APR 26 1963

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IS-626

MASTER

THE INFERENCE OF ADSORPTION FROM DIFFERENTIAL
DOUBLE LAYER CAPACITANCE MEASUREMENTS.

II. DEPENDENCE OF SURFACE CHARGE DENSITY ON
ORGANIC NON-ELECTROLYTE SURFACE EXCESS^{1, 2}

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Abstract

Dependences of boundary tension and capacitance at the mercury-aqueous 0.1 N HClO₄ interface on polarization and organic solute concentration were determined for the solutes n-amyl alcohol and phenol. The surface charge density at fixed polarization varied linearly with surface excess in the case of n-amyl alcohol, but contained both linear and cubic terms in surface excess in the case of phenol suggesting a change in phenol orientation with increasing coverage. Near the electrocapillary maximum the differential capacitance varied linearly with coverage in both cases.

The theory of inference of adsorption from capacitance measurements is further discussed. It is pointed out that the "thermodynamic" inference based on double integration of non-static capacitance curves introduces (by integrating across desorption peaks) serious errors where solutes are strongly adsorbed at small concentrations. Criteria

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for estimating the errors thus introduced are suggested. An earlier treatment proposed by this Laboratory⁵ based on a (non-thermodynamic) assumption of linear variation of surface charge density with coverage appears adequately justified for inference of fractional surface coverages near the electrocapillary maximum, but must be considered approximate for evaluation of molar areas at full coverage in cases where linear variation of charge with coverage has not been demonstrated.

Introduction

This Laboratory has recommended⁵ a method for inference of adsorption from differential double layer capacitance measurements claimed to be especially suited for systems exhibiting monomolecular adsorption. The method stems from earlier work by Frumkin⁶ and is indicated in outline by Eqs. (1-4).

If

$$\frac{\theta}{1 - \theta} = B_0 a e^{2\alpha\theta} \quad (V = 0) \quad (1)$$

then

$$\frac{\sigma}{1 - \theta} = B_0 a e^{2\alpha\theta} e^{-(S\Phi/RT)} \quad (V \text{ general}) \quad (2)$$

where

$$\Phi = \int_0^V [Q_w - C'(V - V_N)] dV \quad (3)$$

and parameters may be established by observing the dependence of the quantity θ_{app} on V and a , where

$$\theta_{app} = \frac{C_w - C}{C_w - C'} = \theta \left[1 - (S/RT) \frac{1 - \theta}{1 - 2\alpha\theta(1 - \theta)} \frac{\{Q_w - C'(V - V_N)\}^2}{C_w - C} \right] \quad (4)$$

In these equations, θ is the fractional surface coverage, a the solute activity, Q_w the interfacial charge density with the base solution at polarization V , C_w and C the differential capacitances per unit area in absence and in presence of adsorbate, C^1 the capacitance when $\sigma = 1$, V_N the electrocapillary maximum potential when $\theta = 1$, S the molar area of adsorbate when $\theta = 1$, B_0 and α are adjustable constants.

Since our work appeared an article by Parsons⁷ has criticized the assumption of linear variation of capacitance with coverage and conclusions derived from this assumption. It should be noted that our previous treatment assumed linear variation of charge density with coverage, and as should be evident from the form of Eq. (4) derived on the basis of this assumption this does not imply a linear variation of capacitance with coverage in general. An excellent article by Breiter and Delahay⁸ has compared surface excesses inferred from capacitance curves (treating data in a manner somewhat similar to ours) and electrocapillary curves, for the system mercury-1M NaClO_4 - amyl alcohol, and found results obtained by the two methods to be in good general agreement. Breiter and Delahay emphasize the importance of using static (zero frequency) capacitances for the inference of adsorption. This point is well taken; Frumkin and Melik-Gaikazyan^{9,10} have demonstrated both theoretically and experimentally that differential capacities may be expected to be highly frequency dependent at potentials near the desorption peaks in capacity-polarization curves.

The present work is an investigation of the dependence of surface charge on adsorbate surface coverage in the systems mercury-0.1M HClO_4 - *n* - amyl alcohol and mercury-0.1M HClO_4 - phenol. We shall

also extend the theory presented in our earlier papers, and discuss its applicability critically with respect to the findings of Parsons,⁷ Breiter and Delahay⁸ and the present investigation.

Theoretical

We shall be concerned with the dependence of interfacial properties on polarizing potential and activity of an adsorbable organic solute in a solution containing electrolytes whose chemical potentials are kept constant, the system being at constant temperature. Then

$$-d\gamma = Q dV + RT\Gamma d \ln a \quad (5)$$

where γ is the interfacial tension, Q the charge per unit area on the electrode side of the double layer, V the potential of the polarizable electrode (mercury in the present work) with respect to a reference electrode (we shall refer V to the electrocapillary maximum potential at $a = 0$), Γ is the surface excess of the adsorbable component per unit area and a is its activity.

From Eq. (5) we obtain

$$\left(\frac{\partial \ln a}{\partial V}\right)_{\Gamma} = -\frac{1}{RT} \left(\frac{\partial Q}{\partial \Gamma}\right)_V \quad (6)$$

Hence if we define $F(a)$ by

$$F(a) = \Gamma(a, V = 0) \quad (7)$$

we have

$$\Gamma(a, V) = F(a e^{-(S\Phi/RT)}) \quad (8)$$

where

$$\Phi = -\frac{1}{S} \int_0^V \left(\frac{\partial Q}{\partial \Gamma}\right)_V dV. \quad (9)$$

Equations (6-9) are of purely thermodynamic origin; no assumptions as to adsorption model are implicit in them. For subsequent model

discussions we define S as the molar areas of the adsorbate in a complete monolayer, but evidently Eq. (8) with Φ defined by Eq. (9) is valid for any choice of S .

If a certain value, say Γ_0 , of the surface excess occurs at an activity a_0 when $V = 0$ and at an activity a' at a polarization V' , then from Eq. (8)

$$(S\Phi/RT) = \ln a' - \ln a_0 \quad (\Gamma = \Gamma_0) \quad (10)$$

In this way the function $(S\Phi/RT)$ can be evaluated experimentally. It is convenient to suppose $(S\Phi/RT) = f(\Gamma, V)$ for the purpose of model discussions.

We define the spreading pressure π by

$$\pi(a, V) = \gamma(0, V) - \gamma(a, V) \quad (11)$$

and obtain by use of Eq. (5)

$$d\pi = (Q - Q_w) dV + RT\Gamma d \ln a \quad (12)$$

where Q_w is the surface charge density at polarization V when $a = 0$.

From Eq. (12) we find

$$\left(\frac{\partial \ln a}{\partial V}\right)_\pi = \frac{Q_w - Q}{\Gamma RT} \quad (13)$$

Hence if we define $G(a)$ by

$$G(a) = \pi(a, V=0)$$

we have

$$\pi(a, V) = G(a e^{-(S\psi/RT)}) \quad (14)$$

where

$$\psi = \frac{1}{S} \int_0^V \frac{Q_w - Q}{\Gamma} dV. \quad (15)$$

If a certain value, say π_0 , of the spreading pressure occurs at an activity a_0 when $V = 0$ and at an activity a' at polarization V' , then from Eq. (14)

$$(S\psi'/RT) = \ln a' - \ln a_0 \quad (\pi = \pi_0) \quad (16)$$

In this way the function $(S\psi/RT)$ can be evaluated experimentally. Most conveniently, we obtain $(S\psi/RT)$ as a function of π and V by plotting experimental values obtained at a given value of π against V and repeating for as many values of π as desired; for the purpose of model discussions, however, it is most useful to obtain the function $(S\psi/RT) = g(\Gamma, V)$. Equations (11-17) are also purely thermodynamic in character and contain no assumptions as to adsorption model.

If and only if Q varies linearly with Γ at fixed V , ϕ and ψ will be equal and independent of Γ . If the linear dependence of Q on Γ is limited to a range $0 \leq \Gamma \leq \Gamma_0$, ϕ and ψ will be equal and independent of Γ in this range. Finally, if ϕ or ψ can be shown to be independent of Γ for some range of Γ , say $0 < \Gamma < \Gamma_0$, then ϕ and ψ are equal in this range and Q must vary linearly with Γ at fixed V in this range.

If Q varies linearly with Γ , ψ depends on V only and, where G' and G'' are the first and second derivatives of $G(a e^{-(S\psi/RT)})$ after its argument we obtain from Eqs. (12) and (14)

$$Q - Q_w = \left(\frac{\partial \pi}{\partial v}\right)_a = - \frac{Sa}{RT} e^{-S\psi/RT} \frac{d\psi}{dv} G' \quad (17)$$

$$C - C_w = \left(\frac{\partial^2 \pi}{\partial v^2}\right)_a = - \frac{Sa}{RT} e^{-\frac{S\psi}{RT}} \frac{d^2 \psi}{dv^2} G' + \left[\frac{Sa}{RT} e^{-\frac{S\psi}{RT}} \right]^2 \cdot [G' + \frac{G'}{a} e^{\frac{S\psi}{RT}}] \left(\frac{d\psi}{dv}\right)^2 \quad (18)$$

$$\Gamma = \left(\frac{\partial \pi}{RT \partial \ln a}\right)_v = \frac{a}{RT} e^{-S\psi/RT} G' \quad (19)$$

From Eqs. (18) and (19)

$$C_w - C = S\Gamma \frac{d^2\psi}{dV^2} - (S\Gamma \frac{d\psi}{dV})^2 \left[\frac{G''}{(G')^2} + \frac{1}{aG'} e^{\frac{S\psi}{RT}} \right]. \quad (20)$$

Equation (19) shows that Γ also depends only on $ae^{-(S\psi/RT)}$; where Γ' is its derivative after this argument

$$\Gamma' = \frac{1}{RT} (G' + ae^{-(S\psi/RT)} G''). \quad (21)$$

From Eqs. (18-21)

$$C_w - C = \Gamma S \frac{d^2\psi}{dV^2} - a\Gamma' e^{-(S\psi/RT)} (S \frac{d\psi}{dV})^2 \quad (22a)$$

or

$$C_w - C = \Gamma S \frac{d^2\psi}{dV^2} - (S \frac{d\psi}{dV})^2 \frac{d\Gamma}{d \ln (ae^{-(S\psi/RT)})}. \quad (22b)$$

Suppose that Q is linear in Γ at fixed V for $0 \leq \Gamma \leq \Gamma_o$, $-V' \leq V \leq V''$.

V' and V'' are positive, so that the range of V includes the electrocapillary maximum for the base solution, and Γ_o is a fixed number (independent of V). Let Q_o be the value of Q when $\Gamma = \Gamma_o$, $C_o = \frac{dQ_o}{dV}$. Then

$$Q = Q_w + (Q_o - Q_w) \frac{\Gamma}{\Gamma_o} \quad (23)$$

$$\frac{d\psi}{dV} = \frac{1}{S} \frac{Q_w - Q}{\Gamma} = \frac{Q_w - Q_o}{S\Gamma_o} \quad (24)$$

$$\frac{d^2\psi}{dV^2} = \frac{C_w - C_o}{S\Gamma_o} \quad (25)$$

Substituting these results in Eqs. (20) and (22) we obtain

$$C_w - C = \frac{\Gamma}{\Gamma_o} (C_w - C_o) - \left[\frac{\Gamma}{\Gamma_o} (Q_w - Q_o) \right]^2 \left[\frac{G''}{(G')^2} + \frac{1}{aG'} e^{\frac{S\psi}{RT}} \right] \quad (26)$$

$$C_w - C = \frac{\Gamma}{\Gamma_o} (C_w - C_o) - a\Gamma \left[-\frac{S\psi}{RT} \left(\frac{Q_w - Q_o}{\Gamma_o} \right)^2 \right] \quad (27a)$$

$$C_w - C = \frac{\Gamma}{\Gamma_o} (C_w - C_o) - \left(\frac{Q_w - Q_o}{\Gamma_o} \right)^2 \frac{d\Gamma}{d \ln [ae^{-S\psi/RT}]} \quad (27b)$$

Equations (26-27) are generalizations of Eq. (10) of reference (5), and Eq. (18) is similar in content to Parsons' ⁷ Eq. (8); Parsons has not assumed linear variation of charge with coverage, so his analogs of $\frac{d\psi}{dV}$ and $\frac{d^2\psi}{dV^2}$ are partial derivatives.

It should be noted that, if Q varies linearly with Γ at fixed V , C will not be linear in Γ in general. This is clear from Eqs. (22-23); more generally

$$C = \left(\frac{\partial Q}{\partial V} \right)_a = \left(\frac{\partial Q}{\partial V} \right)_\Gamma + \left(\frac{\partial Q}{\partial \Gamma} \right)_V \left(\frac{\partial \Gamma}{\partial V} \right)_a \quad (28)$$

The term $\left(\frac{\partial Q}{\partial V} \right)_\Gamma$ is linear in Γ if Q is linear in Γ , but the term

$\left(\frac{\partial Q}{\partial \Gamma} \right)_V \left(\frac{\partial \Gamma}{\partial V} \right)_a$ is not and is the term responsible for the well-known de-

sorption peaks in capacitance-polarization curves obtained with solutions containing adsorbable non-electrolytes. In the neighborhood of the electrocapillary maximum $\left(\frac{dQ}{d\Gamma} \right)_V$ (approximately proportional to V) and $\left(\frac{d\Gamma}{dV} \right)_a$ are both small, the second term in Eq. (28) is hence substantially negligible, and in this region linearity of Q in Γ implies linearity of C in Γ .

Experimental

The capillary electrometer used in this research incorporates several ideas presented by previous workers ¹¹⁻¹³ and is shown schematically in Fig. 1. Because the design and operation of a capillary

electrometer is not described fully in any of the generally accessible modern literature, we feel that a description of our apparatus is warranted although the general principles of operation have been known for more than eighty years.

The tapering capillary was formed from precision bore Pyrex capillary tubing of internal diameter 0.0025 ± 0.005 inches. This tubing was drawn out in a gas flame to the extent that the original outside diameter of 5 mm became approximately 2 mm at the narrowest constriction. The tubing was cut just above this point of minimum diameter, producing a tapering capillary with an internal diameter of approximately 0.03 mm at the tip.

The mercury reservoir directly above the capillary was approximately 27 cm in height. A tungsten wire sealed through the glass near the top served as lead to the polarizing source. All ball joints and standard tapers attached or leading to the cell proper were greaseless. The large ball joint connecting the mercury reservoir to the manometer system was lubricated lightly with Apiezon N which was also used on the three stopcocks attached to the manometer system.

A Leeds and Northrup K-2 Potentiometer monitored the voltage supplied by three two-volt cells of a wet-cell storage battery which were wired in parallel. The potential of the mercury electrode was measured in reference to a saturated calomel electrode in contact with the 0.10 normal perchloric acid solution. The porous plug separating the cell proper from the compartment containing the reference electrode minimized the transfer of chloride ion to the solution.

The gas pressure above the mercury reservoir was increased by addition of tank nitrogen controlled by a standard regulator valve or decreased by venting nitrogen to the atmosphere through a stopcock and tapering vent prepared from 1 mm I. D. capillary tubing. A 1-liter ballast reservoir further increased the ease with which the pressure could be adjusted to a high degree of precision. The system was designed in such a way as to allow the operator to increase pressure via the nitrogen tank or decrease it by venting nitrogen to the atmosphere while simultaneously observing the level of the mercury in the capillary through a microscope.

The manometer was constructed of large bore (20 mm I. D.) tubing to eliminate the need for any correction for capillary depression effect. An opaque white background was provided, and each meniscus was illuminated from the side by a small flashlight. Movable brass cylinders around each arm of the manometer served to eliminate interfering glare from above. A Gaertner cathetometer was used to measure pressures with a reproducibility of 0.05 mm. The aspirator bulb attached to the atmosphere side of the manometer insured complete wetting of the capillary walls. The bulb was used to oscillate the mercury in the capillary before and after each measurement to make sure that the position of the meniscus in the capillary was truly the equilibrium position.

A Gaertner Scale Micrometer microscope, M 105A, with objective of 48 mm effective focal length and a magnification of 23 diameters, was used to observe the meniscus in the capillary. The focal distance was large enough to permit the meniscus and the tip of the capillary to be viewed simultaneously, thus allowing the tip to serve as a

convenient reference point. During measurement, the meniscus was always brought to a point about 0.20 mm from the tip as seen through the eyepiece scale of the microscope. The capillary was illuminated from behind by a small electric bulb placed behind a white translucent background. A flat piece of glass fused to the front side of the electrometer cell allowed the capillary to be viewed through optically plane glass.

After cleaning the cell components in a hot bath of 3-1 sulfuric-nitric acid, followed by rinsing with conductivity water, the cell was assembled and the capillary was allowed to soak in conductivity water for a day or two before any interfacial tension measurements were made. We found, as had Craxford previously,¹¹ that the capillary radius tends to increase significantly in size with soaking until it reaches a constant value.

The radius of the capillary at the null point was determined by standardization against a solution of known surface tension. Smolder's value of 426.2 ± 0.2 dynes/cm¹⁴ for the interfacial tension of mercury—0.05 molar sodium sulphate at the electrocapillary maximum at $25.0 \pm 0.3^\circ\text{C}$. was used for this purpose.

The electrometer was thermostatted only by the air-conditioning of the building. Measurements were made at a temperature of $26.5 \pm 0.9^\circ\text{C}$.; such a temperature fluctuation generates errors of the order of 0.2 dynes/cm in the interfacial tension.

Differential double layer capacitances were measured by a substitution technique with an impedance bridge whose schematic design is shown in Fig. 2. A Leeds and Northrup shielded ratio box, catalog number 1553, served as the central connecting terminal. A shielded stepdown transformer is incorporated in this box. Shielded binding

Figure 2. Impedance bridge.

posts made connection to the various external pieces of equipment. All electrical connections were made with high quality shielded cables.

The input signal to the transformer in the ratio box was supplied by a Hewlett-Packard Model 200 CD wide range oscillator. The signal from the oscillator was attenuated by use of a simple potential divider constructed from precision resistors. This permitted operation of the oscillator at a high output level where best frequency stability was observed while allowing use of a low level signal for the operation of the bridge.

The measuring arm of the bridge consisted of a Freed Transformer Co. Model 1350 decade capacitor and a non-inductively wound Leeds and Northrup decade resistance, catalog No. 4764, in series connection. The lowest capacitance range was covered by a continuously variable air capacitor with a maximum value of 100 micro-microfarads. Four decades in units of 0.001, 0.01, 0.1, and 1 microfarad extended the range of the decade capacitor to 11 microfarads. The decade resistance had six units variable in increments of 0.01, 0.1, 1, 10, 100, and 1000 ohms, respectively, and covered the range from 0.01 to 11,000 ohms. Contact resistances were negligible in both of these circuit elements and the reproducibility in settings were consequently limited only by other factors in the measurement.

A second pair of elements like the above were used in the substitution procedure to be described later. The connections to this cell analog were made as nearly identical to those to the cell proper as could be achieved.

The null detector for the bridge was based on a DuMont Type 304-H cathode ray oscilloscope with both X and Y input terminals. The output signal from the bridge was of such low level that amplification was necessary prior to display on the oscilloscope screen. The bridge output was first amplified by a Hewlett-Packard wide band amplifier, Model 450 A, operating at a gain of 100 to 1. This signal was in turn amplified by a twin-tee narrow band amplifier designed and constructed in this Laboratory. Pairs of tees used in the measurement were constructed for use at nominal frequencies of 100, 500, 5000, and 10,000 cycles per second. The filtered, amplified signal from the twin tee produced the Y displacement on the cathode ray oscilloscope screen.

To gain some additional sensitivity in the measurements, a phase sensitive technique was used. A second Hewlett-Packard Model 450 A wide band amplifier was connected to the bridge so that the input signal to the bridge could be amplified and used to produce the X deflection on the oscilloscope screen. Thus, a series of Lissajou figures showed the amplitude of the output signal from the bridge and the phase of this signal with respect to the input. A horizontal straight line indicated a balance condition. The X axis of the cathode ray oscilloscope was calibrated and used to measure the input signal to the bridge.

The mercury electrode was polarized by means of a Leeds and Northrup Student Potentiometer. To eliminate effectively the path available for the alternating current flow parallel to the path through the double layer and solution, a 100,000 ohm resistor was placed in series with this polarizing source. A Rubicon Type B high precision

potentiometer, shown in Fig. 2, was used to measure the polarization of the mercury surface in reference to the standard hydrogen electrode. The Rubicon potentiometer (but of course not the polarizing potentiometer) was switched out of the circuit during capacity measurements, thus removing any alternate path for the A.C. current flow. C_k was a 60 microfarad condenser which essentially eliminated the direct current path from the electrodes through the oscillator transformers. C_k was in series with the cell capacitance, but its small contribution to the impedance was corrected for by substitution.

Six volt storage batteries supplied current to the potentiometers. The Rubicon potentiometer slide wire was calibrated against an Eppley Laboratories standard cell, catalog No. 100. A Rubicon galvanometer, catalog No. 3411, with a sensitivity of 1.5 microvolts per millimeter was used in the calibration. The potentiometer was completely enclosed in a grounded metal box for shielding.

A Simpson microammeter with a full scale deflection of 25×10^{-6} amperes was connected in series with the cell and potentiometer to detect and measure any direct current in the system. Capacitance measurements were not made whenever this current exceeded 0.5 microamps.

A schematic diagram of the cell used in the capacitance measurements is shown in Fig. 3. The container for the solution was formed from a 55/60 Pyrex double walled standard taper, outer. The ring seal at the bottom completed a thermostating jacket through which water from a constant temperature source could be circulated. The temperature of a solution in the cell was maintained at $25 \pm 0.15^\circ\text{C}$.

Figure 3. Impedance Bridge cell.

A 55/60 Pyrex standard taper, inner, closed the cell against the atmosphere and served as a support for the various components of the cell. A gas dispersing tube was connected to this support by a ring seal, and a Teflon-plug stopcock directed the incoming gas through this tube when closed, or, when open, forced the gas to bypass the tube while maintaining an atmosphere of hydrogen above the solution. The platinum gauze reference electrode was also connected to the support by a firm platinum wire sealed through a glass sheath, which in turn was ring-sealed to the support.

The dropping mercury electrode was inserted through a Teflon plug, the outside of which had been machined to fit tightly the 12/30 Pyrex standard taper, outer, which was attached to the top of the cell support. The electrode was fed by a reservoir of large cylindrical cross-section in order that flow of mercury through the capillary during the course of a day would not significantly change the height of mercury above the electrode tip, and hence would cause no change in the volume flow rate of the mercury. A greaseless ball joint connected this reservoir to the electrode in order to facilitate removal of the electrode from the cell when necessary.

The dropping mercury electrode was formed from the same precision bore capillary tubing used in the construction of the capillary electrometer. A central segment of this tubing about two inches in length was heated over a wide gas flame and, when soft, was pulled to give an extension about two inches in length. The diameter of the capillary, both inner and outer, decreased as a result. A head of about 40 cm of mercury applied to the

capillary was necessary to produce a flow rate of approximately 10^{-4} grams per sec. A drop of mercury was formed and fell from the tip in 60 to 100 sec.

Desicote, a Beckman product which forms a hydrophobic surface layer when applied to clean air-dry glass, was drawn into the tube by capillary action and, after rising some 3 or 4 cm up the tube, was forced out with nitrogen. After rinsing the capillary interior with acetone, Desicote was again applied in the same manner, and after rinsing again with acetone the capillary was dried by forcing nitrogen through the tubing for several hours. We found that this procedure markedly reduced the frequency dependence of the capacitance measured in solutions containing no organic solutes; this result suggests that solution creeping between mercury and capillary walls may lead to an apparent dispersion of the double layer capacitance.

The procedure for measurement involved setting a capacitance value on the variable arm of the bridge and observing the variation of the Lissajou figure depicting the state of bridge balance. If the resistance of the variable arm of the bridge is adjusted properly, the Lissajou figure passes through a horizontal straight line configuration. At this instant, the size of the droplet is such that its double layer capacitance and its resistance are just the proper values necessary to balance the bridge. If the surface area of the drop at this instant is known, then one can easily calculate the capacitance per unit area of electrode surface. By determining the volume flow rate of the mercury through the capillary, and assuming a spherical shape for the mercury droplet at

the instant of balance, the age of the drop can be used as a measure of the surface area. The relationship

$$\log A = 2/3 \log (0.7843 Z t)$$

can be shown to represent the area of a spherical mercury droplet at time t and flow rate Z when the density of mercury is taken as 13.56 gram/cm³. Thus, to determine the surface area, the age of the droplet t was measured with a stopwatch, and flow rate Z measured by weighing the mercury expended from the electrode over a period of several hours. This mercury was washed well with conductivity water and acetone, and then dried thoroughly prior to weighing. All times were measured with a reproducibility of 0.2 sec. in 70 sec.

A substitution technique was used to eliminate effects due to asymmetries in the bridge network and in the electrical leads and the capacitor C_k . The cell was replaced by a series combination of a decade resistance with a decade capacitance. This cell analog combination became the adjustable arm of the bridge in the calibration procedure. The resistance and the capacitance which initially balanced the cell impedance were in turn balanced by adjusting the resistance and capacitance in the analog. By using identical shielded electrical leads for connecting both the cell and the analog to the bridge terminals, the identity of the impedance of the analog with that of the cell was insured.

Materials

Goldsmith Brothers triply distilled mercury was further purified by washing with 5% nitric acid, rinsing with conductivity water, drying, and finally by vacuum distillation. The mercury was added to the electrode reservoir through a pin hole filter which removed any dust which might have collected on the surface.

The conductivity water used in making up solutions was prepared by redistilling tap distilled water through an all fused silica continuous double distillation column obtained from Englehard Industries, Inc. The first stage of this column contained enough sulfuric acid to make the concentration of the solution there approximately one molar when the column was in operation. This acid reacted with any long chain amines present in the tap distilled water; using this procedure, the surface tension of the product of the double distillation as measured with a commercial Cenco-DuNoüy Tensiometer was always within 0.2 dynes/cm of the literature value.

The electrolytic solution was 0.10 normal perchloric acid. Pre-electrolysis was carried out for several hours on a number of solutions studied early in the investigation. It was thought that this would insure the removal of any ions which might have interfered in the measurement of the double layer capacity; however, repeating these runs using solutions which had not been subjected to this treatment showed that the pre-electrolysis had no measureable effect on the results obtained, indicating that any interfering ions had already been removed in preceding purification steps, and hence the pre-electrolysis was discontinued.

Carefully purified hydrogen was used to outgas the solutions and, in conjunction with the platinized platinum gauze, served as the reversible reference electrode for the capacitance measurements. The hydrogen entered the cell through a fritted glass filter stick which dispersed the gas in a stream of fine bubbles, and left the cell through a water bubbler. Provision was made for bypassing the hydrogen stream above the

solution when measurements were being taken; thus the cell was continuously flushed and was under a positive pressure of hydrogen at all times.

When measurements were being made on a solution containing a volatile component, e.g. n-amyl alcohol, phenol, etc., the hydrogen was bubbled through a solution of the same concentration as that being studied prior to its admittance to the cell. The bubbler was used in the cell for only 30-60 min. in such cases, and the gas pressure was always adjusted to such a level that only enough hydrogen necessary to maintain a positive pressure inside the cell was admitted. To check on any possible change in concentration over the course of a run, the first point taken was always repeated at the end of the run. In every case, the readings were identical within normal experimental error.

Mallinckrodt A. R. grade phenol was fractionally frozen and distilled in a single stage glass still. The corrected boiling point of the product was $181.4 \pm 0.1^\circ \text{C}$. A concentrated aqueous solution was prepared and standardized by bromination; all phenol solutions were subsequently made up from this solution. Eastman n-amyl alcohol was distilled through a 30 plate Oldershaw column at a reflux ratio of ten to one; the boiling point of the product was $137.8 \pm 0.1^\circ \text{C}$. at S. T. P. N-butylacetamide was used as received from Eastman.

Results

Electrocapillary data for solutions of n-amyl alcohol and phenol are shown in Figs. 4 and 5 respectively. The mercury electrode potential is expressed in volts relative to the electrocapillary maximum for

Figure 4. Electrocapillary curves: interface mercury-0.1N HClO₄ + indicated n-amyl alcohol concentration and interface mercury-0.05M Na₂SO₄ (standardization).

Figure 5. Electrocapillary curves: interface mercury-0.1N HClO₄ - indicated phenol concentration.

the base solution, 0.1M HClO_4 . For each concentration, experimental points were obtained at 25 millivolt intervals over the polarization range.

Figure 6 shows typical dependence of capacitance on frequency at the mercury-base solution + n-amyl alcohol interface. Frequency dependence of capacitance in the neighborhood of the desorption peaks is pronounced as is to be expected.^{8,9,10} Generally, some dispersion of capacitance occurred even at polarizations substantially removed from desorption peaks. The capacitance of the mercury-base solution system varied about 8% near the capacitance "hump", less than 4% elsewhere as the frequency varied from 100 cps to 10,000 cps. It is suspected that variations in capacitance with frequency observed in the base solution system and in systems with adsorbable solutes at polarizations well removed from the desorption peaks result from imperfect electrode design, although a theory attributing them to interfacial properties has been advanced.^{15,16}

Figure 7 shows the dependence of static differential capacitance on phenol concentration and polarizing potential at the mercury-base solution + phenol interface. The static differential capacitance was obtained at each polarization and concentration by plotting capacitances measured at frequencies of 100, 500, 4910, and 9050 cycles/sec. against square root of frequency and extrapolating to zero frequency. For each concentration, static capacitances were thus obtained at 50 millivolt intervals over the range of polarizations. Electrocapillary maxima, as obtained from the previously obtained electrocapillary curves, are shown on each curve. The charge density at a given concentration and polarization can be obtained by integrating the capacitance curve for

Figure 6. Frequency dependence of differential capacitance at the interface mercury-0.1N HClO_4 + 0.031M n-amyl alcohol.

Figure 7. Dependence of zero frequency differential capacitance on polarization, interface mercury-0.1N HClO_4 + indicated phenol concentration. Electrocapillary maximum potential for each concentration is indicated.

that concentration from the electrocapillary maximum potential to the polarization of interest; Fig. 8 shows the dependence of charge density on polarization and phenol concentration obtained by integrating static capacitance curves in this manner. The interfacial tension at a given concentration and polarization can be obtained by integrating the charge density curve for that concentration from the electrocapillary maximum potential to the polarization potential and subtracting the result from the interfacial tension for that concentration at the electrocapillary maximum; electrocapillary curves thus obtained agreed with those determined directly within experimental error.

Figures 9 and 10 show isotherms for the adsorption of n-amyl alcohol and phenol at their respective mercury-base solution interfaces at various polarizations. These were obtained graphically by a method based on the equation

$$\Gamma = \frac{1}{RT} \left(\frac{\partial \pi}{\partial \ln C} \right)_V \quad (29)$$

Because the dependence of π on c at fixed V was rather closely approximated by a Volmer type isotherm over a large part of the concentration range, it was convenient to represent the dependence of π on c by a Volmer term plus a correction term, obtaining Γ by analytical differentiation of the Volmer term and graphical differentiation of the correction term. Thus

$$\ln \frac{c}{\pi} = \alpha + \beta \pi + \Delta \ln \frac{c}{\pi} \quad (V \text{ fixed}) \quad (30)$$

implies

$$\frac{1}{\Gamma} = \frac{RT}{\pi} + \beta RT + RT \left[\frac{\partial (\Delta \ln \frac{c}{\pi})}{\partial \pi} \right]_V \quad (31)$$

Figure 8. Dependence of interfacial charge density of polarization, interface mercury- 0.1N HClO_4 + indicated phenol concentration.

Figure 9. Isotherms for the adsorption of n-amyl alcohol at the mercury-0.1N HClO₄ interface at various polarizations. (C_0 is saturation concentration of n-amyl alcohol in 0.1N HClO₄; taken as 0.222M.)

Figure 10. Isotherms for the adsorption of phenol at the mercury-0.1N HClO_4 interface at various polarizations.

This method is of course exact in principle; in practice constants α and β could be chosen so that the correction term was very small except at very small spreading pressures, and evaluation of Γ was convenient and highly objective except at very small spreading pressures. Most of the data in Figs. 9 and 10 were obtained in this way. An alternate method based on the Langmuir isotherm is outlined by Eqs. (32) and (33)

$$\pi = \Gamma_m RT \ln(1 + bc) + \Delta\pi \quad (V \text{ constant}) \quad (32)$$

$$\Gamma = \frac{\Gamma_m bc}{1 + bc} + \frac{1}{RT} \left(\frac{\partial \Delta\pi}{\partial \ln C} \right)_V \quad (33)$$

For suitable choices of the parameters Γ_m and b , the Langmuir term, $\Gamma_m RT \ln(1 + bc)$ represented π well for small c , but deviated significantly at moderate c and markedly at large c , so that this method was less satisfactory than that outlined by Eqs. (30) and (31) over most of the concentration range. The "Method 2" curve for $V=0.175$ in Fig. 10 was obtained by application of Eqs. (32) and (33).

Figure 11 shows the dependence of $(S\psi/RT)$ on π and V at the mercury-base solution + n-amyl alcohol interface. Evidently $(S\psi/RT)$ is substantially independent of π (and so also of Γ) at this interface. Similar plots showed that $(S\psi/RT)$ varied systematically with π at fixed V at the mercury-base solution + phenol interface; for interpretation of this behavior in terms of a model the dependence of $(S\psi/RT)$ on Γ and V was therefore investigated. Within experimental error this dependence was represented by

$$(S\psi/RT) = F_1(V) + \Gamma^2 F_2(V) \quad (34)$$

This result is shown graphically in Fig. 12. To good approximation $F_1(V) = 6.57 V^2 - 3.02 V$, $F_2(V) = 1.28 \times 10^{19} V$ for the phenol system, V being expressed in volts relative to the base solution electrocapillary maximum.

Discussion

Dependence of spreading pressure on concentration and polarization at the interface mercury-0.1N HClO_4 + n-amyl alcohol found in this work agrees generally with that obtained by Breiter and Delahay;⁸ these workers used a 1M NaClO_4 + 0.001 HClO_4 base solution so their results are not quantitatively comparable to ours. Derived adsorption isotherms are also generally in accord with those inferred from capacitance results in our earlier work,⁵ and this result also confirms findings of Breiter and Delahay.

Isotherms for the adsorption of phenol at the mercury-0.1N HClO_4 interface shown in Fig. 10 agree generally with those found by Blomgren, Bockris, and Jesch¹⁷ using a 0.1N HCl base solution. Although capacitance results obtained in our earlier work are in general agreement with those found here at comparable concentrations, adsorption isotherms shown in Fig. 10 accord very poorly with those which would be calculated from a Frumkin isotherm using parameters previously reported. This stems basically from the fact, apparent from Fig. 10, that the phenol data cannot be represented by a Frumkin isotherm, and our earlier work, limited to three concentrations ranging from 0.1 to 0.2M in phenol, was insufficiently extensive to make this fact obvious. By choosing parameters in the Frumkin equation to represent data at these three concentrations, an isotherm equation was obtained which grossly underestimates the adsorption at substantially lower concentrations.

Figure 11, which demonstrates that the quantity $(S\psi/RT)$ is independent of surface excess when the adsorbate is n-amyl alcohol, therefore also shows that the surface charge is linear in Γ at fixed V for all V and Γ investigated. This result justifies the basic assumption in our earlier work⁵ for this system. Figure 12 shows, however, that when the adsorbate is phenol the quantity $(S\psi/RT)$ varies linearly with Γ^2 at fixed V , and that the surface charge is therefore not linear in Γ at fixed V in this system. From Eqs. (34), (13), and (16) we find

$$Q_w - Q = RT \Gamma [F'_1(V) + \Gamma^2 F'_2(V) - 2\Gamma^3 RT F_2(V) \frac{\partial^2 (S\psi/RT)}{\partial \pi \partial V}] \quad (35)$$

in which $F'_1 = \frac{dF_1}{dV}$, $F'_2 = \frac{dF_2}{dV}$. The last term on the right proved to be negligible at all concentrations and polarizations studied. Hence to good approximation

$$Q_w - Q = RT \Gamma [F'_1(V) + \Gamma^2 F'_2(V)] \quad (36)$$

and

$$C_w - C = \Gamma RT [F'_1(V) + \Gamma^2 F'_2(V)] + RT [F'_1(V) + 3\Gamma^2 F'_2(V)] \left(\frac{\partial \Gamma}{\partial V}\right)_a \quad (37)$$

From Eq. (36), if Γ is small in first order Q will be linear in Γ to terms of second order in Γ , but this linearity does not extend to large values of Γ . Our earlier treatment is therefore not justified for the phenol system at all polarizations and surface excesses. Near the electrocapillary maximum the second term in Eq. (37) becomes negligible, and since $F_2(V)$ was found experimentally to be linear in V , $F'_2(V) = 0$, so the capacitance must be linear in Γ for all Γ near the electrocapillary maximum for both the n-amyl alcohol and phenol containing systems.

Figure 11. Dependence of $\frac{Sv}{RT}$ (see Eqs. 14-17 of text) on polarization and spreading pressure, interface mercury-0.1N HClO_4 +n-amyl alcohol.

Figure 12. Dependence of $\frac{S\Psi}{RT}$ (see Eqs. 14-17 of text) on polarization and surface excess, interface mercury-0.1N HClO_4 + phenol.

Linear dependence of Q on Γ at fixed V was first assumed by Frumkin⁶ in the form

$$Q = (1 - \theta)C_w V + \theta C' (V - V_N) \quad (38)$$

(quantities as defined following Eq. (4)). Capacitances were assumed independent of polarizations; this assumption is unnecessary but is consistent with the degree of approximation in the discussion to follow. Frumkin's assumption is most easily pictured as supposing the double layer to consist of a water-filled condenser and an organic-filled condenser connected in parallel. This implies that a zero net charge at intermediate values of θ corresponds to non-zero charges, equal but opposite in sign, on the organic-filled and water-filled condensers,¹⁸ and this implication is not entirely attractive physically. Instead of Eq. (38) we might also suppose

$$Q = [(1 - \theta)C_w + \theta C'] [V - \theta V_N], \quad (39)$$

i.e. that both capacitance and electrocapillary maximum potential varied linearly with coverage. Equation (39) implies a quadratic dependence of Q on θ , and therefore does not agree with results obtained with either *n*-amyl alcohol or phenol adsorbates. We shall therefore retain Frumkin's model, rewrite Eq. (38) in the form

$$\frac{C_w V - Q}{\theta} = (C_w - C') V + C' V_N \quad (40)$$

and compare this with the result obtained for phenol, Eq. (36), using the experimental values $F'_1(V) = 13.14 V - 3.02$, $F'_2(V) = 1.28 \times 10^{19}$. We have

$$\frac{Q_w - Q}{\Gamma} = RT(13.14 V - 3.02 + 1.28 \times 10^{19} \Gamma^2). \quad (41)$$

Comparison of Eqs. (40) and (41) suggests that the term in Q not linear in Γ in the phenol system is associated with a variation in V_N with coverage, probably due to a change in orientation of the phenol molecules as coverage increases. A model leading to a dependence of V_N on Γ of approximately the form suggested by comparison of Eqs. (40) and (41) is one in which adsorbed molecules are distributed at random on fixed sites, and each molecule has one orientation if it has zero or one neighbor, a different orientation if it has two or more neighbors. This could be considered a "quasi-lattice" representation for a monolayer without fixed adsorption sites, which is physically more likely in the cases here studied. The adsorption isotherms for phenol shown in Fig. 10 show some evidence of reaching limiting surface excesses at high concentrations, but these limits are certainly not well defined over the range of concentrations studied, and vary markedly from polarization to polarization. This may again reflect a change in orientation with increasing coverage.

It is of course possible to obtain adsorption isotherms from capacitance data by doubly integrating capacitance-polarization curves to obtain electrocapillary curves, and differentiating the function $\gamma(a, V)$ thus obtained after $RT \ln a$. As mentioned in the results section, electrocapillary curves obtained by double integration of our capacitance-polarization curves agreed within experimental error with those obtained directly, provided static capacitance (obtained by extrapolating observed capacitance data to zero frequency) were used. This result was also noted for the adsorbate *n*-amyl alcohol by Breiter and Delahay.⁸ Two constants of integration result from double integration of the capacitance curves. It is attractive to base evaluation of surface excess on Eq. (12), and to

fix these two constants by setting $\pi = 0$, $Q = Q_w$ at some potential well beyond one of the desorption peaks (i.e. at a polarization such that desorption can be supposed complete with negligible error). This procedure guarantees that isotherms calculated between desorption peaks (the only polarization region where appreciable adsorption occurs) have been based on two integrations over a desorption peak, and the area under this peak is known to be highly frequency dependent in many cases. Unless zero-frequency capacitance values are used in these integrations isotherms derived from them not only have no special "thermodynamic" justification, but are also very likely to be seriously in error. A recently published treatment of the adsorption of thiourea at the mercury-electrolyte interface by Schapink et al.¹⁹ and further treatment of the data of Schapink and coworkers by Parsons²⁰ and Devanathan²¹ are open to criticism in this respect. Two criteria can be suggested for testing whether or not capacitance data obtained at other than zero frequency can be safely substituted for zero frequency capacitances in thermodynamic treatments. In the first place, if desorption peaks on both sides of the electrocapillary maximum have been documented, the integral

$$I = \int_{-\infty}^{\infty} (C_w - C) dV \quad (42)$$

(the infinite limits can of course not be realized in practice, but the integral should cover the range of polarizations over which C_w and C differ appreciably) should be zero. If $I \neq 0$, some error must surely be introduced into quantities derived from treating such capacitances as thermodynamic. Let V' , V'' be the points of intersection of the curves $C(V)$, $C_w(V)$, and let $I' = \int_{V'}^{V''} (C_w - C) dV$ (i.e. I' is the area between C_w and C

between desorption peaks); the error referred to is probably of the order I/I' . In the second place, diffusion places a lower bound on the time required for re-equilibration of adsorption following polarization change. The fractional error in capacitance $\Delta C/C$ due to diffusional time lag in non-zero frequency capacitance measurements can be shown from the theory of Frumkin and Melik-Gaikazyan⁹ to be $(\frac{\partial \Gamma}{\partial C})_V \sqrt{\frac{2\pi\nu}{D}}$ to first order for low frequencies, in which D is the diffusion coefficient, ν the frequency (cycles/sec.). Where $c_{1/2}$ (moles/liter) is the concentration required for adsorption of half a monolayer at the desorption peak potential and Γ_m (moles/cm²) the full monolayer surface excess, we may suppose $(\frac{\partial \Gamma}{\partial C})_V \sim 1/4 \times 10^3 \Gamma_m / c_{1/2}$. Taking $\Gamma_m \sim 5 \times 10^{-10}$ moles/cm², $D \sim 10^{-5}$ cm²/mole we find $(\Delta C/C) \sim 1 \times 10^{-4} \nu^{1/2} / c_{1/2}$. For $\nu = 1000$ cps, $(\Delta C/C)$ would hence exceed 10% if $c_{1/2} < 0.03M$ if only diffusion limited re-equilibration, and the error would be more serious if other rate processes were limiting.

We turn finally to the method of inference of adsorption parameters used by Hansen, Minturn, and Hickson⁵ and its justification in terms of the present work. The parameters B_0 and α of Eq. (1) and C' of Eq. (4) were obtained from the dependence of capacitance on concentration at the electrocapillary maximum potential of the base solution assuming (a) linear dependence of capacitance on coverage at the electrocapillary maximum, (b) possibility of adequately representing adsorption by the Frumkin Eq. (1). Assumption (a) has been shown to be well justified for the adsorbates *n*-amyl alcohol and phenol in the present work. Validity of assumption (b) can hence be tested in these cases (and presumably more generally) from capacitance measurements alone; with an additional

adjustable parameter the Frumkin isotherm is more versatile than the Langmuir isotherm, but as previously mentioned it is inadequate for representation of adsorption of phenol at the mercury-base solution interface. The parameter V_N of Eq. (3) was then established to best represent the capacitance data near the polarization of maximum adsorption for given solute activity. From Eq. (5) we obtain

$$\left(\frac{\partial \Gamma}{\partial V}\right)_a = \frac{1}{RT} \left(\frac{\partial Q}{\partial \ln a}\right)_v = \frac{1}{RT} \left(\frac{\partial Q}{\partial \Gamma}\right)_v \left(\frac{\partial \Gamma}{\partial \ln a}\right)_v \quad (43)$$

i. e. $\left(\frac{\partial \Gamma}{\partial V}\right)_a = 0$ when $\left(\frac{\partial Q}{\partial \Gamma}\right)_v = 0$. If Q is linear in Γ the potential at which $\left(\frac{\partial \Gamma}{\partial V}\right)_a = 0$ should be independent of Γ (and so of a), and if Frumkin's assumption as indicated by Eq. (38) were valid the potential of maximum adsorption should be $V_{\max} = -\frac{C' V_N}{C - C'}$ (independent of a). In our earlier work it was noted that such constancy of $V_{\max}$ was not always observed; in the present work Q was found to be linear in Γ for *n*-amyl alcohol but not strictly so for phenol. Finally, the parameter S was established by (essentially) fitting the curvature of plots of θ_{app} against polarization in the neighborhood of the plot maxima. From Eq. (43) we have

$$\frac{\partial^2 \Gamma}{\partial V^2} = \frac{1}{RT} \frac{\partial^2 Q}{\partial v \partial \ln a} = \frac{1}{RT} \left(\frac{\partial C}{\partial \ln a}\right)_v \quad (44)$$

and so

$$\frac{\partial^2 \theta}{\partial V^2} = \frac{S}{RT} \left(\frac{\partial C}{\partial \ln a}\right)_v \quad (45)$$

Equation (45) implies a relation between curvature of a plot of θ_{app} against V and molar area at full coverage, but does not furnish a basis for calculation of molar area from capacitance data alone. This is because $\frac{\partial^2 \theta_{\text{app}}}{\partial V^2}$ differs strongly from $\frac{\partial^2 \theta}{\partial V^2}$ even near the electrocapillary

maximum where to good approximation $\theta = \theta_{app}$. It therefore appears impractical to avoid a model in calculation of molar area if double integration of capacitance curves is to be avoided. Choice of molar area to provide representation of curvature of plots of θ_{app} against V near their maxima must be considered to give only an approximation to this parameter if dependence of Q on Γ is not known to be linear, and results obtained with phenol in the present work show that such linearity cannot be safely assumed.

References

- (1) Based in part on a dissertation submitted by Dennis J. Kelsh to the Graduate College, Iowa State University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1962.
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- (5) R. S. Hansen, R. E. Minturn, and D. A. Hickson, *J. Phys. Chem.*, 60, 1185 (1956); 61, 953 (1957).
- (6) A. Frumkin, *Z. Physik*, 35, 792 (1926).
- (7) R. Parsons, *Trans. Faraday Soc.*, 55, 999 (1959).
- (8) M. Breiter and P. Delahay, *J. Am. Chem. Soc.*, 81, 2938 (1959).
- (9) A. Frumkin and V. I. Melik-Gaikazyan, *Doklady Akad. Nauk, U. S. S. R.*, 77, 855 (1951).
- (10) V. I. Melik-Gaikazyan, *Zhur. Fiz. Khim.*, 26, 560 (1952).
- (11) S. R. Craxford, "Dissertation," Oxford, 1936.
- (12) L. A. Hansen and J. W. Williams, *J. Phys. Chem.*, 39, 439 (1935).
- (13) F. O. Koenig, *Z. Physik. Chem., A*, 54, 454 (1931).
- (14) C. A. Smolders, *Rec. trav. chim.*, 80, 635 (1961).
- (15) J. O'M. Bockris, W. Mehl, B. E. Conway, and L. Young, *J. Chem. Phys.*, 25, 776 (1956).
- (16) J. O'M. Bockris and B. E. Conway, *Ibid.*, 28, 707 (1958).
- (17) E. Blomgren, J. O'M. Bockris, and C. Jesch, *J. Phys. Chem.*, 65, 2000 (1961).

- (18) This point was called to the attention of one of us (R. S. H.) by J. Th. G. Overbeek in a discussion in September 1959.
- (19) F. W. Schapink, M. Oudeman, K. W. Leu, and J. N. Helle, *Trans. Faraday Soc.*, 56, 415 (1960).
- (20) R. Parsons, *Proc. Roy. Soc.*, 261A, 79 (1961).
- (21) M. A. V. Devanathan, *Ibid.*, 264A, 133 (1961).

Figure Captions

- Figure 1. Capillary electrometer.
- Figure 2. Impedance bridge.
- Figure 3. Impedance bridge cell.
- Figure 4. Electrocapillary curves: interface mercury-0.1N HClO_4 + indicated n-amyl alcohol concentration and interface mercury-0.05M Na_2SO_4 (standardization).
- Figure 5. Electrocapillary curves: interface mercury-0.1N HClO_4 + indicated phenol concentration.
- Figure 6. Frequency dependence of differential capacitance at the interface mercury-0.1N HClO_4 + 0.031M n-amyl alcohol.
- Figure 7. Dependence of zero frequency differential capacitance on polarization, interface mercury-0.1N HClO_4 + indicated phenol concentration. Electrocapillary maximum potential for each concentration is indicated.
- Figure 8. Dependence of interfacial charge density of polarization, interface mercury-0.1N HClO_4 + indicated phenol concentration.
- Figure 9. Isotherms for the adsorption of n-amyl alcohol at the mercury-0.1N HClO_4 interface at various polarizations. (C_0 is saturation concentration of n-amyl alcohol in 0.1N HClO_4 , taken as 0.222M.)
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- Figure 11. Dependence of $\frac{S\psi}{RT}$ (see Eqs. 14-17 of text) on polarization and spreading pressure, interface mercury-0.1N HClO_4 + n-amyl alcohol.

Figure 12. Dependence of $\frac{S\psi}{RT}$ (see Eqs. 14-17 of text) on polarization and surface excess, interface mercury-0.1N HClO_4 + phenol.

END