for not only does a study of this adsorption have considerable academic value as a tool in the understanding of the nature of surfaces and of surface-solute interactions, but such a study may also lead to results which have considerable industrial worth. The corrosion of metals and the inhibition of that corrosion, the lubrication of metallic surfaces, the flotation and separation of ores, the spreading and adherence of paints and varnishes, the process of heterogeneous catalysis, and the purification of solutions by selective adsorption are but several of the many phenomena upon which a study of adsorption from solution could conceivably shed light.

In the past, most investigations of adsorption from solution by metals have been limited to those adsorbents which could be prepared with a very large specific surface area. This limitation has been necessitated by the manner in which the extent of adsorption was followed. In most cases, changes in adsorbate concentration in the bulk solution were determined in order to obtain adsorption isotherms. Other investigators determined the amount of material adsorbed by weighing the adsorbent before and after the adsorbate was admitted to the solution. Such studies of adsorption by metals were consequently limited to powdered metal samples (1,2,3), and these are notoriously difficult to rid of surface impurities and occluded contaminants, or to bundles of metal strips, which have small area to weight ratios and are therefore not given to accurate measurements. Some attempts (4,5) have been made to determine adsorption by single metal strips or plates by observing the changes in the contact angle water makes with the surface of the plate, but because of experimental difficulties such as adsorbate evaporation from the surface and hysteresis of contact angles, such studies are hardly more than qualitative. Franklin and Sothorn (6) employed a coulometric method for measuring the competitive adsorption from aqueous solutions of hydrogen and nitriles on platinized platinum, but their data too were quite irreproducible and give only qualitative information.

Butler and numerous co-workers (7,8,9,10,11,12) calculated

what they called "adsorption curves", actually surface tension lowering versus electrode potential curves, for various organic adsorbates upon liquid mercury. Their data were not sufficiently extensive to allow adsorption isotherms to be determined, and the method itself is somewhat inaccurate due to the small magnitude of the variations in surface tension and to the difficulty in obtaining really sensitive surface tension measurements. Ch'iao and Mann (13) studied the adsorption of amines on iron, utilizing steady state current-overvoltage measurements while Barclay and Butler (14) calculated an adsorption isotherm for tertiary amyl alcohol on mercury from their data on changes in the electrical double layer capacity as calculated from initial potential buildup measurements. Hansen and Clampitt (15) used both of the above methods to study the adsorption of sundry organic compounds by solid metals.

B. The Electrical Double Layer

The method utilized in this investigation to determine the extent of adsorption from solution involves the measurement of the changes in the electrical double layer capacity as a function of adsorbate concentration. Quincke (16) first visualized the existence of an electrical double layer at the interface between two immiscible phases, but his concept of the double layer as two simple layers of charge, one positive and one negative, is now known to be overly simplified. Present thinking (17,18,19) has the electrical double layer consisting of a

layer of electrons, if one phase is metallic, a layer of adsorbed ions, and a neighborhood, called the diffuse layer, in which there exists an excess of ions of one charge and a defect of ions of the opposite sign. This excess of a particular kind of ion falls off rapidly away from the electrode, with the half-thickness of the excess charge density generally less than about 100 angstrom units. At the surface of the metallic phase, there may exist a monomolecular layer of neutral molecules if there is no specific adsorption of ions by the metallic surface. In addition to ions, neutral polar molecules may be oriented at the surface and will consequently constitute part of the electrical double layer.

If the metallic phase is polarized by an external source of potential, there is a range of potentials over which only a very small current flows to or from the metal, for the electrical double layer acts as an electrical condenser of very large specific capacity. The range of potentials over which this condition exists depends upon the electrode material used; for solids such as silver and copper this range is quite small, of the order of 0.4 or 0.5 volts, while for mercury the range is about 1.2 volts or better. Upon polarization of the electrode, the effect of the concentration changes due to the direct current that does flow upon the measured properties of the electrode is negligible compared to experimental error if the current is kept small (20). Such currents in practice are not allowed to exceed one or two microamperes. The extent of

the negligible-current range depends in part upon the hydrogen overvoltage at the metal surface. At a mercury surface, which at a given current density has a high overvoltage compared to most other metals, there is a negligible rate of hydrogen deposition at polarizations less than a volt. Appreciable hydrogen deposition occurs on most other metal surfaces at much lower polarizing potentials, and the resulting flow of current is correspondingly large. Consequently, the method used in this investigation is most suited to the study of mercury surfaces, although it is applicable to the study of adsorption from solution by many metals. In addition to having a high hydrogen overvoltage, mercury is relatively easy to purify, it forms an electrode free of strains and easily changed, and mercury is relatively chemically inert. It is, consequently, preeminently fitted for an investigation of the present kind.

C. The Differential Capacity

When a mercury electrode is polarized, its surface tension changes. Lippman (21,22,23) first studied this effect using the electrometer which bears his name. As the electrode is made negative, its surface tension increases to a maximum and then decreases as the negative potential is increased still more. At the maximum in the surface tension versus potential curve, called the electrocapillary curve, the net charge on the mercury surface is zero. At potentials more positive than that of the electrocapillary maximum, the electrode is charged

positively; at potentials more negative, the electrode has a net negative charge. At constant composition the change in surface tension with potential should satisfy the equation

$$\frac{d\sigma}{dV} = -q,$$

where σ is the surface tension, V the potential difference, and q the charge per unit area (11,p.58).

If one plots the charge per unit area of surface against the electrode potential, he obtains a curve the slope of which at any point is the electrical double layer differential capacity C . That is, at constant composition,

$$C = \frac{dq}{dV}.$$

Friedrich Kruger (24) made the first quantitative measurements of the electrical double layer capacity of a mercury electrode by using an alternating current impedance bridge and a null detector. He studied the effect of electrode size, of solution composition, of frequency, and of polarizing voltage on the measured capacity. Since that time, there have been many such studies, increasing in accuracy and range as the quality of available electronic equipment has improved. Grahame has published an extensive series of papers elucidating the structure of the double layer (20,25,26,27,28,29,30), and an excellent review article on the electrical double layer and the theory of electrocapillarity (17). Proskurnin and Frumkin (31)

first pointed out in 1935 the large effects surface active molecules have upon the double layer capacity. They demonstrated that in a saturated solution octyl alcohol strongly depresses the differential capacity curve in the neighborhood of the electrocapillary maximum and pointed out the danger of contaminants in the measurement of the electrical properties of clean surfaces. Loveland and Elving (32) recently developed a rapid, although less sensitive, oscillographic technique for determining the differential capacity of the double layer. They obtained a current versus potential oscillogram and calculated the capacity from this. They assumed that the differential capacity as a function of applied potential is independent of the rate at which the potential is changed, despite the evidence to the contrary (8). Melik-Gaikazyan (33) postulated the formation of polymolecular layers of adsorbed molecules from the shape of the curves of the dependence of the differential capacity on the potential of the electrode. He observed that for saturated n-hexyl alcohol solutions and for n-octyl alcohol solutions at concentrations approaching saturation there was an additional lowering of the capacity curve below that curve which, according to him, corresponded to a complete monolayer on the surface of the mercury. He had demonstrated in a paper on the kinetics of the adsorption of surface-active substances on the mercury electrode (34) that with increasing volume concentration of the surface active substance the minimum of the capacity curve will lower and flatten out. By some line of

reasoning that is neither obvious nor stated, he concluded that the flat minimum corresponds to a monomolecular layer of adsorbate on the surface of the electrode. The range of concentrations employed by Melik-Gaikazyan was small, and he made no attempts to infer adsorption isotherms from his data. Kheifets and Krasikov have reported the measurement of the electrical double layer capacity of a platinum electrode in a recent paper (35). In addition, they observed that the effect of added organic materials on the measured capacity was similar to that that has been observed for mercury electrodes. No experimental data pertaining to the capacity measurements are given directly, but the range of polarizing potentials used was two or three volts. Platinum has a very small hydrogen overvoltage, and one is forced to conclude that at the potentials used considerable polarizing current must have been flowing. This current flow would not, of course, invalidate the qualitative information that can be gleaned from the capacity curves.

Relatively few of the large number of people interested in the properties of the electrical double layer have regarded the profound effect of strongly adsorbable components on the double layer capacity as anything more than extremely unfortunate, for the bulk of the work in this field has been concerned solely with solutions of electrolytes. The opportunity to utilize this effect in a quantitative measurement of adsorption has consequently been largely ignored until the present time.

II. OBJECTIVES

The objectives of this investigation were twofold. Initially, the aim of the research was to develop an accurate general method of obtaining adsorption isotherms for metal adsorbents of small specific surface area. Then, the object was to utilize the newly developed method to study the adsorption characteristics of a series of organic compounds so chosen as to allow one to correlate quantitatively (1) the effect of functional group on the extent of adsorption, (2) the effect of chain length upon the extent of adsorption, and (3) the effect of inorganic acid strength in the bulk solution upon the extent of adsorption.

In addition, since electrical measurements are becoming much more important in the study of interfacial properties of metal-liquid systems, the investigation of the effects of applied potential differences upon the adsorptive properties of the metal was of interest. Information gleaned from such an investigation should lead to an informative evaluation of previous work in this field where electrode potential values were unknown.

III. EXPERIMENTAL

A. Choice and Preparation of Solutions

Perchloric acid was chosen to fix the acid strength of the primitive solutions. This choice was prompted by two factors. First, the perchlorate ion has little tendency to complex other ions in solution, and consequently with its use there was no need for concern about ionic concentration and activity effects, and secondly, the perchlorate ion is not specifically adsorbed by mercury except under conditions of large positive polarization (17, p. 469). One solution about 0.1 molar in acid and another about 0.01 molar in acid were prepared by diluting a measured volume of Baker and Adamson reagent grade perchloric acid with water redistilled from basic permanganate. Because the capacity of the double layer is relatively insensitive to small variations in the ionic strength, it was not deemed necessary to control the acid strength more closely than this.

To provide an ion reversible to the silver-silver chloride reference electrode, each solution was made 0.001 molar in sodium chloride by adding a weighed amount of Baker Analyzed Reagent grade NaCl to the solution before it was diluted to volume.

B. Mercury

The mercury used as the electrode material in this

investigation was purified in the following way. Goldsmith Bros. triple-distilled mercury was fed dropwise through a sixty centimeter column of fifty percent by volume nitric acid. This operation was repeated twice to oxidize any base metals that might be present. The oxides formed were filtered off and the mercury was distilled at slightly reduced pressure in a stream of clean dry air. Again the oxides formed were filtered off, and the mercury was then distilled under vacuum to remove the last traces of the oxides that had been formed by the previous treatment.

C. Adsorbates

1. Octanoic acid

Eastman's best grade n-caprylic acid was distilled in a 30-plate Oldershaw column at a reflux ratio of twenty to one. The boiling point range of the central fraction retained, corrected to 760 mm. pressure, was 238.7 to 238.9 degrees centigrade. Lange (36) reports a value of 237.5°C.

2. Pentanenitrile

The exact history of the pentanenitrile used is not known. The only locally available sample had been synthesized some time ago by an unknown person in the Department of Organic Chemistry at Iowa State College, and was somewhat discolored before purification. It was distilled in a 30-plate Oldershaw column at a reflux ratio of ten to one. The boiling point

range at 760 mm. pressure of the fraction retained for use was 141.55 to 141.57 degrees centigrade. This narrow range is a good indication that the product used was quite pure, and it agrees with the value 141-142°C. reported by Lange (36).

3. Pentanoic acid

Eastman's best grade n-valeric acid was distilled in the Oldershaw column at a reflux ratio of ten to one. The fraction retained for use boiled at 186.5 to 186.8 degrees centigrade at 760 mm. pressure. Lange's value (36) is 187°C.

4. 1-Pentanol

Eastman's best grade n-amyl alcohol was distilled in the Oldershaw column. The fraction retained had a boiling point range of 138.41 to 138.56 at 760 mm. pressure, somewhat higher than the literature value 137.8-137.9°C. (36).

5. 3-Pentanone

Eastman's best grade 3-pentanone was distilled with a Helipak column. The central fraction, boiling at 102.01 degrees centigrade was retained. Lange's value (36) is 101.7°C.

D. Inert Atmosphere

The helium gas used as an inert atmosphere in the adsorption cell was purified by leading tank helium across a bed of finely divided uranium, prepared by thermally decomposing the

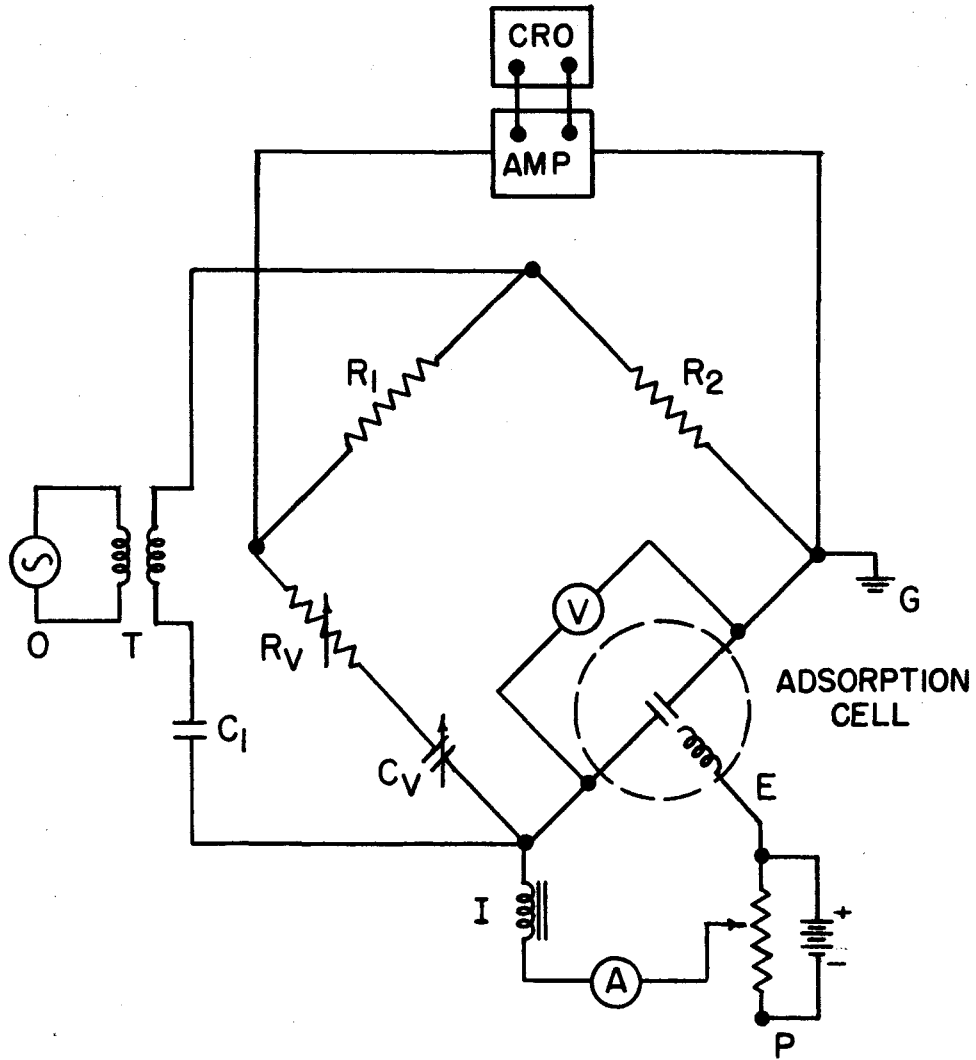
hydride and maintained at a temperature of 240 degrees centigrade. The helium then passed through a bed of activated charcoal maintained at liquid nitrogen temperature. Another liquid nitrogen trap removed stopcock grease from the helium stream immediately before it entered the cell.

E. Apparatus

1. Electronic components

The capacity measurements were made by means of an impedance bridge, shown in Figure 1, similar to that designed by Grahame (27,29). The equal resistance arms R_1 and R_2 consisted of small temperature coefficient wire-wound resistors of 1004.5 ohms each. The variable arm used to balance the impedance of the adsorption cell consisted of a decade resistor R_v in series with parallel decade capacitors C_v . R_v was variable in 0.10 ohm steps from zero to 11,000 ohms, while C_v , which was calibrated against a Beco Model 250-C Impedance Bridge, was continuously variable from zero to eleven microfarads. The power source O, a Hewlett-Packard audio oscillator, fed a 1000-cycle ac signal into the 10:1 step-down transformer T and was adjusted to maintain approximately a two millivolt drop, as measured by meter V, across the electrodes of the adsorption cell. The unbalanced signal across the bridge was amplified by the 1000-cycle high-gain amplifier AMP and detected on CRO, a DuMont type 323 cathode ray oscilloscope.

Figure 1. Electronic schematic diagram of differential capacity apparatus



The potentiometer P was adjusted to apply the desired polarizing voltage on the test electrode, utilizing the reversible electrode E as a reference. The microammeter A measured the dc current through the cell. The 3 henry inductance I was included to choke ac signal out of the potentiometer circuit, and the 2 microfarad condenser C₁ eliminated a direct current path from the electrodes through the transformer.

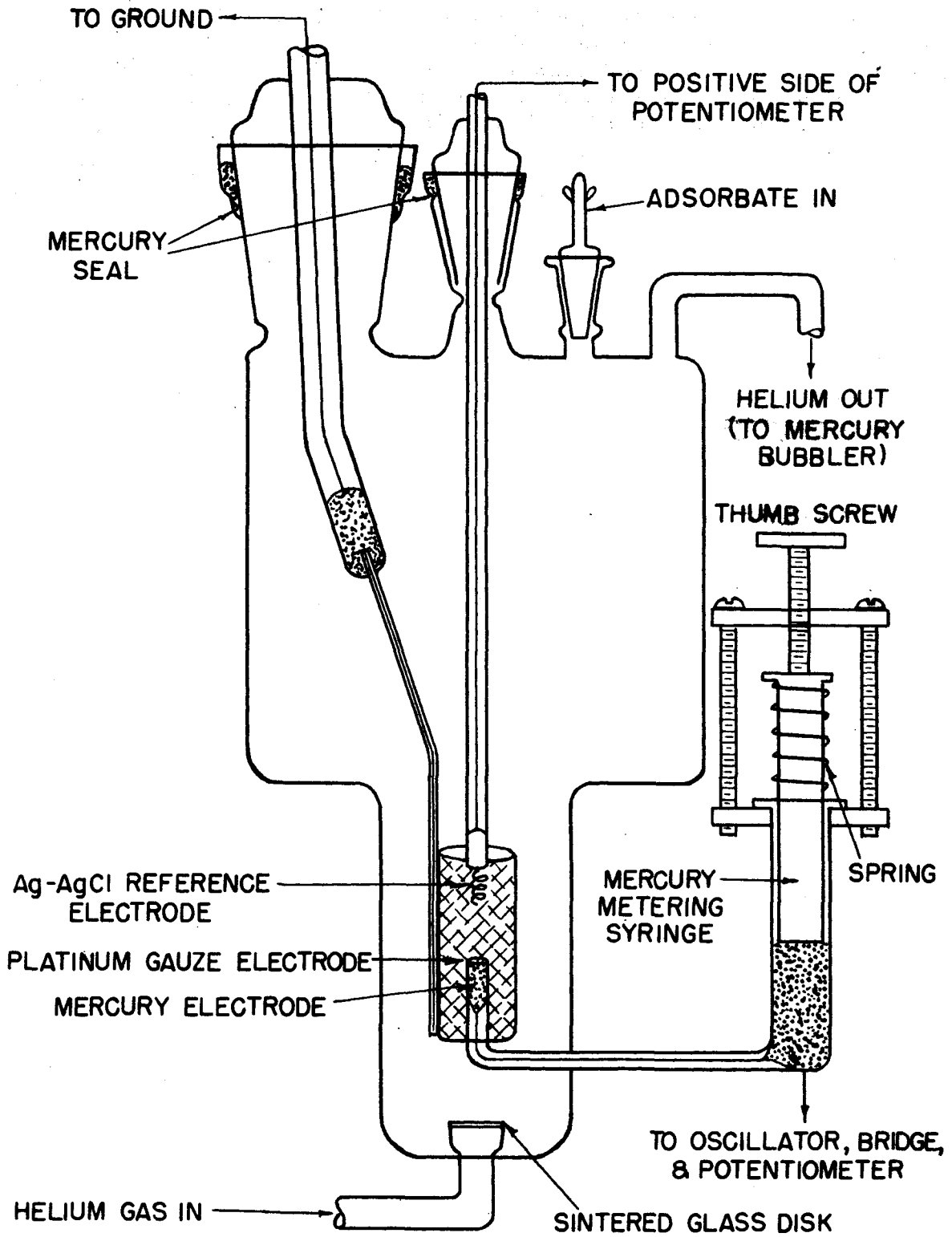
2. The adsorption cell

The Pyrex adsorption cell is sketched in Figure 2. Helium, entering at the bottom of the cell, served a dual purpose in that it both stirred the solution and provided an inert atmosphere. The mercury bubbler and mercury seals on the larger standard tapers prevented contaminating gases from entering the cell. The positive pressure in the cell minimized oxygen contamination when adsorbate was added through the appropriate taper. The mercury electrode surface was renewed when desired by turning the thumb screw controlling the plunger in the mercury metering syringe. The contaminated mercury spilled over the tip of the capillary and collected at the bottom of the cell. There was no contact between either solution or vapors with stopcock greases.

3. The electrodes

The adsorption cell contained three electrodes. The reference electrode was a Ag-AgCl electrode made by the

Figure 2. The adsorption cell



thermal-electric method of Harned (37). The test electrode was a hemispherical drop of mercury formed in a small vertical Pyrex tube in the center of the adsorption cell. The area of the mercury electrode, calculated from the diameter of the tube and assuming a perfect hemispherical shape for the drop, was 0.0982 square centimeters. Concentric with the tube containing the mercury electrode was placed a platinum screen cylinder. This cylinder was in series with the mercury electrode in the ac circuit. Because the area of the platinum electrode was very large compared to that of the mercury, its electrical double layer capacity had little effect on the total measured impedance of the cell. Even if the capacity of the platinum electrode changed markedly during an adsorption run, as it undoubtedly did, the ratio of mercury capacity to platinum capacity should have remained negligible, and the platinum contribution to cell impedance should therefore also have been negligible.

F. Method of Procedure

Two or three milliliters of purified mercury were transferred to the mercury metering syringe and the plunger and thumb screw assembly attached. The platinum electrode was inserted and the cell was flushed for several minutes with helium before three hundred milliliters of the prepared perchloric acid - sodium chloride solution were measured and added. The reference electrode was inserted and the remaining

taper closed to seal the cell. Helium was bubbled vigorously through the cell for at least an hour before any measurements were made to rid the cell of most of the dissolved contaminating gases.

The electrical leads to the bridge were attached to the cell and a new mercury surface was prepared by turning the thumb screw until the old surface spilled over the end of the electrode tube and fell to the bottom of the cell. The flow of helium was stopped. The bridge was energized, and the oscillator amplifier adjusted to give an ac voltage drop of about two millivolts across the electrodes. The potentiometer was calibrated against a standard cell and then adjusted to place a polarizing voltage of -0.10 volt, relative to the Ag-AgCl electrode in 0.001 N. chloride, between the mercury and reference electrodes. A null signal was obtained on the oscilloscope by adjusting the decade resistors and capacitors to balance the impedance of the cell. The capacity needed to achieve this balance was read and recorded as the differential capacity of the electrical double layer of the mercury surface. The polarizing voltage was decreased by 0.10 volt and the bridge again balanced. This operation was repeated throughout the polarizing potential range from -0.1 volt to -1.10 volts. After recording the capacity of the electrode at a polarizing potential of -1.10 volts, a new mercury surface was formed. The capacities of this new surface were measured and recorded as

the polarizing potential was increased in 0.10 volt steps to -0.10 volts. After the potentiometer was again balanced against the standard cell, a given amount of adsorbate was added by micropipette to the cell and stirred by bubbling helium through the solution for a short period of time. Without changing mercury electrode, the capacities were again measured as a function of decreasing potential. At -1.10 volts, the surface was again renewed, and the capacities measured with increasing potential at the same concentration.

With this method of operation it was possible to guard against any differences in capacity resulting from direction of change of potential, and it was also possible to get two measurements of capacity at each polarizing potential for a given adsorbate concentration.

The size of the mercury electrode varied each time it was changed, indicating that some wetting of the walls of the tube by the mercury prevented the mercury from forming a truly hemispherical surface. To eliminate spurious capacity changes due to change in electrode size, the size of the new electrode was adjusted by manipulating the thumb screw until the same capacity value was obtained as had the previous electrode at the same polarizing potential of -1.10 volts.

IV. EXPERIMENTAL RESULTS

The data collected in this investigation were the values of the electrical double layer capacity of the mercury electrodes at different polarizing potentials and adsorbate concentrations. One adsorbate, pentanoic acid, was studied in two solutions of different strength in perchloric acid, 0.009 normal and 0.10 normal. The data for the perchloric acid solutions without added adsorbate are given in Table 1. The uncertainties indicated are the standard deviations of the experimental values during the course of several runs. Tables 2 through 7 record the double layer capacities in microfarads per square centimeter as functions of polarizing potential and adsorbate reduced concentrations C/C_0 for the adsorbates octanoic acid, pentanoic acid (in two different acid solutions), pentanenitrile, 3-pentanone, and 1-pentanol. The reduced concentrations, which are the adsorbate concentrations divided by its saturation concentration, were used as close approximations to the adsorbate activities, which were unavailable. In the figures following each of these tables, Figures 3 through 8, are drawn representative capacity versus potential curves for the given adsorbates at various molal concentrations. The values plotted are the average values of the two measurements made at each potential for each adsorbate concentration. The lengths of the vertical lines intersecting the "clean mercury" curves in Figures 3 through 8 indicate graphically the uncertainties listed in Table 1.

In Table 8 are listed the saturation concentrations for the various adsorbates. The saturation concentrations for pentanoic acid, pentanenitrile, 3-pentanone, and 1-pentanol in 0.10 N. HClO_4 were determined by adding slight excesses of the adsorbate to the acid solution in a slender buret and estimating the amount undissolved after long equilibration through agitation. The accuracy of this method as used is believed to be about one percent.

Table 1. Differential capacity at the mercury-aqueous solution interface. Aqueous phase 0.001 N. NaCl with indicated concentration of HClO₄. Potentials in volts relative to Ag-AgCl electrode in 0.001 N. NaCl. Capacities in microfarads/cm².

0.10 N. HClO ₄		0.009 N. HClO ₄	
Potential	Capacity	Potential	Capacity
-0.1	23.51 ± 0.20	-0.1	25.2 ± 0.8
-0.2	19.76 ± 0.19	-0.2	20.7 ± 0.7
-0.3	18.64 ± 0.31	-0.3	16.6 ± 0.4
-0.4	18.49 ± 0.40	-0.4	14.8 ± 0.3
-0.5	19.96 ± 0.10	-0.5	13.5 ± 0.4
-0.6	20.03 ± 0.06	-0.6	10.50 ± 0.09
-0.7	18.23 ± 0.13	-0.7	9.30 ± 0.03
-0.8	17.11 ± 0.09	-0.8	10.63 ± 0.06
-0.9	15.33 ± 0.10	-0.9	10.60 ± 0.02
-1.0	14.27 ± 0.11	-1.0	10.03 ± 0.00
-1.1	13.78 ± 0.03	-1.1	9.49 ± 0.00

Table 2. Dependence of differential capacity at mercury-aqueous solution interface on polarizing potential and concentration of octanoic acid in 0.10 N. aqueous perchloric acid solution. Capacity in microfarads/cm². Potential in volts relative to Ag-AgCl in 0.001 N. chloride solution.

C/C ₀	Hg.	<u>Electrode Potential</u>										
		-0.1	-0.2	-0.3	-0.4	-0.5	-0.6	-0.7	-0.8	-0.9	-1.0	-1.1
0.044	a	25.05	20.65	19.45	18.63	10.89	7.04	6.09	6.20	7.74	11.78	13.33
	b	24.51	20.82	19.71	15.88	10.02	7.22	6.24	6.21	7.01	9.33	13.31
0.088	b	25.36	21.88	20.63	12.02	6.54	5.02	4.58	4.61	5.11	6.58	10.44
	c	26.18	22.68	21.05	11.51	6.61	5.08	4.59	4.56	4.97	6.27	10.50
0.133	c	26.56	23.51	21.19	9.95	5.81	4.63	4.28	4.30	4.64	5.68	8.60
	d	26.52	23.61	20.35	10.02	5.90	4.66	4.26	4.22	4.53	5.50	8.59
0.265	d	27.75	27.89	15.66	6.55	4.53	3.92	3.70	3.68	3.87	4.37	5.63
	e	30.46	31.17	15.61	6.73	4.65	4.02	3.78	3.74	3.91	4.38	5.62
0.398	e	29.73	31.89	10.42	5.13	3.92	3.50	3.36	3.35	3.45	3.76	4.48
	f	31.46	34.38	10.50	5.20	3.97	3.54	3.38	3.36	3.45	3.76	4.49
0.531	f	33.70	28.22	8.08	4.40	3.57	3.28	3.17	3.16	3.26	3.48	4.01
	g	33.09	27.43	7.98	4.40	3.56	3.28	3.17	3.16	3.26	3.47	3.99
0.708	g	44.58	19.08	4.58	2.85	2.53	2.53	2.68	2.90	3.08	3.30	3.65
	h	38.02	19.04	5.73	2.99	2.46	2.47	2.62	2.86	3.07	3.28	3.65
0.885	h	38.89	17.15	3.42	1.98	1.82	1.81	1.88	2.06	2.43	2.97	3.46
	i	43.28	16.75	3.72	1.97	1.81	1.80	1.87	2.04	2.39	2.95	3.46

Figure 3. Differential capacity versus electrode potential for octanoic acid on mercury in 0.10 N. perchloric acid

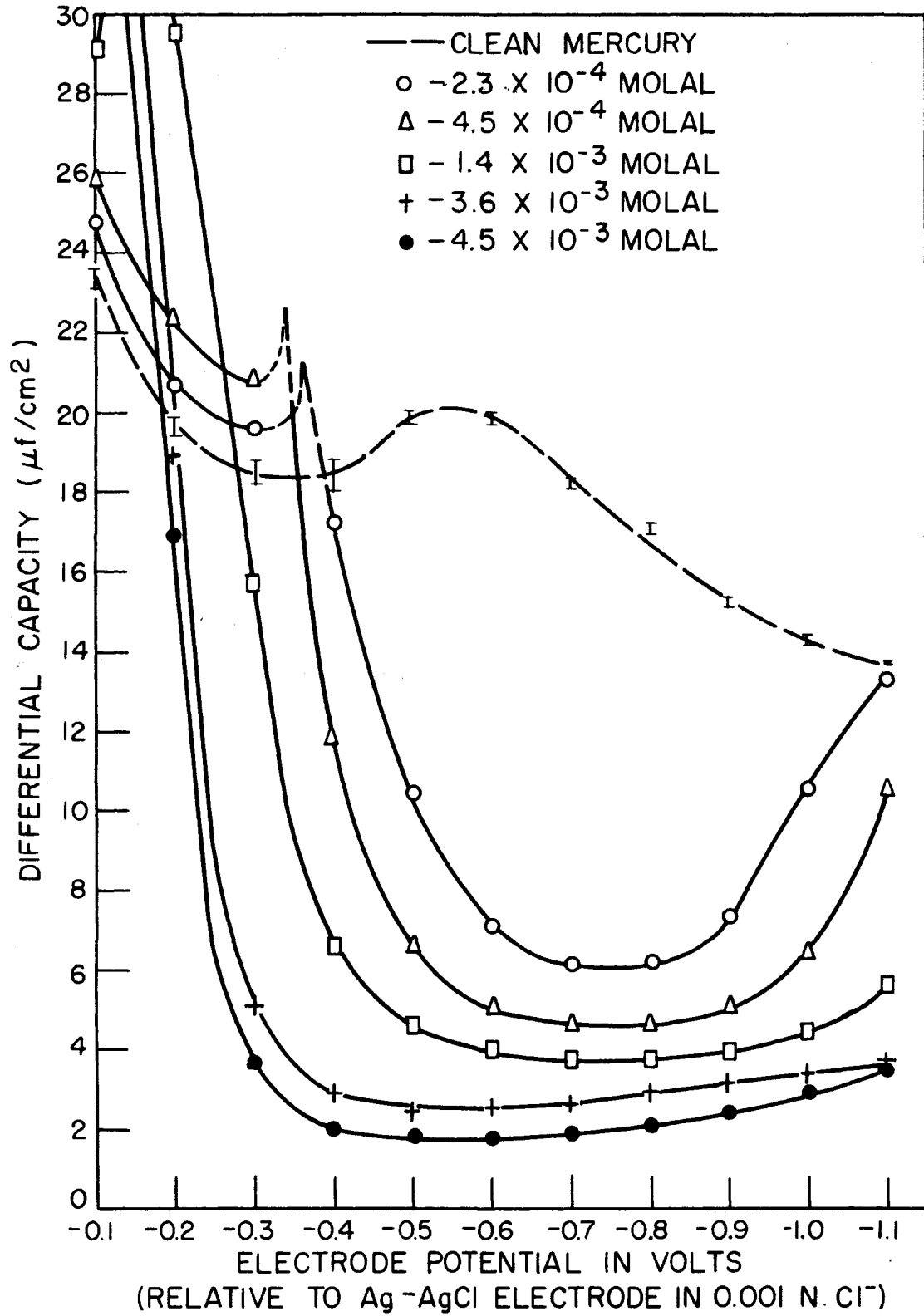


Table 3. Dependence of differential capacity at mercury-aqueous solution interface on polarizing potential and concentration of pentanoic acid in 0.10 N. aqueous perchloric acid solution. Capacity in microfarads/cm² Potential in volts relative to Ag-AgCl in 0.001 N. chloride solution

c/c _o		Electrode Potential										
		-0.1	-0.2	-0.3	-0.4	-0.5	-0.6	-0.7	-0.8	-0.9	-1.0	-1.1
0.0084	a	23.69	20.19	19.59	20.76	22.13	21.41	18.50	16.22	15.12	14.47	14.22
	b	24.16	20.65	19.91	20.09	21.38	20.50	17.84	15.90	15.39	14.75	14.30
0.0168	b	24.00	20.57	20.15	21.35	22.28	20.09	16.68	15.19	14.99	14.83	14.55
	c	24.44	21.12	20.65	20.96	21.28	19.24	16.13	15.30	15.13	14.97	14.61
0.0504	c	24.67	22.00	23.15	26.15	20.07	11.35	8.57	9.18	12.64	16.88	17.58
	d	24.37	21.91	22.88	24.82	19.94	11.32	8.55	9.16	12.58	16.83	17.26
0.084	d	24.67	23.21	27.48	27.30	13.25	7.72	6.33	6.47	8.26	13.49	20.88
	e	24.87	23.42	27.57	27.47	13.25	7.71	6.30	6.44	8.15	13.48	20.87
0.151	e	26.30	28.33	35.59	17.09	8.30	5.85	5.13	5.06	5.62	7.47	13.32
	f	27.92	30.65	37.32	17.99	8.47	5.92	5.16	5.08	5.64	7.50	13.86
0.235	f	30.91	41.21	29.78	11.98	6.69	5.21	4.68	4.60	4.86	5.76	8.32
	g	30.88	39.94	30.27	12.20	6.76	5.24	4.72	4.60	4.85	5.73	8.36
0.403	g	40.13	42.54	18.32	8.26	5.58	4.69	4.36	4.26	4.37	4.80	5.92
	h	40.96	43.99	18.75	8.43	5.64	4.72	4.37	4.26	4.37	4.78	5.91
0.689	h	52.2	27.87	11.44	6.07	4.76	4.36	4.20	4.15	4.20	4.42	5.00
	i	52.7	28.66	11.80	6.17	4.81	4.38	4.20	4.15	4.19	4.42	4.98
1.00	i	38.01	24.53	8.76	4.12	3.50	3.64	4.06	4.49	4.68	4.74	5.02
	j	40.7	26.40	9.21	4.18	3.49	3.62	4.05	4.48	4.67	4.74	5.01

Figure 4. Differential capacity versus electrode potential for pentanoic acid on mercury in 0.10 N. perchloric acid

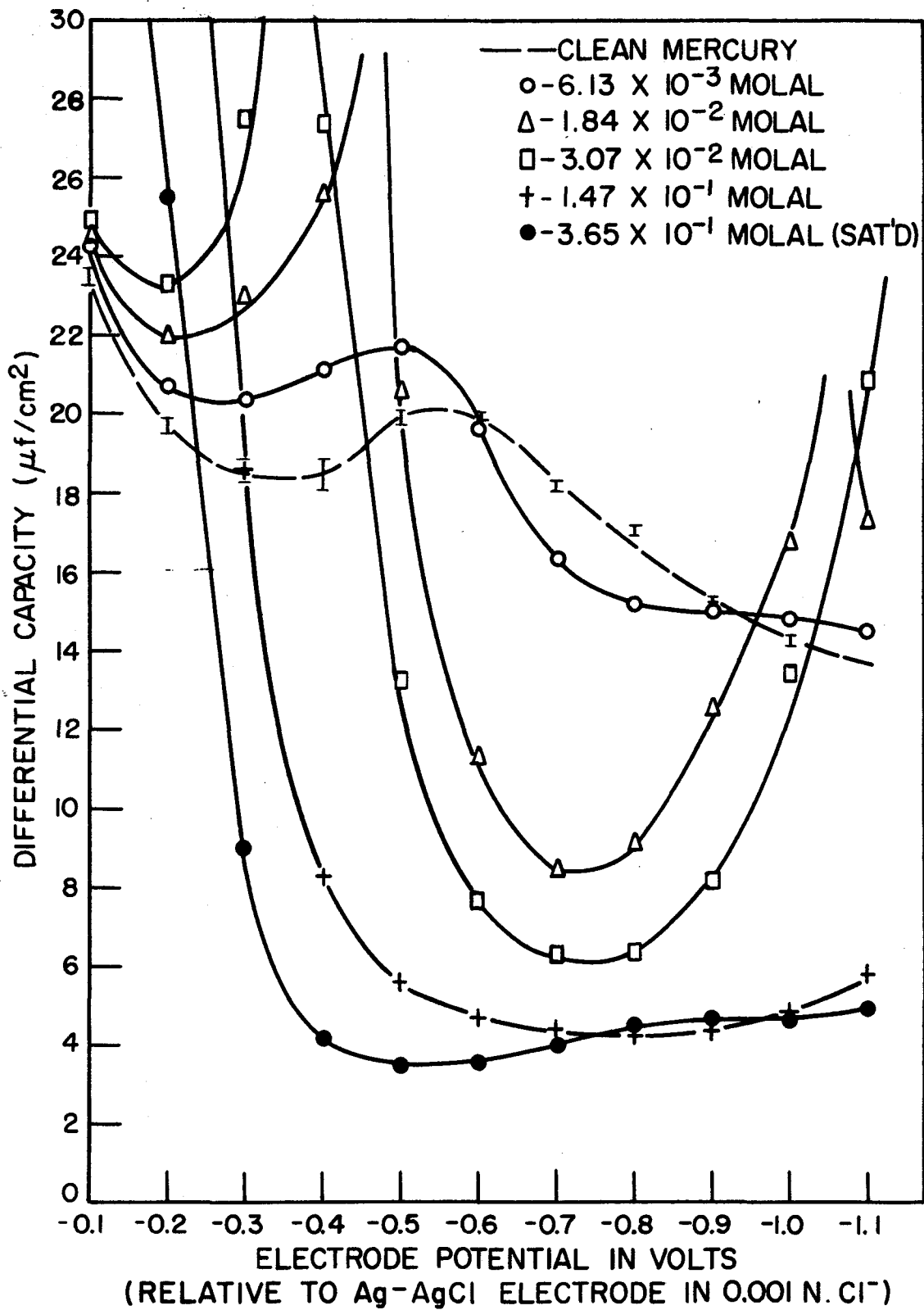


Table 4. Dependence of differential capacity at mercury-aqueous solution interface on polarizing potential and concentration of pentanoic acid in 0.009 N. aqueous perchloric acid solution. Capacity in microfarads/cm². Potential in volts relative to Ag-AgCl in 0.001 N. chloride solution

C/C _o	Hg.	<u>Electrode Potential</u>										
		-0.1	-0.2	-0.3	-0.4	-0.5	-0.6	-0.7	-0.8	-0.9	-1.0	-1.1
0.016	a	27.2	22.3	21.3	20.7	17.33	11.44	10.00	11.31	12.46	13.04	12.97
	b	27.5	23.0	22.2	22.2	18.2	10.87	9.39	10.57	11.93	13.00	12.97
0.049	b	28.7	25.3	27.0	24.0	10.48	6.41	5.95	6.47	8.38	12.73	15.97
	c	28.9	25.7	28.2	23.4	9.65	6.22	5.69	6.04	7.56	11.35	15.97
0.082	c	30.4	30.1	35.5	15.5	6.89	5.23	4.90	5.02	5.80	8.38	16.01
	d	31.5	31.4	39.4	15.3	6.98	5.32	4.97	5.03	5.68	7.96	16.01
0.132	d	34.3	43.4	29.6	9.80	5.64	4.76	4.48	4.46	4.80	5.85	9.44
	e	34.2	43.7	30.9	9.69	5.54	4.60	4.31	4.29	4.59	5.63	9.44
0.214	e	41.6	55.0	17.1	7.08	4.85	4.26	4.04	3.99	4.15	4.66	6.10
	f	41.2	62.4	17.1	7.03	4.86	4.29	4.06	4.01	4.16	4.64	6.10
0.395	f	78.9	30.4	10.4	5.58	4.38	4.00	3.85	3.80	3.86	4.09	4.65
	g	82.7	30.8	9.99	5.39	4.27	3.94	3.80	3.77	3.84	4.07	4.65
0.675	g	50.1	20.48	7.83	4.30	3.95	3.77	3.76	3.77	3.84	3.97	4.27
	h	53.4	21.1	8.12	4.64	3.86	3.68	3.68	3.74	3.81	3.96	4.27
1.00	h	52.4	25.2	7.46	4.22	3.33	3.14	3.35	3.88	4.10	4.22	4.37
	i	44.9	27.6	10.1	4.13	3.26	3.27	3.53	3.86	4.10	4.21	4.37

Figure 5. Differential capacity versus electrode potential for pentanoic acid on mercury in 0.009 N. perchloric acid

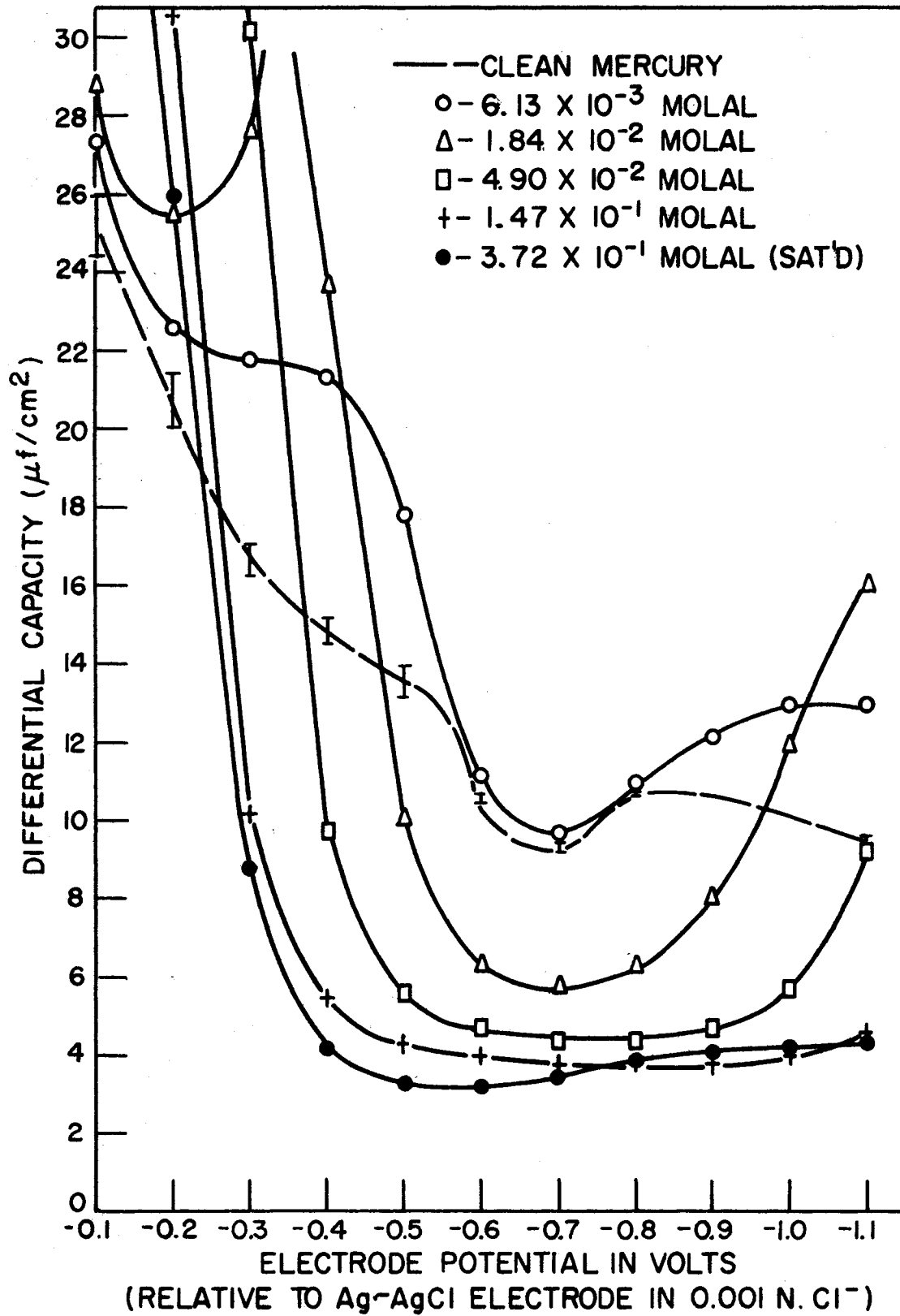


Table 5. Dependence of differential capacity at mercury-aqueous solution interface on polarizing potential and concentration of pentanenitrile in 0.10 N. aqueous perchloric acid solution. Capacity in microfarads/cm² Potential in volts relative to Ag-AgCl in 0.001 N. chloride solution

C/C _o	Hg.	<u>Electrode Potential</u>										
		-0.1	-0.2	-0.3	-0.4	-0.5	-0.6	-0.7	-0.8	-0.9	-1.0	-1.1
0.012	a	24.07	20.22	19.41	19.91	21.46	21.90	19.66	16.86	15.11	14.12	13.52
	b	23.46	20.02	19.39	20.25	21.47	21.63	19.26	16.61	15.04	14.12	13.54
0.024	b	23.07	19.72	19.09	19.85	21.34	21.52	18.88	16.08	14.58	13.84	13.40
	c	23.25	19.93	19.36	20.38	21.87	21.71	18.91	16.09	14.61	13.86	13.40
0.047	c	23.19	20.00	19.55	20.57	22.10	21.28	17.53	14.66	13.78	13.69	13.57
	d	23.10	19.89	19.42	20.58	22.08	21.28	17.51	14.64	13.78	13.69	13.57
0.094	d	23.24	20.32	20.18	22.20	25.04	18.62	11.31	8.98	8.57	10.37	15.28
	e	23.57	20.43	20.30	22.36	25.30	18.89	11.43	9.02	8.56	10.26	15.25
0.142	e	23.66	20.95	21.40	26.15	26.95	13.05	9.26	7.91	7.28	7.21	8.56
	f	24.70	21.63	22.17	27.25	27.96	13.48	9.44	8.00	7.36	7.26	8.56
0.236	f	23.90	21.90	25.40	36.32	15.09	10.13	8.35	7.40	6.81	6.45	6.37
	g	24.08	21.89	25.32	36.82	15.51	10.28	8.42	7.45	6.85	6.47	6.38
0.426	g	25.37	26.28	44.92	17.38	11.42	9.13	7.92	7.13	6.58	6.18	5.94
	h	25.73	26.62	46.51	17.96	11.56	9.16	7.94	7.13	6.57	6.18	5.95
0.64	h	29.38	49.42	21.23	13.24	10.07	8.49	7.54	6.88	6.39	6.03	5.76
	i	28.14	48.22	20.53	13.53	10.26	8.56	7.54	6.84	6.36	6.03	5.78
0.91	i	34.35	41.93	17.80	12.03	9.40	8.11	7.34	6.78	6.36	6.02	5.76
	j	31.41	36.75	17.80	12.36	9.55	8.19	7.39	6.81	6.38	6.04	5.76
1.00	j	39.23	33.51	16.88	11.44	9.03	7.94	7.26	6.76	6.36	6.04	5.80
	k	36.14	30.38	17.04	11.92	9.29	8.11	7.39	6.84	6.41	6.05	5.80

Figure 6. Differential capacity versus electrode potential for pentanenitrile on mercury in 0.10 N. perchloric acid

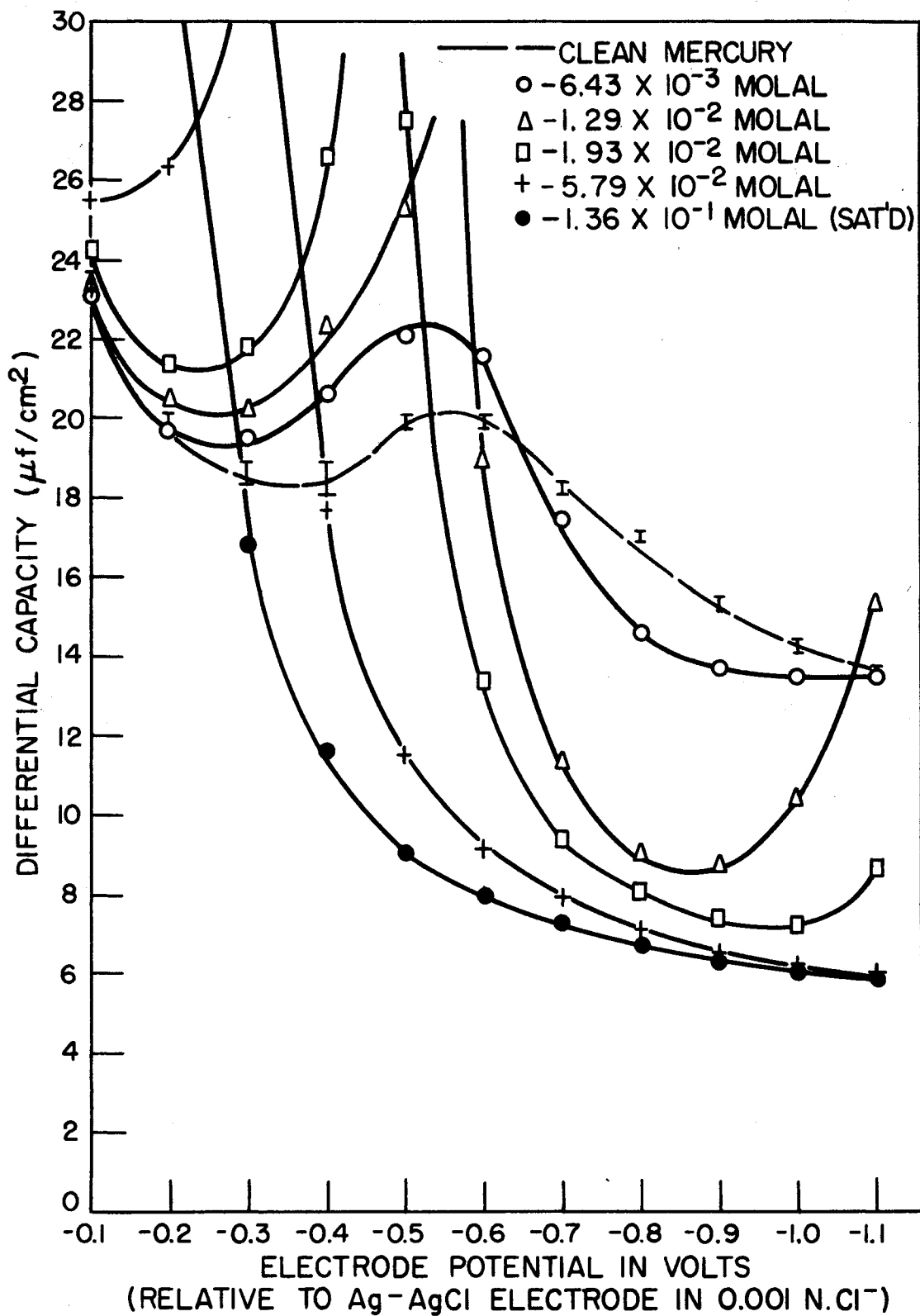


Table 6. Dependence of differential capacity at mercury-aqueous solution interface on polarizing potential and concentration of 3-pentanone in 0.10 N. aqueous perchloric acid solution. Capacity in microfarads/cm² Potential in volts relative to Ag-AgCl in 0.001 N. chloride solution

C/C _o	Hg.	Electrode Potential										
		-0.1	-0.2	-0.3	-0.4	-0.5	-0.6	-0.7	-0.8	-0.9	-1.0	-1.1
0.010	a	23.48	19.85	19.0	20.22	22.46	21.89	18.06	14.51	13.05	12.94	13.24
	b	23.62	20.23	19.80	20.99	22.50	21.89	18.04	14.55	13.11	12.97	13.28
0.02	b	23.67	20.32	20.14	21.93	23.95	22.44	15.34	10.63	9.17	9.88	12.55
	c	23.90	20.69	20.57	22.20	24.25	22.65	15.53	10.71	9.21	9.88	12.61
0.031	c	23.88	20.65	20.80	23.13	26.41	21.74	12.21	8.65	7.49	7.41	8.78
	d	24.14	21.07	21.28	23.53	26.89	22.05	12.34	8.70	7.52	7.42	8.81
0.061	d	24.53	21.95	23.28	29.57	28.78	13.56	8.95	7.30	6.54	6.20	6.18
	e	24.99	22.44	23.82	30.50	29.53	13.75	9.03	7.35	6.56	6.21	6.19
0.112	e	25.43	23.78	28.40	37.32	17.50	10.51	8.01	6.86	6.23	5.90	5.73
	f	25.21	23.78	28.54	37.35	17.57	10.55	8.04	6.87	6.23	5.89	5.72
0.215	f	26.62	27.86	39.56	22.51	12.86	9.19	7.50	6.56	6.01	5.66	5.47
	g	27.13	28.21	40.42	23.04	13.03	9.30	7.55	6.60	6.03	5.67	5.47
0.368	g	29.86	37.04	30.71	17.06	11.34	8.67	7.28	6.44	5.91	5.56	5.35
	h	30.09	37.28	30.80	17.04	11.31	8.64	7.26	6.44	5.91	5.57	5.36
0.573	h	33.91	37.82	22.86	14.47	10.28	8.23	7.08	6.35	5.85	5.49	5.28
	i	34.74	38.64	23.06	14.62	10.37	8.27	7.11	6.37	5.86	5.51	5.28
0.819	i	37.62	32.44	20.45	13.30	9.72	8.02	7.01	6.34	5.85	5.49	5.26
	j	38.58	33.02	20.73	13.48	9.82	8.07	7.05	6.37	5.88	5.51	5.28
1.00	j	41.80	29.58	19.28	12.35	9.30	7.91	7.03	6.40	5.92	5.57	5.31
	k	40.41	29.07	19.17	12.38	9.31	7.91	7.02	6.39	5.90	5.53	5.27

Figure 7. Differential capacity versus electrode potential for 3-pentanone on mercury in 0.10 N. perchloric acid

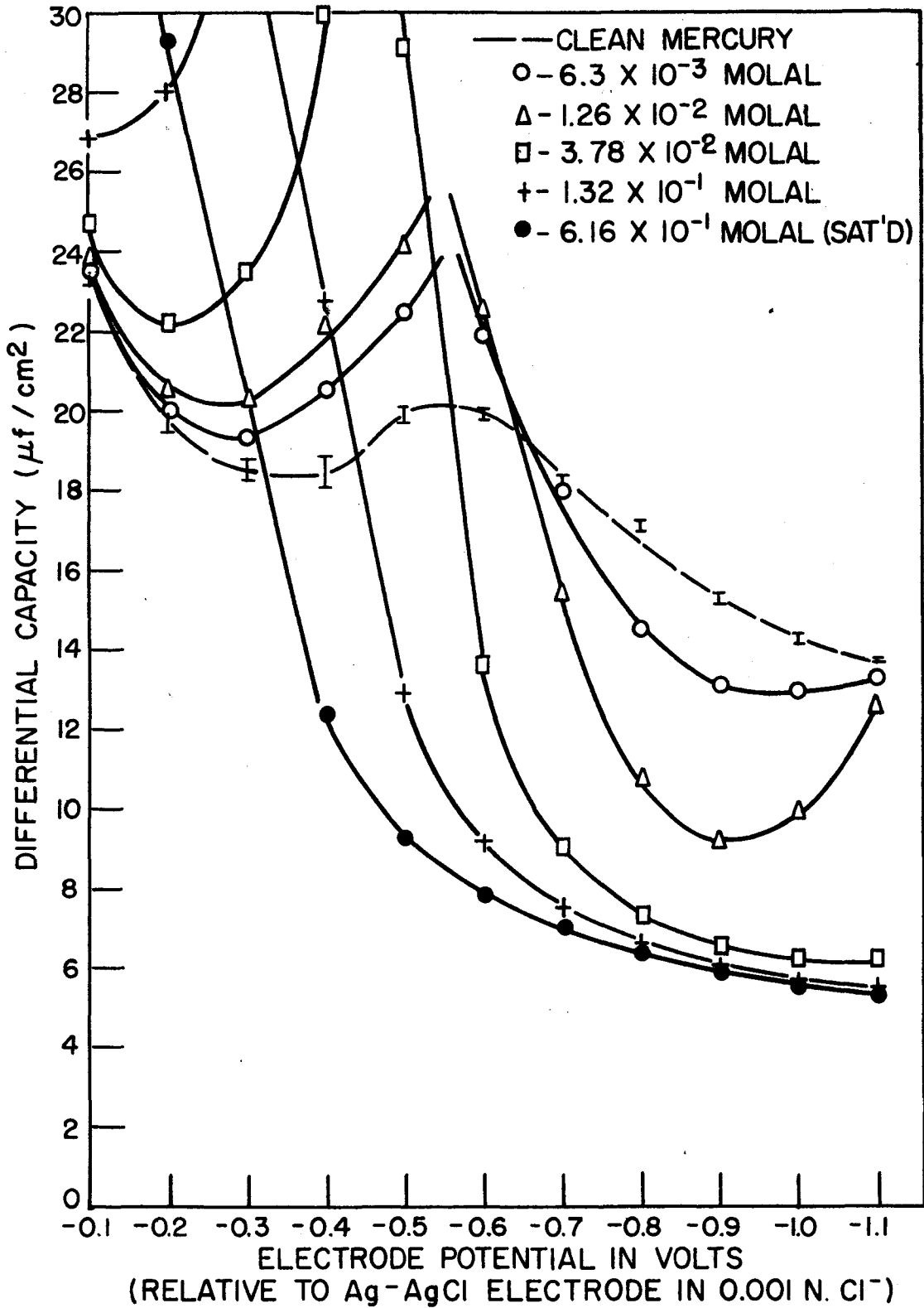


Table 7. Dependence of differential capacity at mercury-aqueous solution interface on polarizing potential and concentration of 1-pentanol in 0.10 N. aqueous perchloric acid solution. Capacity in microfarads/cm² Potential in volts relative to Ag-AgCl in 0.001 N. chloride solution

C/C _o	Hg.	<u>Electrode Potential</u>										
		-0.1	-0.2	-0.3	-0.4	-0.5	-0.6	-0.7	-0.8	-0.9	-1.0	-1.1
0.014	a	25.30	21.21	20.40	21.47	23.44	23.08	19.34	16.37	15.18	14.69	14.34
	b	25.53	21.59	20.90	22.04	23.60	22.68	18.95	16.20	15.09	14.74	14.34
0.028	b	25.46	21.57	20.98	22.47	24.58	20.73	14.65	13.22	14.14	14.93	14.94
	c	25.46	21.78	21.30	22.84	24.53	20.46	14.48	13.09	14.06	14.96	14.95
0.042	c	25.44	21.76	21.70	24.09	26.21	15.22	10.01	10.10	12.72	15.47	15.97
	d	25.57	22.03	21.89	24.40	25.91	15.02	9.98	10.05	12.60	15.46	15.96
0.083	d	25.80	22.90	25.76	37.14	14.45	7.60	6.35	6.67	8.36	12.38	19.17
	e	26.34	23.53	26.26	37.15	14.55	7.66	6.37	6.67	8.34	12.59	19.30
0.139	e	26.78	25.83	42.32	21.91	8.83	6.01	5.43	4.18	6.56	8.80	14.36
	f	27.96	26.55	43.28	22.50	8.97	6.06	5.46	5.67	6.57	8.79	14.44
0.222	f	29.09	34.10	42.65	13.43	6.96	5.34	4.97	5.14	5.74	7.07	10.15
	g	29.68	34.84	43.59	13.74	7.05	5.37	4.99	5.15	5.74	7.05	10.14
0.333	g	32.62	56.98	24.45	9.84	5.98	4.90	4.65	4.78	5.23	6.11	7.94
	h	33.50	58.76	25.42	10.08	6.05	4.93	4.66	4.78	5.22	6.09	7.92
0.472	h	40.95	51.15	17.63	8.26	5.48	4.66	4.47	4.58	4.93	5.59	6.83
	i	42.17	53.06	18.24	8.47	5.55	4.67	4.53	4.57	4.91	5.58	6.81
0.694	i	66.68	31.59	13.94	7.28	5.16	4.49	4.34	4.42	4.70	5.21	6.06
	j	55.7	32.50	14.24	7.42	5.21	4.51	4.35	4.42	4.68	5.20	6.05
1.00	j	39.09	29.09	13.59	7.13	5.15	4.49	4.33	4.40	4.65	5.14	6.00
	k	39.96	30.38	14.38	7.35	5.24	4.54	4.35	4.41	4.66	5.14	6.00

Figure 8. Differential capacity versus electrode potential
for 1-pentanol on mercury in 0.10 N. perchloric acid

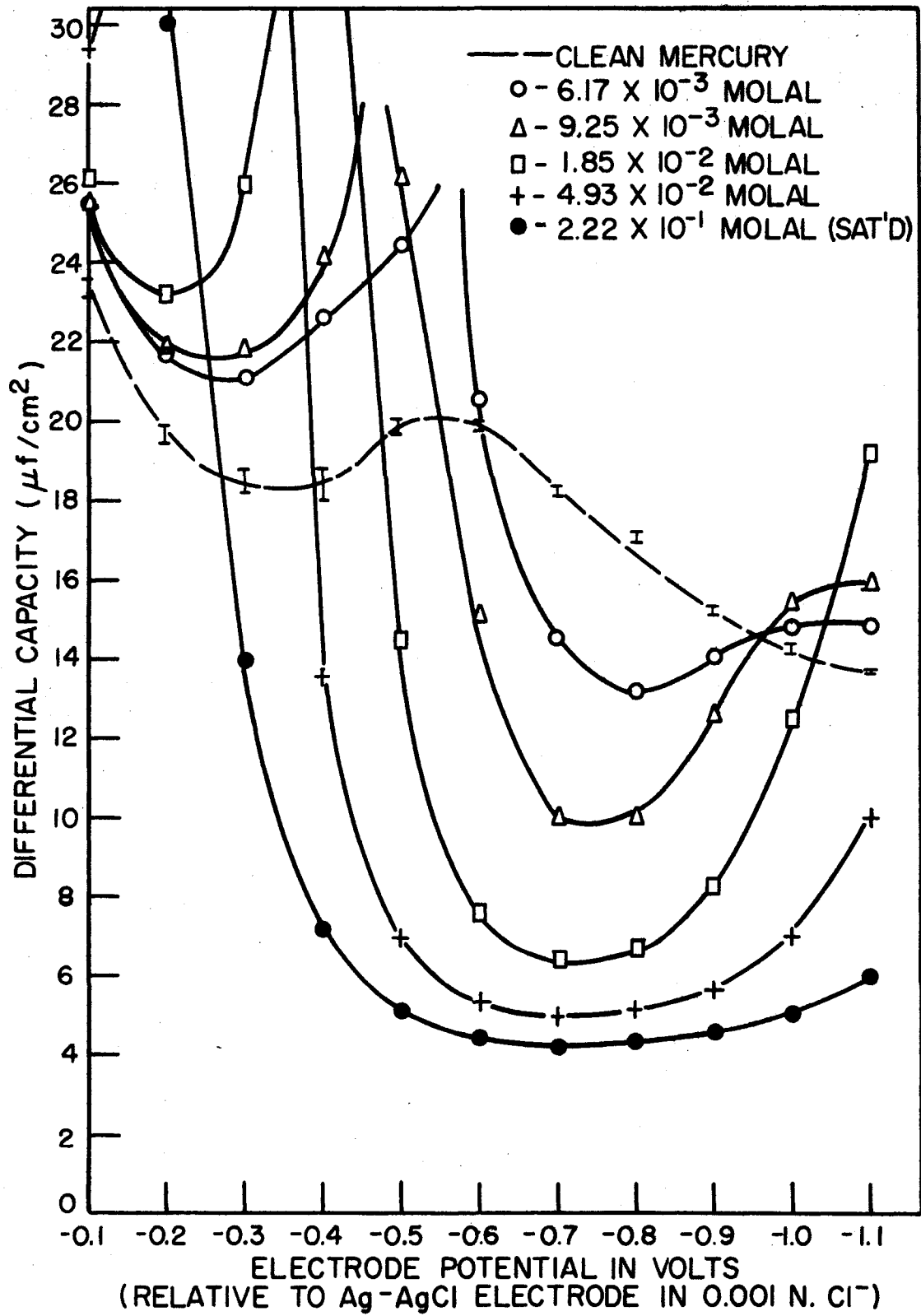


Table 8. Saturation concentrations of adsorbates in experimental media

Medium	Compound	Saturation Molality
0.10 N. HClO_4 , 0.001 N. NaCl	Octanoic acid	0.0051 ^a
	Pentanoic acid	0.365
	Pentanenitrile	0.136
	3-Pentanone	0.616
	1-Pentanol	0.222
0.009 N. HClO_4 , 0.001 N. NaCl	Pentanoic acid	0.372 ^b

^aDetermined by B. H. Clampitt, Thesis, Iowa State College (1954).

^bTaken as that solubility in pure water as determined by R. P. Craig, Thesis, Iowa State College (1952).

V. DISCUSSION

A. Status of the Theory of the Electrical Double Layer in
Absence of Adsorbable Non-electrolytes

A complete discussion of the theories in existence pertinent to the study of the electrical double layer at the mercury surface in ionic solutions is beyond the scope of this dissertation. It is, in addition, worthy of extensive investigation in itself, for, although the object of much research in the past, it has not yet been placed on a sound theoretical basis. Perhaps the best review of the present status of work along this line is that of Grahame previously mentioned (17). More recently, attempts have been made by MacDonald (18), Devanathan (19), and Devanathan and Peries (38) to manufacture a quantitatively correct theory. In each case, however, it has been necessary in the end to adjust parameters arbitrarily to obtain a fit between calculated and experimental results. This resort to experiment is not difficult to understand when one pauses to consider the obstacles the theorist faces when he cogitates electrical phenomena at interfaces. As indicated earlier, one may consider the electrical double layer to act as a condenser of extremely high specific capacity. This high capacity is a result of the minuteness of the spacing between the "plates", which is of atomic dimensions, and of the high charge densities near the interface. Unlike more familiar condensers, the capacity of the electrical double layer is not constant with changing

potential difference across the plates, for the extremely high fields associated with even a small potential drop across so small a distance tend to warp and deform the ions and molecules which constitute one plate of the condenser, so that with increasing potential the plates crowd ever more closely together. The dielectric properties of the medium between the electrical centers of the double layer array of ions and dipoles and the mercury surface cannot even be inferred from those of the bulk medium, for again the high fields associated with the double layer prevent the components from behaving in their ordinary way. In addition to the "compact" double layer, i.e. that associated with specifically adsorbed ions and molecules and across which the fall in potential is believed to be linear, one need consider the "diffuse" double layer, which extends out into the solution and in which the potential gradient is an exponential function of distance from the surface. The compact and diffuse double layers act electrically as condensers in series with each other. Except at low polarizing potentials, the capacity of the diffuse layer is much greater than that of the compact layer and it consequently contributes little to the impedance of the interface.

Additional discussions of the electrical double layer and of electrocapillarity in general may be found in Butler (12) and in a recent volume edited by Bockris (39).

B. Theory of Changes in Differential Capacity Curves in Solutions of Adsorbable Non-electrolytes

1. Introduction

Fortunately for the present purpose, it is not necessary to possess an adequate theory explaining differential capacity as a function of potential in electrolytic solutions. It is only necessary that the variation of capacity with potential be measurable, for it is from changes in this dependence that one hopes to derive adsorption isotherms. Suffice it here to develop a theory which adequately treats the changes in the capacity curves with increasing concentration of adsorbate.

The following treatment is based in part on an early theory of Frumkin (40) which he applied with some success in the interpretation of surface tension lowering versus potential curves for amyl alcohol on mercury.

2. Dependence of actual adsorption on potential

At constant temperature, boundary tension changes at an ideal polarizable electrode must satisfy the differential equation (41,42, see also 17)

$$d\sigma = - Q dV - RT \sum_1 \Gamma_1 d \ln a_1, \quad (1)$$

where σ is the boundary tension, Q the charge per unit area on the electrode side of the double layer, V the potential of the

electrode relative to a reference electrode, and Γ_1 the surface excess of component 1 whose activity in solution is a_1 . Solubility of solution components in the electrode is assumed negligible.

If only the electrode potential and the activity of one adsorbable component is allowed to vary, equation (1) becomes

$$d\sigma = -Q dV - RT\Gamma da, \quad (2)$$

in which Γ and a refer to surface excess and activity of the adsorbable component. Strictly, the Γ here is the $\Gamma_s^{(1)}$ of Gibbs (41), and is the surface excess of the adsorbable component at a mathematical interface so situated that at the interface the surface excess of water is zero. In dilute solutions, such as encountered in the present work, Γ can be identified with small error as the number of moles of adsorbate per square centimeter at the electrode surface. Then

$$\left(\frac{d\Gamma}{dV}\right)_a = \frac{1}{RT} \left(\frac{dQ}{d \ln a}\right)_V = \frac{1}{RT} \left(\frac{dQ}{d\Gamma}\right)_V \left(\frac{d\Gamma}{d \ln a}\right)_V, \quad (3)$$

and

$$\frac{1}{RT} \left(\frac{dQ}{d\Gamma}\right)_V = \left(\frac{d\Gamma}{dV}\right)_a \left(\frac{d \ln a}{d\Gamma}\right)_V = - \left(\frac{d \ln a}{dV}\right)_\Gamma. \quad (4)$$

Consequently, if the dependence of charge at constant polarization on the amount adsorbed can be established, then the activity change needed to so compensate a polarization change as to keep the adsorption constant can be determined. Assume

that

$$Q = Q_w(1-\Gamma S) + C'\Gamma S(V-V_N), \quad (5)$$

where Q_w is the double layer charge that would be present in absence of adsorbate, S is the molar surface area of the adsorbate, C' is the double layer capacity per unit area when the surface is completely covered with adsorbate, and V_N is the potential of the electrocapillary maximum for the electrode in this condition. This amounts to assuming that the electrode surface can be considered composed of two parts, an adsorbate-free part and an adsorbate-covered part, which charge independently. For convenience, it is further assumed that the capacity of the adsorbate-covered surface is independent of polarization. This assumption could be eliminated in a more refined treatment.

From equation (5)

$$\left(\frac{dQ}{d\Gamma}\right)_V = -Q_w S + C' S(V-V_N), \quad (6)$$

and therefore from equation (4)

$$\left(\frac{d \ln a}{dV}\right)_\Gamma = \frac{S}{RT} [Q_w - C'(V-V_N)]. \quad (7)$$

Let

$$\Phi = \int_0^V [Q_w - C'(V-V_N)] dV, \quad (8)$$

in which the potential of the electrode of interest at the electrocapillary maximum in the absence of adsorbate is now selected as the reference potential, i.e. the potential at

which $V=0$.

Integrating equation (7), one has

$$\ln \frac{a_V}{a_0} = \frac{S\Phi}{RT}, \quad (9)$$

in which a_V is activity of adsorbate at a potential V necessary to give the same surface excess as obtained with activity a_0 at the electrocapillary maximum.

Given equation (9), if the dependence of amount adsorbed on activity of adsorbate in absence of polarization is known, then one can establish the general dependence of amount adsorbed on adsorbate activity for arbitrary polarization. A simple equation derived by Fowler and Guggenheim (43, p.430-3) for monolayer adsorption of gases was used by Frumkin (40) for this purpose. The equation is

$$B_0 a = \frac{\theta}{1-\theta} e^{-2\alpha\theta}, \quad (10)$$

where $\theta = \Gamma S$, B_0 is a constant pertaining to the interaction of the adsorbate molecules with the electrode surface, and α is a constant pertaining to the interactions between adsorbate molecules. The character of these constants will be discussed in greater detail in a later section. Combining equations (9) and (10), there results

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

where

$$B = B_0 e^{-\frac{S\Phi}{RT}} \quad (12)$$

Equation (11) indicates the general dependence of adsorption on adsorbate activity and electrode polarization.

It may be remarked at this time that in equation (8) Q_w and $C'V$ have the same sign as V . Consequently, ignoring for the moment V_N , Φ will be positive if $Q_w > C'V$, negative if $Q_w < C'V$, and will be greater in numerical magnitude the greater V . In the former case, B and therefore θ will decrease with increasing numerical magnitude of V ; in the latter B and θ will increase. Simply stated, this means that at high polarizations the material of higher dielectric constant will concentrate at the interface, the region of high field. In the present case, $Q_w > C'V$, since water has a higher dielectric constant than the adsorbates studied, and displacement of the adsorbate at high polarization is to be expected. As the solvent begins to displace the adsorbate from the surface under the influence of a high polarization, sharp peaks occur in the capacity curves (see Figures 3 through 8) to the right and left of the region of maximum capacity depression. At the potential at which these peaks occur, a small change in polarization causes a large change in surface charge and there is a correspondingly large increase in measured capacity. At the potentials of the maxima, which are not fully developed on the right or negative side in the figures indicated because the measurements were not carried to sufficiently negative

potentials, the amount of solute adsorbed by the electrode is a very sensitive function of potential. To the left of the left maxima and to the right of the right maxima, the solutes are almost completely desorbed from the electrode surface since the strong fields associated with the large potentials greatly favor the concentration of the higher dielectric water at the interface.

3. Dependence of differential capacity and apparent adsorption on solute activity and polarizing potential

An electrode at a polarization V in an aqueous solution containing adsorbate at an activity a may be imagined to have been achieved in two steps: (1) charging the electrode in absence of adsorbate to potential V , and (2) adding adsorbate at constant potential V until the activity is a . The total change in boundary tension is given by the sum of the changes during these two processes as computed from equation (2).

Thus

$$\sigma_0 - \sigma = \int_0^V Q_w dV' + RT \int_0^a \Gamma_V d \ln a', \quad (13)$$

in which Q_w is the charge per unit area of electrode at potential V' and $\Gamma_V(a')$ is the number of moles adsorbate adsorbed at potential V and activity a' . Since the boundary tension is a state property, equation (13) is valid regardless of the path used to achieve the final state.

By using $\Gamma_V = \theta/S$ and equation (11), one can integrate

the second term on the right of equation (13). Equation (13) becomes

$$\begin{aligned}\sigma_0 - \sigma &= \int_0^V Q_w dV' + \frac{RT}{S} \int_0^a \left(1 + \frac{\theta}{1-\theta} - 2\alpha\theta\right) d\theta \\ &= \int_0^V Q_w dV' - \frac{RT}{S} [\ln(1-\theta) + \alpha\theta^2].\end{aligned}\quad (14)$$

Since the differential capacity C is given by $(\partial Q/\partial V)_a$, and since from equation (2) $Q = -(\partial\sigma/\partial V)_a$, then

$$\begin{aligned}C &= -\left(\frac{\partial^2\sigma}{\partial V^2}\right)_a \\ &= C_w - \frac{RT}{S} \frac{\partial^2}{\partial V^2} [\ln(1-\theta) + \alpha\theta^2],\end{aligned}\quad (15)$$

in which $C_w = (\partial Q_w/\partial V)_{a=0}$ is the differential capacity at the electrode surface per unit area in the absence of adsorbate.

Now

$$\begin{aligned}\frac{\partial^2}{\partial V^2} [\ln(1-\theta) + \alpha\theta^2] &= \frac{\partial}{\partial V} \left[-\frac{1}{1-\theta} + 2\alpha\theta \right] \left(\frac{\partial\theta}{\partial V} \right) \\ &= \left[-\frac{1}{1-\theta} + 2\alpha\theta \right] \frac{\partial^2\theta}{\partial V^2} + \left[-\frac{1}{(1-\theta)^2} + 2\alpha \right] \left(\frac{\partial\theta}{\partial V} \right)^2.\end{aligned}$$

Substituting into equation (15), one has

$$C = C_w + \frac{RT}{S} \left[\frac{1-2\alpha\theta(1-\theta)}{1-\theta} \left(\frac{\partial^2\theta}{\partial V^2} \right) + \frac{1-2\alpha(1-\theta)^2}{(1-\theta)^2} \left(\frac{\partial\theta}{\partial V} \right)^2 \right].\quad (16)$$

From equation (11)

$$\ln B + \ln a = \ln \theta - \ln(1-\theta) - 2\alpha\theta,$$

or

$$\frac{d \ln B}{dV} = \left[\frac{1}{\theta} + \frac{1}{1-\theta} - 2\alpha \right] \left(\frac{d\theta}{dV} \right)_a,$$

and

$$\left(\frac{d\theta}{dV} \right)_a = \frac{\theta(1-\theta)}{1-2\alpha\theta(1-\theta)} \frac{d \ln B}{dV}. \quad (17)$$

The second derivative of θ with respect to V becomes, after simplification,

$$\left(\frac{d^2\theta}{dV^2} \right)_a = \frac{\theta(1-\theta)}{1-2\alpha\theta(1-\theta)} \left\{ \frac{d^2 \ln B}{dV^2} + \frac{1-2\theta}{[1-2\alpha\theta(1-\theta)]^2} \left(\frac{d \ln B}{dV} \right)^2 \right\}. \quad (18)$$

Substituting the results of equations (17) and (18) into equation (16) and simplifying, one gets

$$C = C_w + \theta \frac{RT}{S} \left[\frac{d^2 \ln B}{dV^2} + \frac{1-\theta}{1-2\alpha\theta(1-\theta)} \left(\frac{d \ln B}{dV} \right)^2 \right]. \quad (19)$$

From equations (12) and (8),

$$\begin{aligned} \ln B &= \ln B_0 - \frac{S\Phi}{RT} \\ &= \ln B_0 - \frac{S}{RT} \left[\int_0^V (Q_w - C'(V-V_N)) dV \right]. \end{aligned} \quad (20)$$

Therefore

$$\frac{d \ln B}{dV} = - \frac{S}{RT} [Q_w - C'(V-V_N)], \quad (21)$$

and

$$\frac{d^2 \ln B}{dV^2} = - \frac{S}{RT} (C_w - C'). \quad (22)$$

Equation (19) now becomes

$$C = C_w - \theta \left\{ (C_w - C') - \frac{S}{RT} \frac{(1-\theta) [C_w - C' (V - V_N)]^2}{1 - 2\theta(1-\theta)} \right\}. \quad (23)$$

The terms in this equation can be simply interpreted in light of the chosen model. The term $C_w - \theta(C_w - C')$ is the capacity of two condensers which act in parallel, the one of size $(1-\theta)$ and capacity per unit area C_w and the other of size θ and capacity C' per unit area. This is the capacity per unit area the electrode would have in terms of the model if θ did not change with potential. The remaining term of equation (23) is the contribution to differential capacity resulting from a change of θ with V . This contribution may be termed a pseudocapacity, since it does not arise from a single conceivable condenser.

Hansen and Clampitt (15) originated the term "apparent adsorption" to designate the surface coverage calculated by the expression

$$\theta_a = 1 - \frac{C}{C_0}, \quad (24)$$

where θ_a is the apparent fractional surface coverage, C is the measured capacity at a given adsorbate activity, and C_0 the capacity of the electrode before any adsorbate had been added to the solution. Implicit in the definition of θ_a by equation (24) is the assumption that a monolayer of adsorbed non-electrolyte would cause the double layer capacity to fall to zero. The above authors realized this might not be the case, and it was demonstrated not to be the case by a rough measurement in the present work of the capacity of a mercury electrode in a dilute solution of perchloric acid in pure 1-pentanol.

The minimum capacity observed was about seven microfarads per square centimeter. Unfortunately, the results were not directly comparable to the aqueous case of Table 7 since it was necessary to make the pentanol solution several times more concentrated in perchloric acid to make it sufficiently conducting. In an earlier work, Parson and Devanathan (44), studying the electrocapillary curves of mercury in methanol-water mixtures, found that the maximum in the electrocapillary curve was decreased by less than ten per cent by increasing the methanol mole fraction from zero to one.

One may re-define apparent fractional surface coverage as that fractional coverage that would be computed from capacity data if pseudocapacity were ignored. Using the model described earlier, apparent coverage would then be defined by the expression

$$C = C_w(1-\theta_a) + C' \theta_a,$$

or

$$\theta_a = \frac{C_w - C}{C_w - C'} . \quad (25)$$

This expression is identical to one derived by Melik-Gaikazyan (33).

Equation (23) may be rewritten in the form

$$\frac{C_w - C}{C_w - C'} = \theta_a = \theta \left\{ 1 - \frac{s}{RT} \frac{1-\theta}{C_w - C'} \frac{[Q_w - C'(V - V_N)]^2}{1 - 2\theta(1-\theta)} \right\}, \quad (26)$$

which expresses the apparent fractional surface coverage in

terms of the parameters of the foregoing theory.

4. Illustrative calculation of apparent adsorption as a function of electrode potential and adsorbate activity

It is extremely difficult to evaluate all of the parameters of equation (26) from first principles alone. As indicated earlier, no adequate theory exists that describes the complex dependence of the given parameters on the electrode potential. However, it is possible for one to establish values for the parameters that are both physically reasonable and consistent in their ability to fit the apparent adsorption curves for several adsorbate concentrations by selecting and adjusting the constants to fit the curve for one adsorbate activity.

To indicate the technique used to calculate the adsorption curves according to equation (26), the calculation for 1-pentanol at an activity of 0.139 will be made. To do this, one must first establish a value for C' , the differential capacity of the adsorbate-covered surface. For 1-pentanol, this was chosen equal to 4.34 microfarads per square centimeter, the lowest measured differential capacity in the solution saturated with the alcohol. This choice is arbitrary and implies that the adsorbate forms, from saturated solution, a complete monolayer on the mercury surface at that potential at which maximum adsorption occurs. Assigning C' such a value is subject to the assumption, made in the theoretical development, that C' is independent of polarizing potential. From the

measured values of C_w , Table 1, and the measured values of C , Table 7, θ_a was calculated according to equation (25) for each potential and each adsorbate activity. The resulting values are tabulated in Table 9.

Since pseudocapacitive effects can only lower θ_a , θ_a will be a maximum at the same V that θ , the true surface coverage, is a maximum. Assuming that at its maximum $\theta_a = \theta$ for each adsorbate activity, that is, assuming that the choice made for C' is correct and that pseudocapacity is negligible at the potential of the maximum, one may establish values for the parameters B and 2α of equation (11). From that equation,

$$\log \frac{\theta}{a(1-\theta)} = \log B + \frac{2\alpha}{2.303} \theta,$$

and a plot of $\log [\theta/a(1-\theta)]$ against θ would have a slope $2\alpha/2.303$ and an intercept $\log B$.

Representative plots of θ_a versus potential at constant activity for the purpose of selecting the maxima are shown in Figure 9. The selected values are tabulated as a function of adsorbate activity in Table 10. The plot of $\log [\theta/a(1-\theta)]$ against θ , see Figure 10, has a slope of 1.18 and an extrapolated intercept 0.84. Consequently, $2\alpha = 2.72$ and $B = 6.92$ at the potential of the maximum.

Q_w of equation (26) is the charge per unit area of mercury surface in the absence of adsorbate and may be evaluated at each potential V by numerical integration of the capacity values

Table 9. Apparent fractional surface coverages for 1-pentanol on mercury in 0.10 N. aqueous perchloric acid at given polarizing potentials and adsorbate activities. C' taken as 4.34 $\mu\text{f}/\text{cm}^2$. Potential in volts relative to Ag-AgCl in 0.001 N. chloride solution

a	<u>Polarizing Potential</u>										
	-0.1	-0.2	-0.3	-0.4	-0.5	-0.6	-0.7	-0.8	-0.9	-1.0	-1.1
0.014	-0.10	-0.10	-0.14	-0.30	-0.22	-0.18	-0.07	0.06	0.02	-0.04	-0.05
0.028	-0.10	-0.12	-0.18	-0.29	-0.29	-0.04	0.27	0.30	0.11	-0.06	-0.12
0.042	-0.10	-0.14	-0.22	-0.40	-0.39	0.31	0.59	0.55	0.24	-0.12	-0.23
0.083	-0.13	-0.16	-0.52	-1.31	0.35	0.79	0.85	0.81	0.63	0.18	-0.57
0.139	-0.20	-0.41	-1.69	-0.26	0.71	0.89	0.92	0.89	0.79	0.55	-0.06
0.222	-0.30	-0.94	-1.72	0.34	0.83	0.93	0.95	0.94	0.87	0.72	0.39
0.333	-0.50	-2.45	-0.44	0.59	0.89	0.96	0.97	0.96	0.92	0.82	0.62
0.472	-0.94	-2.06	-0.05	0.71	0.92	0.98	0.99	0.98	0.95	0.87	0.74
0.694	-1.96	-0.79	0.31	0.78	0.94	0.99	1.00	0.99	0.96	0.91	0.81
1.000	-0.84	-0.64	0.32	0.79	0.94	0.99	1.00	0.99	0.96	0.92	0.82

Figure 9. Apparent fractional surface coverage versus electrode potential for the purpose of selecting maxima. System 1-pentanol on mercury in 0.10 N. aqueous perchloric acid solution

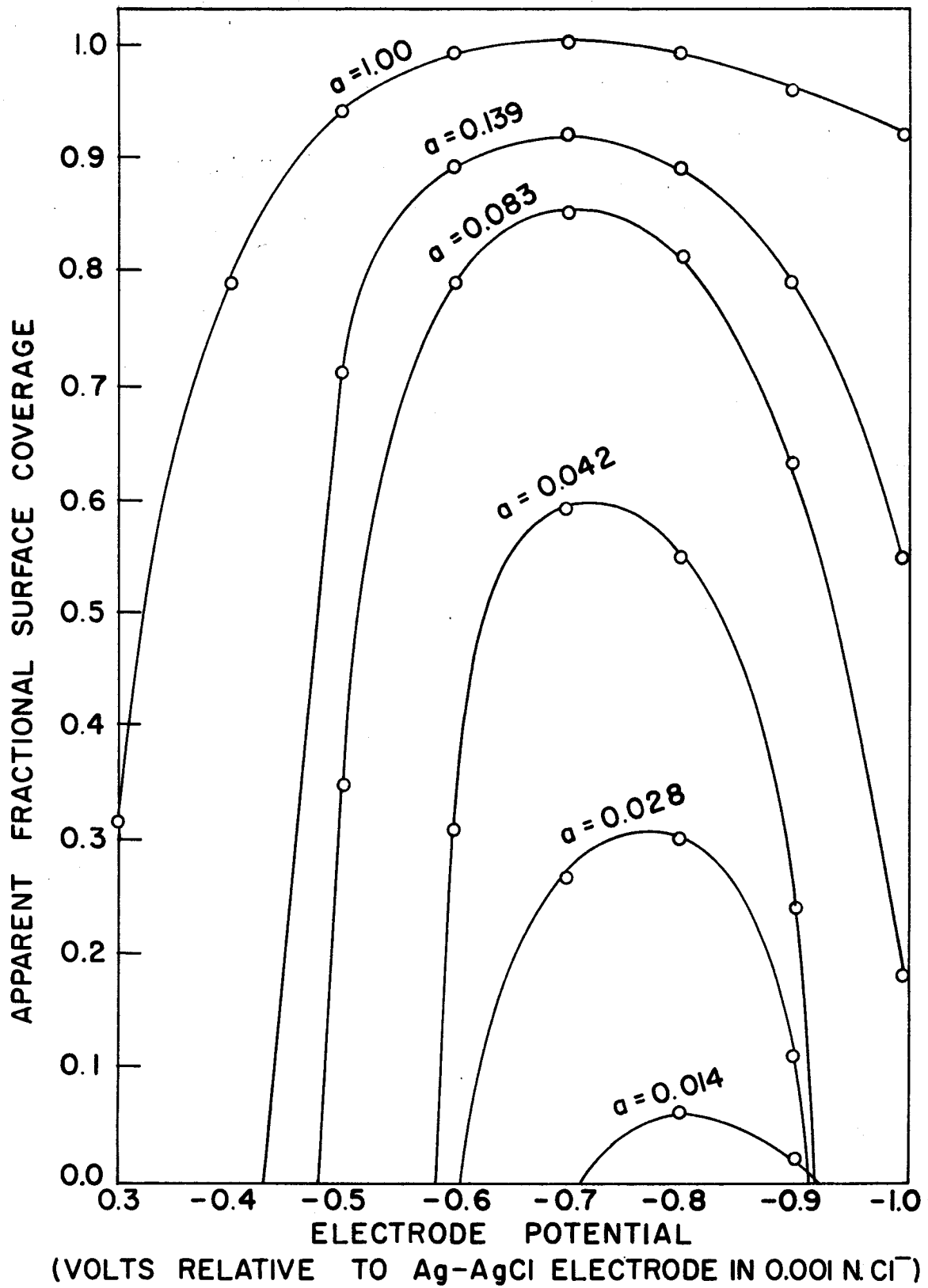
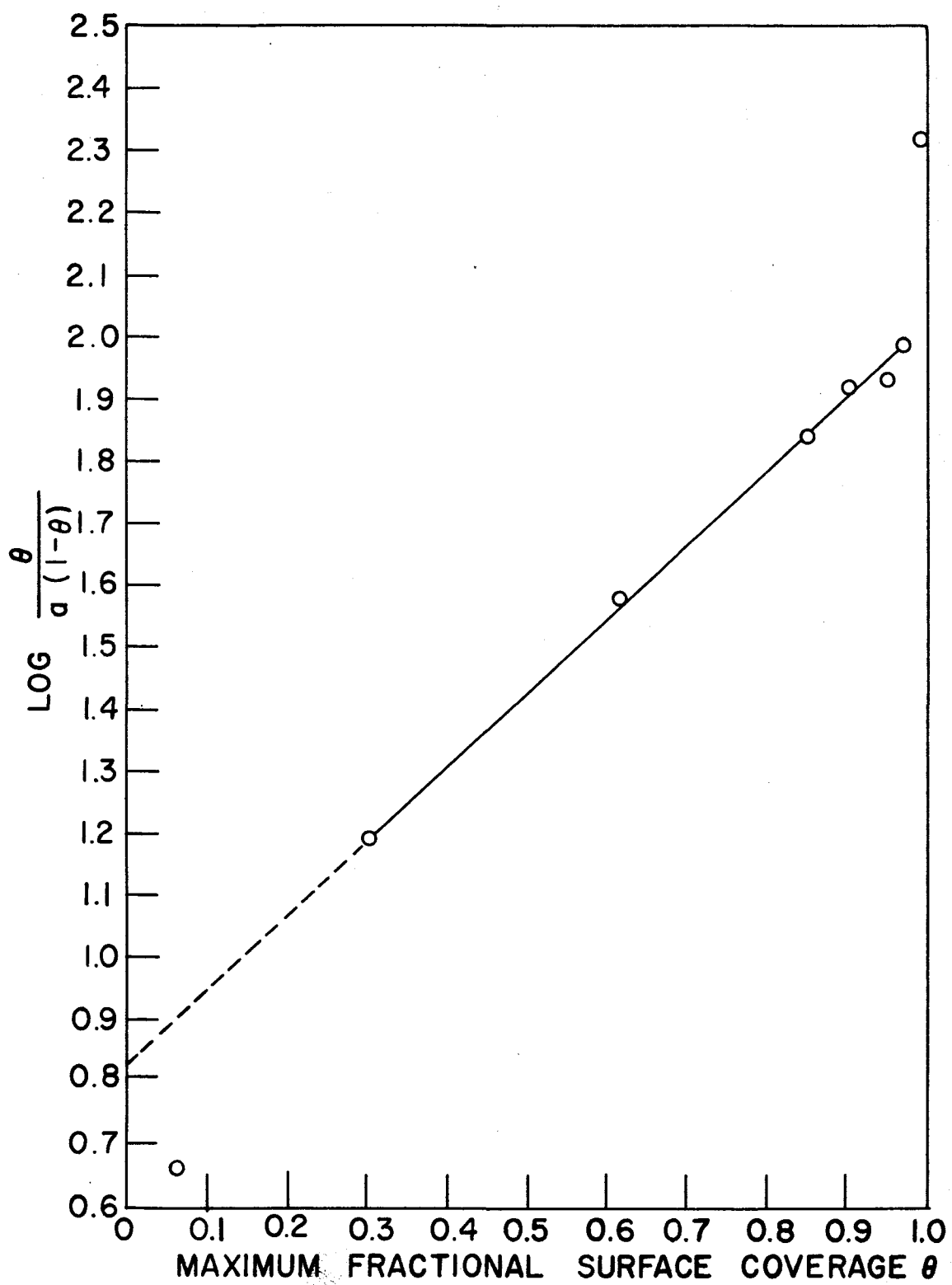


Figure 10. Maximum fractional surface coverage θ versus $\log \theta / a(1-\theta)$ for 1-pentanol on mercury in 0.10 N. aqueous perchloric acid solution



C_w of Table 1, since

$$Q_w = \int_0^V C_w dV.$$

Now the reference or zero potential for this integration is the potential of the electrocapillary maximum. Ruetschi and Delahay (45) cite Klein and Lange (46) as reporting a value

Table 10. Maximum values of apparent fractional surface coverage for 1-pentanol on mercury in 0.10 N. aqueous perchloric acid solution

Adsorbate Activity	Maximum θ_a
0.014	0.06
0.028	0.30
0.042	0.62
0.083	0.85
0.139	0.92
0.222	0.95
0.333	0.97
0.472	0.99
0.694	1.00
1.000	1.00

of -0.33 volt, relative to the normal hydrogen electrode, as the potential of the electrocapillary maximum of a mercury surface in solutions of non-adsorbable electrolytes. Grahame (17), from a consideration of many values reported in the literature, selected -0.23 volt, on the hydrogen scale, as the most representative value for the potential of the electrocapillary maximum. The Ag-AgCl electrode in 0.001 N. chloride solution is 0.40 volt more positive than is the normal hydrogen

electrode. Therefore, following Grahame, the potential of the electrocapillary maximum relative to Ag-AgCl in 0.001 N. chloride solution is -0.63 volt, and this value is used as the zero of potential in the calculation of Q_w .

It remains to establish θ , S , and V_N of equation (26). V_N and S are chosen arbitrarily to give the best fit between calculated and experimental curves of θ_a as a function of potential. For a given set of values of these parameters, θ may be determined in the following way. From equation (12),

$$B = B_0 e^{-\frac{S\bar{\Phi}}{RT}},$$

where $\bar{\Phi}$ is given by equation (8) and B_0 may be calculated since B is known at one value of V , namely the potential of maximum θ_a . Therefore B_a may be calculated for all potentials. But B_a is also known as a function of θ by equation (11), and consequently θ as a function of V may be obtained.

For the adsorbate 1-pentanol at an activity of 0.139, $V_N = 0.45$ volt and $RT/S = 0.8$ microjoules/cm² were found after several trials to give the best fit between experimental and calculated curves. The calculated values for Q_w , $\bar{\Phi}$, B_a , θ , and θ_a are recorded in Table 11.

The calculated curve and the experimental points are compared in Figure 11, which also includes curves similarly calculated for several other activities. Contained in Figure 12 are similar curves for pentanoic acid in 0.10 N. aqueous

perchloric acid. The same values of the parameters used to obtain best fit in this case were then used to calculate the apparent coverage for pentanoic acid in 0.009 N. aqueous perchloric acid, and these results are shown, together with the

Table 11. Values of parameters in calculation of θ_a by equation (26) for 1-pentanol at activity^a 0.139 on mercury in 0.10 N. aqueous perchloric acid. $C' = 4.34 \mu\text{f}/\text{cm}^2$, $V_N = 0.45$ volt, $RT/S = 0.8 \mu\text{joules}/\text{cm}^2$, $B_0 = 6.18$, and $\alpha = 1.36$. V in volts relative to electrocapillary maximum, Q_w in $\mu\text{f}/\text{cm}^2$, Φ in $\mu\text{cb}/\text{cm}^2$

V	Q_w	Φ	Ba	θ	θ_a
0.5	9.84	2.86	0.024	0.025	-0.132
0.4	7.68	1.99	0.071	0.085	-0.415
0.3	5.77	1.26	0.178	0.270	-1.260
0.2	3.93	0.70	0.358	0.715	-0.293
0.1	2.02	0.27	0.614	0.862	0.708
0.0	0.00	0.00	0.860	0.912	0.881
-0.1	-1.92	-0.11	0.990	0.923	0.897
-0.2	-3.69	-0.10	0.972	0.920	0.907
-0.3	-5.30	0.05	0.807	0.905	0.852
-0.4	-6.78	0.31	0.585	0.855	0.444
-0.5	-8.18	0.67	0.373	0.733	-0.172

experimental points, in Figure 13. The dotted curve was added to indicate the qualitative similarity in the shapes of calculated and experimental curves at low concentrations and to emphasize the horizontal displacement one from another. This displacement, which is less apparent at the higher concentrations reflects the effect of the diffuse double layer upon the measured values of the differential capacity. In relatively

Figure 11. Calculated curves and experimental points for apparent fractional surface coverage as a function of potential and adsorbate activity for 1-pentanol on mercury in 0.10 N. aqueous perchloric acid solution. $C' = 4.34 \mu\text{f}/\text{cm}^2$, $V_N = 0.45$ volt, $RT/S = 0.8 \mu\text{joules}/\text{cm}^2$, $B_0^N = 6.18$, and $\alpha = 1.36$

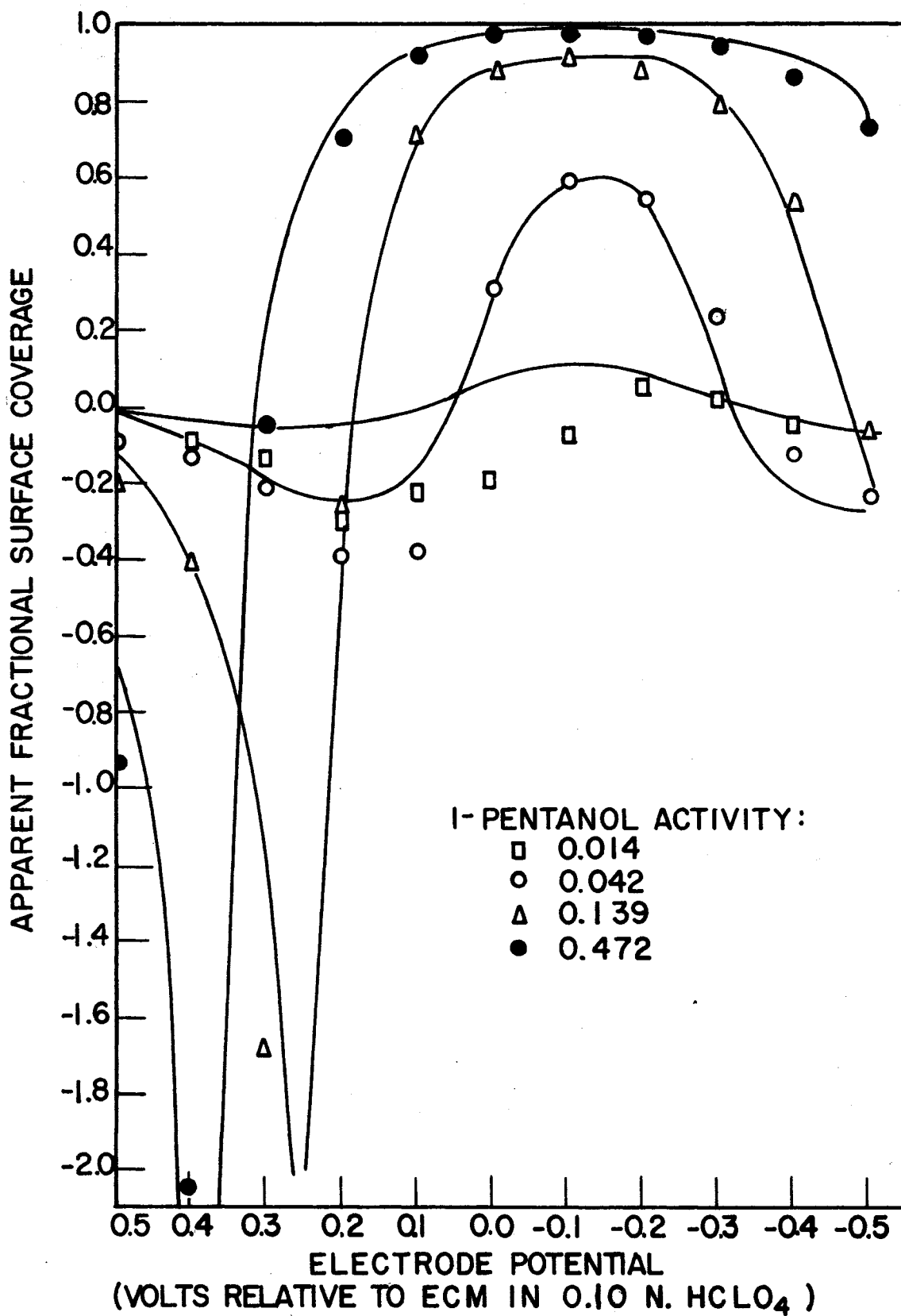


Figure 12. Calculated curves and experimental points for apparent fractional surface coverage as a function of potential and adsorbate activity for pentanoic acid on mercury in 0.10 N. aqueous perchloric acid solution. $C' = 3.50 \mu\text{f}/\text{cm}^2$, $V_s = 0.65$ volt, $RT/S = 1.0 \mu\text{joules}/\text{cm}^2$, $B_0 = 5.30^N$, and $\alpha = 1.38$

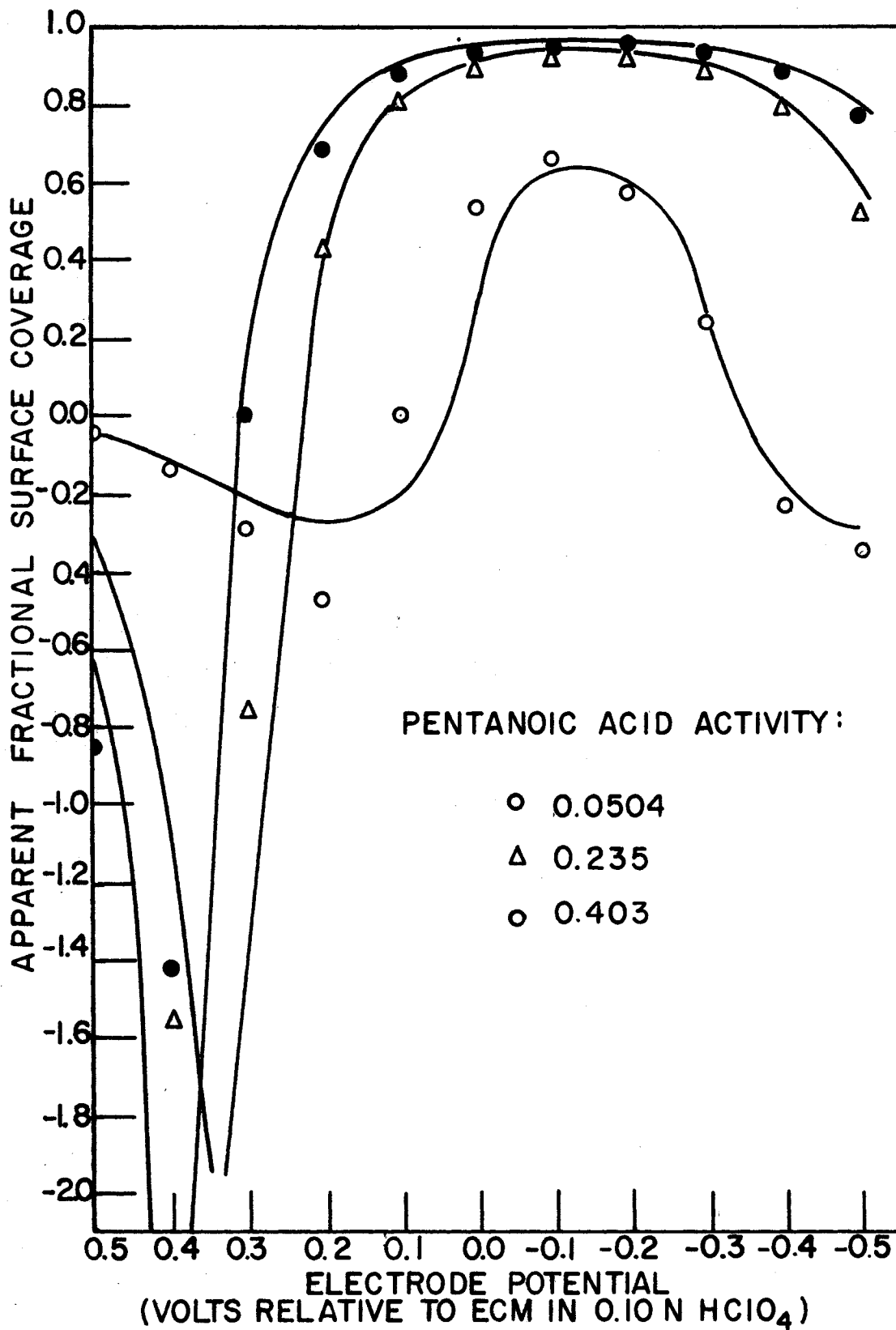
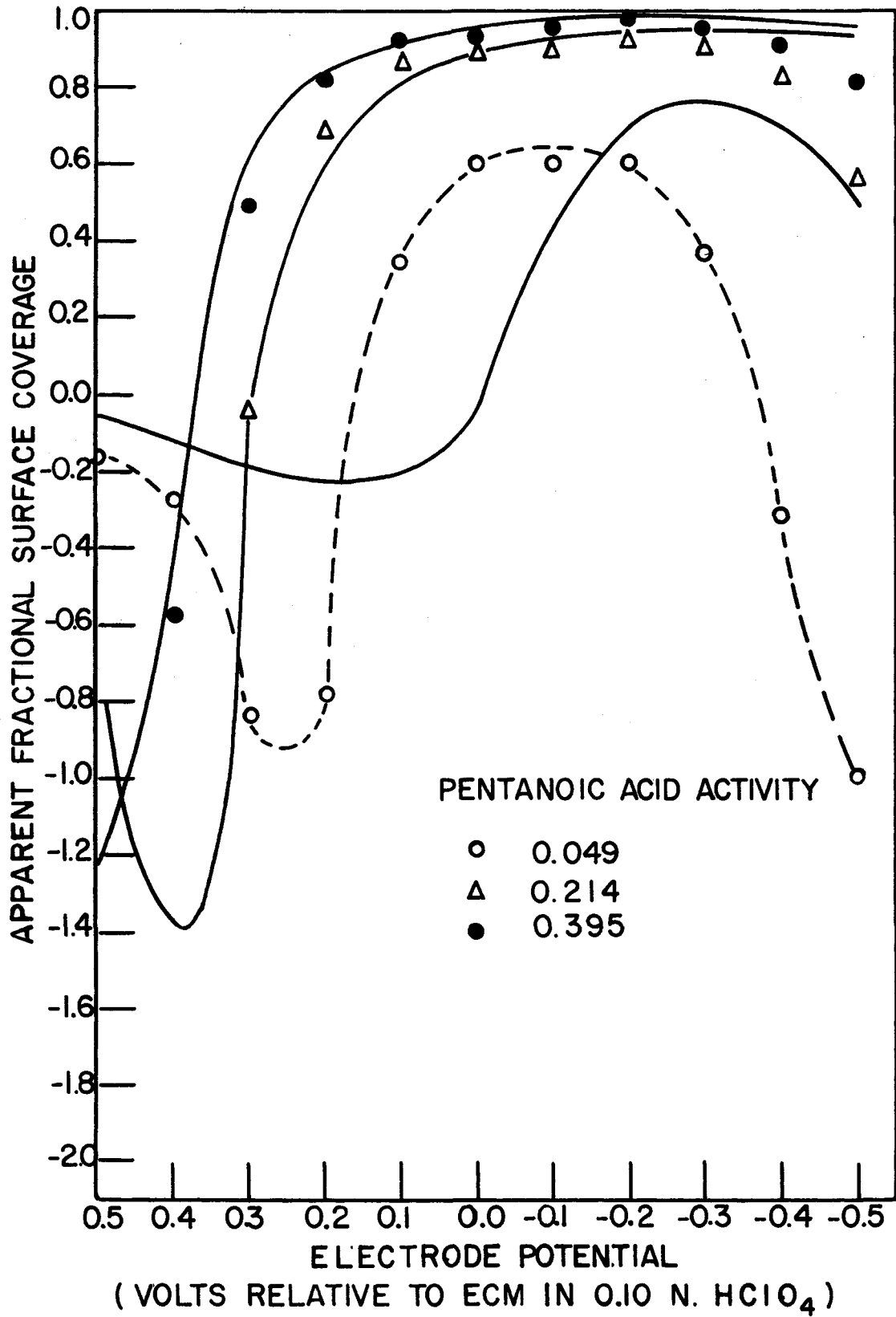


Figure 13. Calculated curves and experimental points for apparent fractional surface coverage as a function of potential and adsorbate activity for pentanoic acid on mercury in 0.009 N. aqueous perchloric acid solution. $C' = 3.5 \mu\text{f}/\text{cm}^2$, $V_N = 0.65$ volt, $RT/S = 1.0 \mu\text{Joules}/\text{cm}^2$, $B_0 = 5.3$, and $\alpha = 1.38$



concentrated electrolytic solutions, the differential capacity of the diffuse double layer is very much greater than that of the compact double layer, and the capacity measured can be assigned with only small error entirely to the compact layer. However, in dilute solutions the impedance of the diffuse layer is much more important and should no longer be ignored. The value chosen for C' for the case of pentanoic acid in dilute acid solution is consequently probably high. In addition, the measured capacity values, assumed by the theory to be representative of the compact layer, also contain an appreciable contribution from the diffuse double layer. The theoretical development is thus less applicable to dilute electrolytic solutions for it should include an operation which prorates the measured capacity correctly between the two contributing layers. In addition to increasing the contribution of the diffuse region to the measured capacity, the lowering of the electrolyte concentration, according to Parson and Devanathan (44), also changes to some extent the potential of the electrocapillary maximum. Now a decrease in the product $C'V_N$, where V_N is as before the potential of the electrocapillary maximum for the adsorbate-covered surface, would cause a shift of maximum apparent coverage in the direction observed in Figure 13.

The calculated curves and experimental points for octanoic acid are shown in Figure 14. In the cases of pentanenitrile and 3-pentanone, Figures 15 and 16 respectively, it was found

Figure 14. Calculated curves and experimental points for apparent fractional surface coverage as a function of potential and adsorbate activity for octanoic acid on mercury in 0.10 N. aqueous perchloric acid solution. $C' = 3.0 \mu\text{g}/\text{cm}^2$, $V_N = 0.64$ volt, $RT/S = 1.0 \mu\text{joules}/\text{cm}^2$, $B_0 = 72$, and $\alpha = 0$

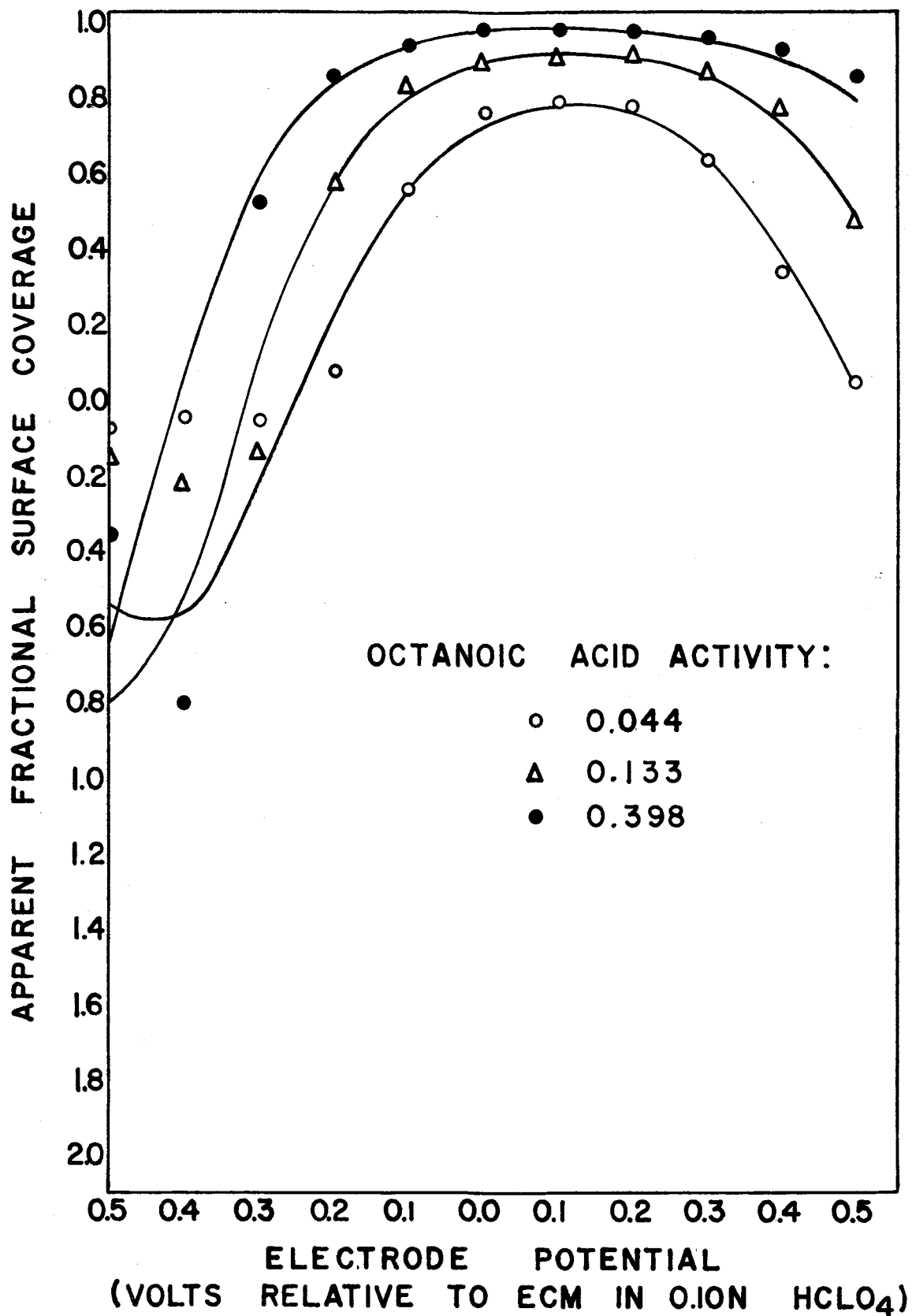


Figure 15. Calculated curves and experimental points for apparent fractional surface coverage as a function of potential and adsorbate activity for pentanenitrile on mercury in 0.10 N. aqueous perchloric acid solution. C' variable (see text), $V_M = 0.42$ volt, $RT/S = 1.2$ μ joules/cm², $B_0 = 1.92$, $d \approx 1.73$

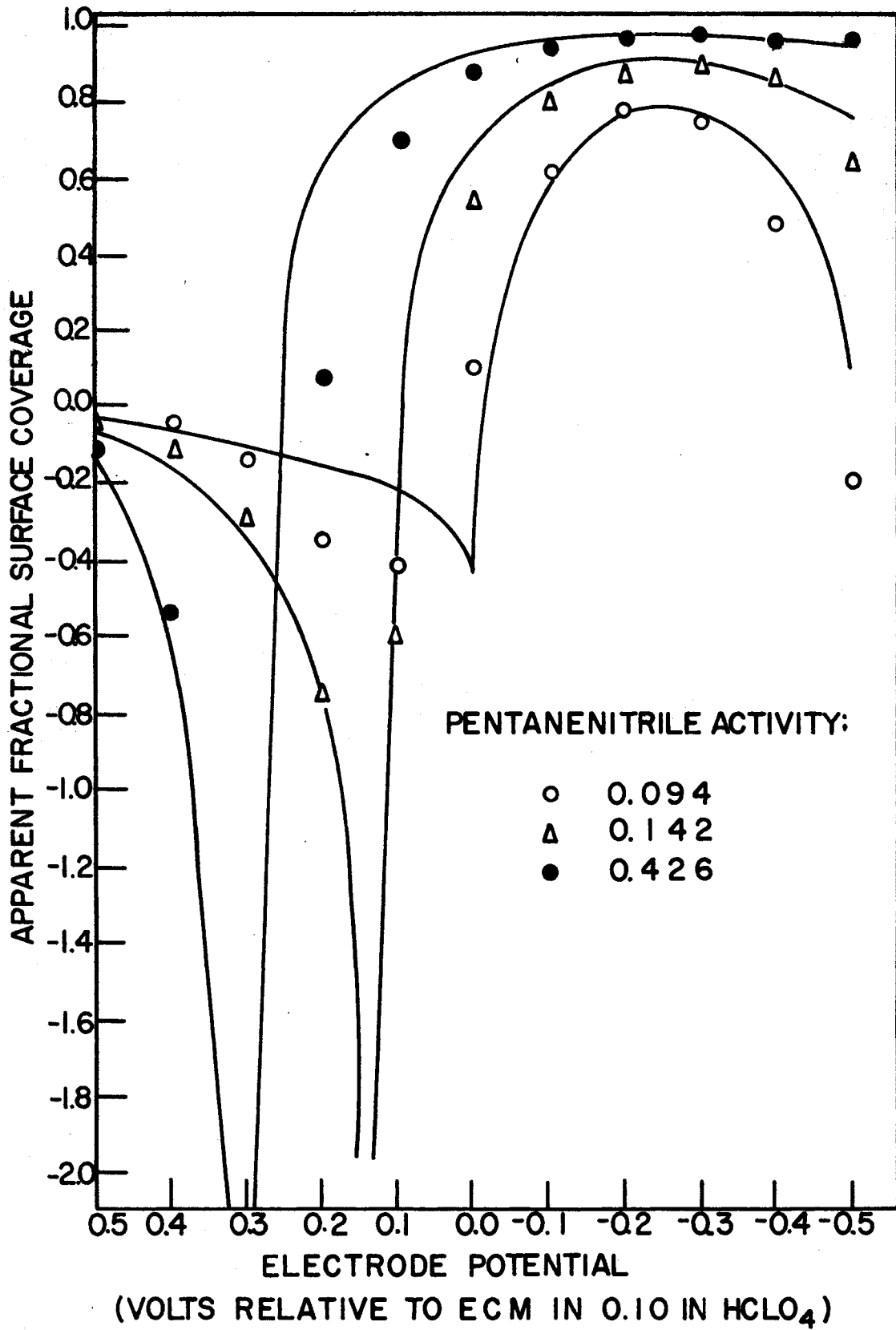
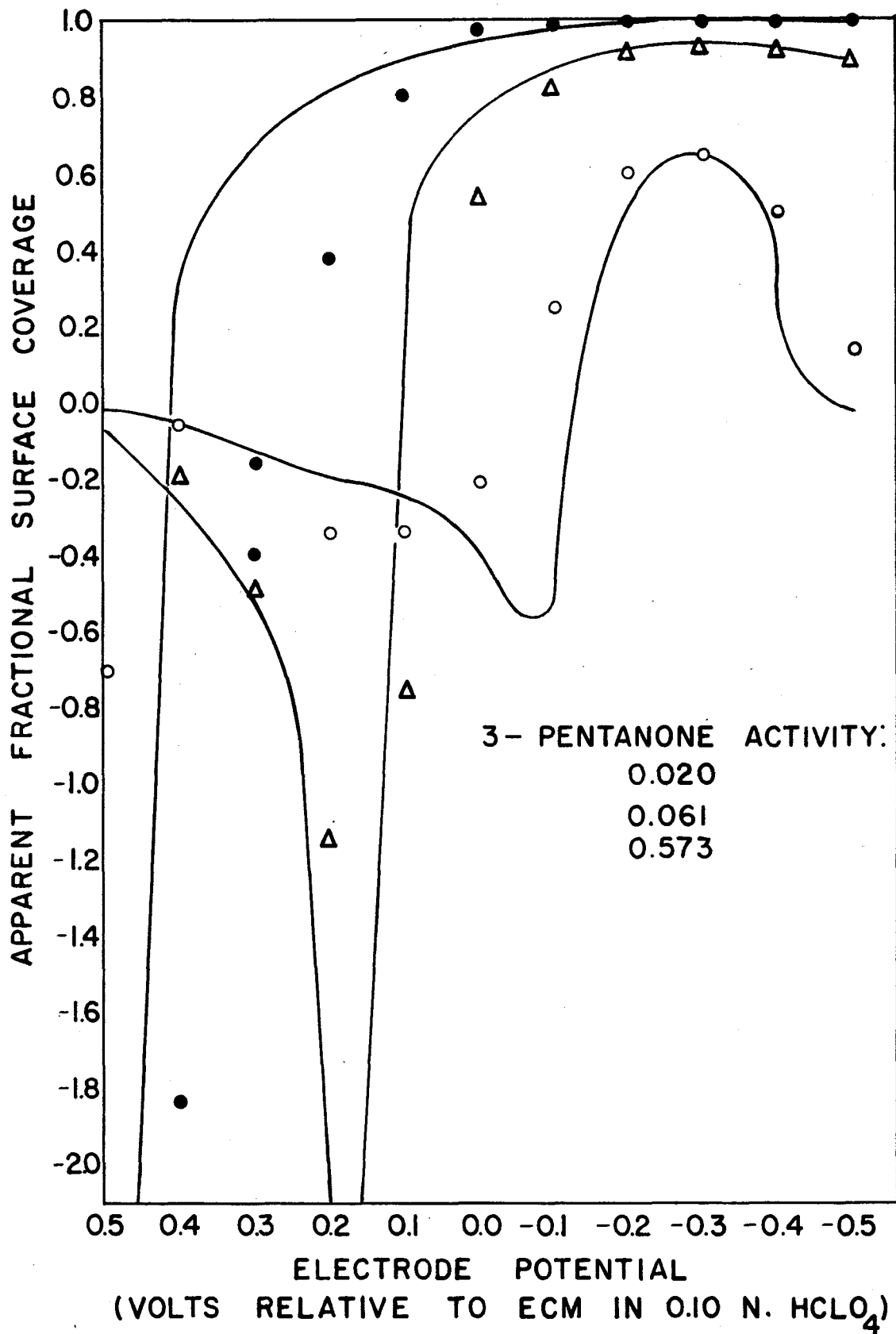


Figure 16. Calculated curves and experimental points for apparent fractional surface coverage as a function of potential and adsorbate activity for 3-pentanone on mercury in 0.10 N. aqueous perchloric acid solution. C' variable (see text), $V_N = 0.60$ volt, $RT/S = 1.2$ μ joules/cm², $B_0 = 6.50$, and $\alpha = 1.73$



necessary to allow C' to vary with potential in order to obtain reasonable coincidence between experimental and calculated results. Where in the former cases it sufficed to assign C' a constant average value, approximating its value throughout the range of maximum capacity depression and neglecting variations throughout those potential ranges wherein pseudocapacitive effects were overriding anyway, in the cases of pentanenitrile and 3-pentanone it became necessary to recognize the change in C' with potential upon increasing the negative polarization of the electrode. For highly polar molecules in the region of the compact layer, there is a sharp decrease in the dielectric constant with increasing polarization due to the onset of dielectric saturation. To water, which has a bulk dielectric constant of about 80 cgse units, MacDonald (18) found that he needed to assign a dielectric constant which varied from 15 to 3 cgse units to properly calculate the double layer capacities. Similarly for pentanenitrile and 3-pentanone, which have bulk dielectric constants of 17.7 and 17.3 cgse units respectively (47, p.88), it is likely that dielectric saturation should cause an appreciable effect on C' as the polarization is increased. The values used for C' at each potential are given in Table 12. The values of the several parameters required to obtain best fit for all adsorbates studied are tabulated in Table 13.

Table 12. Values assigned to C' at each potential for adsorbates pentanenitrile and 3-pentanone in calculating curves shown in Figures 15 and 16. Capacity values in $\mu\text{f}/\text{cm}^2$, potentials in volts relative to ECM in 0.1 N. aqueous perchloric acid solution

Adsorbate	<u>Potential</u>					
	0.5 to 0.0	-0.1	-0.2	-0.3	-0.4	-0.5
Pentanenitrile	7.50	7.10	6.70	6.30	5.90	5.70
3-Pentanone	7.90	7.00	6.40	5.90	5.50	5.30

Table 13. Values of parameters used to obtain best fit between calculated curves and experimental points of apparent fractional surface coverage in Figures 11 through 16. C' in $\mu\text{f}/\text{cm}^2$, V_N in volts relative to ECM in 0.10 N. aqueous perchloric acid solution, RT/S in $\mu\text{joules}/\text{cm}^2$

Adsorbate	C'	V_N	RT/S	B_0	α
1-Pentanol	4.34	0.45	0.8	6.18	1.36
Pentanoic acid	3.50	0.65	1.0	5.30	1.38
Octanoic acid	3.00	0.64	1.0	72.0	0.00
Pentanenitrile	7.5-5.7	0.42	1.2	1.92	1.73
3-Pentanone	7.9-5.3	0.60	1.2	6.50	1.73

C. Conclusions Regarding Applicability of Theoretical Treatment and Meaning of Parametric Values Obtained

1. Applicability of theoretical treatment

The theoretical treatment, as exemplified by equation (26), predicts a strong functional dependence of apparent surface coverage upon polarizing potential at constant adsorbate activity. Inspection of Figures 11 through 16 indicates that this indeed is true. The apparent coverage curves have strong maxima slightly to the cathodic side of the potential of the electrocapillary maximum, undergo a change in sign and pass through pronounced minima on both sides of the maxima. The minima would be more evident on the right or cathodic side had measurements been extended to sufficiently negative polarizations. At sufficiently high polarizations, both anodic and cathodic, the apparent coverage curves approach zero as the organic adsorbates can no longer compete with water with its high dielectric constant for a place in the high field of the compact double layer next to the mercury surface. The theoretical curves correspond almost quantitatively with the experimental points in the region of the maxima and semi-quantitatively over the regions of pronounced curvature. Lack of quantitative representation in the latter regions may be attributed both to experimental error and to shortcomings of the theoretical treatment. In the regions where the measured capacities are very strong functions of potential, i.e. where

pseudocapacity effects are most pronounced, a small error in fixing the potential of the electrode will introduce a large error in the graphical representation of the experimental points. A small potential shift of the mercury electrode may arise from small drifts in the potentiometer emf or from adsorption by the electrode of contaminants such as oxygen, although much care was exercised toward the elimination of such effects. At the more cathodic potentials, the mercury electrode no longer behaved as an ideal polarized electrode in that a small current began to flow. Such a current would probably alter the potential gradient across the compact double layer, and consequently the polarization and hence the contribution to capacity of the molecules in the compact layer would be changed. This effect would be compensated for in the water part of the double layer since the capacity depressions are calculated relative to the capacity of the surface in absence of adsorbate, but it would not be compensated for in the organic portion. Such effect is probably small, however, compared to the effect of shifting electrode potential.

To be strictly rigorous, the theoretical development should have treated V_N as a function of adsorbate activity and C' as a function of potential. That V_N varies with activity is demonstrated in Figure 9 where there is a shift in the maximum to more positive potentials as the adsorbate activity increases. This shift is most likely due to a change in average orientation

of the adsorbate on the surface as the activity increases. The evidence favoring considering C' as dependent upon potential has been previously discussed.

2. Adsorbate molecular area and amount adsorbed

At 300° K., RT/S has a value of $41.4/\bar{s}$ microjoules/cm², where \bar{s} is the effective molecular area in square angstrom units. Adam (48, Table III) reports a value of 21.6 A⁰² per molecule for vertical orientation of alcohols on solids. Kipling (49) reports 17.9 A⁰² per molecule for ethyl alcohol on active charcoal, and Kipling and Norris (50) found 20.5 A⁰² for films of fatty acids. Kipling (47) asserts evidence for parallel orientation for lower fatty acids but does not document his assertion. Taubman (51) calculated an area of 28.5 A⁰² for aliphatic alcohols and 30.5 A⁰² for the acids. The values for \bar{s} calculated from the RT/S values of Table 13 are 51.7 A⁰² for 1-pentanol, 41.4 A⁰² for pentanoic and octanoic acids, and 34.5 A⁰² for pentanenitrile and 3-pentanone. The values for pentanenitrile and 3-pentanone are somewhat high for vertical orientation and close packing but correspond very well with the 35 A⁰² which one would assign these molecules in an orientation parallel to the surface. Octanoic and pentanoic acids might well carry a water molecule with them which would add about 10 A⁰² to their effective molecular area. The value 41.4 A⁰² is still somewhat too high for vertical orientation and cannot be rationalized for both acids by assuming parallel

orientation, but it is certainly correct within a factor two. The value of 51.7 \AA^2 obtained for 1-pentanol seems markedly high regardless of orientation assigned to the adsorbed molecules. Parallel orientation of the molecule with an associated water molecule would cover about 45 \AA^2 , but it is more likely that the value of \bar{s} is somewhat in error. Were the experimental data more plentiful and extended to more negative potential values, less arbitrariness in the selection of RT/S values would be possible. The value assigned RT/S determines the width of the calculated maximum of the apparent adsorption curve and the steepness of its slopes, and consequently only by fitting both sides of the maximum would one establish the one value of RT/S that best represented the data.

In any event, the values obtained for \bar{s} are reasonable ones, at worst less than a factor two different from what one might expect from reasonable models of the molecules studied. Since the theoretical treatment contains the molecular area as an adjustable parameter, it is possible to obtain in principle not only the fraction of the surface covered but also the actual amount of solute adsorbed by a consideration of the dependence upon polarization of the apparent surface coverages. For a computed value of \bar{s} for a given adsorbate, \bar{s} in square centimeters per molecule,

$$\Gamma_0 = \frac{1}{\bar{s}},$$

where Γ_0 is the number of molecules adsorbed per square centimeter

on the completely covered surface. Then the amount adsorbed , in molecules per square centimeter, at a fractional coverage θ is given simply by

$$\Gamma = \theta \Gamma_0.$$

Such information has not been available previously for adsorbents of such small surface area.

3. Standard free energies of adsorption

For the condition of equilibrium between adsorbed molecules and solution molecules

$$\mu_s = \mu_a,$$

where μ_s and μ_a are the chemical potentials of the adsorbate molecules in the solution phase and the adsorbed phase, respectively. Now

$$\mu_s = \mu_s^0 + RT \ln a.$$

In the present work the solute activity referred to pure liquid solute as standard state has been approximated by the reduced concentration (concentration divided by saturation concentration) of the solute. To a better degree of approximation, the reduced concentration is the solute activity referred to solute saturated with water, rather than to pure liquid solute as standard state.

$$\mu_a = \mu_a^0 + RT \ln \gamma_a \frac{\theta}{1-\theta}$$

where γ_a is a surface activity coefficient which would be unity for an ideal monolayer.

Now

$$B_a = \frac{\theta}{1-\theta} e^{-2\alpha\theta},$$

and substituting into the equation for μ_s , one has

$$\begin{aligned} \mu_s &= \mu_s^\circ - RT \ln B + RT \ln \left\{ e^{-2\alpha\theta} \left(\frac{\theta}{1-\theta} \right) \right\} \\ &= \mu_a^\circ + RT \ln \left\{ \gamma_a \frac{\theta}{1-\theta} \right\}. \end{aligned}$$

Consequently,

$$\mu_a^\circ = \mu_s^\circ - RT \ln B,$$

or

$$\mu_a^\circ - \mu_s^\circ = -RT \ln B$$

which is the standard free energy of adsorption with the surface standard state on an infinite dilution basis, and

$$\gamma_a = e^{-2\alpha\theta}.$$

Then

$$RT \ln \gamma_a = -2\alpha\theta RT,$$

which is the interaction free energy per mole at surface coverage θ . Consequently,

$$\Delta F_a^\circ = -RT \ln B - 2\alpha RT$$

is the standard free energy of adsorption with the completely covered surface as the surface standard state.

Values calculated for the standard free energies of adsorption, utilizing the B and α values of Table 13, are roughly

-2.69 Kcal/mole for 1-pentanol, -2.62 Kcal/mole for pentanoic acid, -2.54 Kcal/mole for octanoic acid, -2.43 Kcal/mole for pentanenitrile, and -3.15 Kcal/mole for 3-pentanone. These values indicate that of the adsorbates studied 3-pentanone adsorbs the most strongly, pentanenitrile the least strongly, and pentanoic acid, octanoic acid, and 1-pentanol are about equally adsorbed by mercury with an intermediate standard free energy of adsorption.

4. Reservations regarding inference of adsorption from electrical double layer capacity studies

The general theory of apparent surface coverage presented herein predicts that apparent surface coverages will coincide with actual surface coverages only in the regions of the maxima on the apparent coverage-polarizing potential curves. The character of agreement between experimental and calculated apparent coverages justify an assertion that this feature of the theory is almost certainly correct. It is therefore erroneous to assume that quantitative adsorption information can be gained by gathering capacity data at arbitrary or unfixed electrode potentials. Only when the position of the maximum has been firmly established by means of capacity readings over a wide range of potentials can anything quantitative be said about the adsorption. Even then one must bear in mind that θ is a strong function of electrode potential and a given adsorption isotherm is valid only at that potential at which it was measured.

Since in a study such as this investigation the potential of the adsorbent was carefully controlled, the results gleaned should not be arbitrarily stated to represent the adsorption of the given adsorbates on mercury under all conditions. For a mercury surface free of potential control the adsorption characteristics will, of course, be much altered. The position of the apparent coverage maximum does have, however, considerable practical significance for it allows one to know the conditions under which a given adsorbent will adsorb most strongly a given adsorbate. It conversely allows one to predict which adsorbate will adsorb most strongly under a given set of conditions. For example, if one wanted to protect a metal from attack by acid, he would choose an adsorbate that has a maximum apparent coverage at quite negative potentials, for the adsorption of this compound would be increased by the change in potential of the metal as hydrogen gas is liberated. Conversely, if one wanted an organic film on a metal under conditions from which the metal acquired a positive polarization, one would choose an adsorbate that had an apparent coverage maximum at potentials positive to the position of the electrocapillary maximum.

VI. SUGGESTED MODIFICATIONS AND EXTENSIONS

A. Experimental Modifications

It is suggested that the experimental accuracy would be improved if solutions more concentrated in electrolyte were employed. Better results might be expected in solutions one normal in NaClO_4 , for then the lowered resistance of the solution would make the capacitive reactance a much larger fraction of the total impedance of the cell. In addition an increase in electrolyte concentration increases the capacity of the diffuse double layer, thereby lowering its impedance and again increasing the accuracy of measuring the capacity of the compact double layer.

An ordinary six volt storage battery was used to supply power to the potentiometer circuit in this investigation. It is suggested that a battery specifically designed for potentiometer work, with low temperature coefficient and high voltage stability, be obtained. Voltage fluctuations between standardizations would be thus minimized.

For the slightly soluble adsorbates, it is recommended that a highly soluble slightly adsorbable solvent be employed as an adsorbate diluent to increase the accuracy of concentration measurements. For example, the accuracy of the activities assigned to octanoic acid in aqueous solution could be considerably improved by diluting an easily measurable quantity of acid with methanol. Since the methanol is very soluble in water its activity

in solution would remain negligible over a considerable concentration range and it should interfere negligibly with the adsorption measurements.

Perhaps a better mercury drop metering system could be designed to improve the reproducibility of the size of the mercury electrodes.

B. Suggested Extensions

It would be desirable to study the electrocapillary curves of the systems for which capacity curves have been run. This would indicate the accuracy of the present experimental method and would, in addition, allow one to calculate the extent of pseudocapacity much more accurately. In addition, capacity curves in the pure adsorbate, containing the same concentration of electrolyte, should be obtained in order to better estimate the capacity that should be assigned to the adsorbate covered surface. One must realize, however, that in the pure organic phase the capacity of the diffuse layer would be much less than that in comparable aqueous solutions because of the lower dielectric constant of the organic medium. It would consequently be much more important to accurately pro-rate the measured capacities to the appropriate double layer. This could only be done after a comprehensive treatment of the double layer properties in the organic medium, much the same as that done by Grahame (17) for the aqueous case. This might very well be quite difficult to do.

It would be interesting to study solid metal adsorbents by the present method, for, as indicated in the introduction to this dissertation, no really good method to measure extents of adsorption on small metal surfaces exists at the present time. Preliminary work by the author indicated experimental difficulties in working with solid electrodes, chief among which was an aggravating drift of measured capacity to lower values with time. The capacity fell off exponentially with time, although much care was taken to provide non-contaminated solutions and metal surfaces. Such drift might be eliminated if the electrodes were vacuum degassed prior to immersion in the solution.

Many adsorbates of interest, such as lubricants and some corrosion inhibitors, are too insoluble to study in aqueous solution, but could be readily investigated in non-aqueous solvents by the present method. A correlation between lubricating or inhibiting properties and strength of adsorption would be both interesting and valuable.

In any system studied, measurements should be made over a wider range of polarizing potentials, even though the polarizing current should become appreciable. This is especially important in systems such as 3-pentanone and pentanenitrile in which the capacity curves reach a minimum at the more negative potentials.

VII. SUMMARY

The effect of surface active components on the electrical double layer capacity at the mercury -0.10 N. aqueous perchloric acid solution interface was investigated. Concentrations of the surface active components were varied from zero to saturation and the mercury electrode polarizing potentials were varied from 0.5 volt cathodic to 0.5 volt anodic with respect to the electrocapillary maximum. Surface active components investigated were pentanoic acid, 1-pentanol, 3-pentanone, pentanenitrile, and octanoic acid.

A theory permitting the interpretation of apparent surface coverage by adsorbed surface active components in terms of actual surface coverage was developed, reduced to a form suitable for the treatment of data in the special case of the "regular" monolayer, and the resulting equations applied to the experimental data.

The theoretical treatment predicts, and the experimental results confirm, a strong dependence of apparent surface coverage upon polarizing potential at fixed adsorbate activity. The curve has a maximum in the neighborhood of, but not in general at, the potential of the electrocapillary maximum. To either side of the maximum, the apparent coverage decreases sharply, undergoes a change in sign, and passes through pronounced minima. At high polarizing potentials, both cathodic and anodic, the apparent coverage approaches zero. Curves

calculated from the theoretical treatment represent the data almost quantitatively in the neighborhood of the maximum and semi-quantitatively in the regions of pronounced curvature.

The theoretical treatment contains the molar area as an adjustable parameter, so that in principle not only fractional surface coverages but also actual amounts adsorbed can be calculated from the dependence of the apparent coverage on polarizing potential.

Calculated molar areas are somewhat larger than one would expect from a close packed model and vertical orientation. Areas for 3-pentanone and pentanenitrile indicate the possibility of orientation parallel to the surface, and the areas indicated for pentanoic acid and octanoic acid suggest the possibility that these molecules are hydrated on the surface.

Standard free energies of adsorption are computed, referred to solute saturated with water as solution standard state and complete coverage as the surface standard state. Pentanoic acid, 1-pentanol, and octanoic acid were found to have substantially the same free energies of adsorption ($2.62 \pm .08$ Kcal/mole); the standard free energy of adsorption of pentanenitrile was somewhat less, about 2.44 Kcal/mole, and that of 3-pentanone was markedly higher (3.15 Kcal/mole).

Apparent surface coverages coincide with actual surface coverages only in the neighborhood of the maximum of the

apparent coverage - polarizing potential curve. For reliable inference of adsorption from double layer capacity it is therefore essential that a sufficient range of polarizations be investigated to establish the location of this maximum.

VIII. LITERATURE CITED

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