[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

Adsorption of Neutral Substances from Electrocapillary Curves and Double Layer Differential Capacities

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Three methods of study are compared for the adsorption of neutral substances on electrodes: (I) determination of the surface excess Γ from electrocapillary curves for different concentrations of the adsorbed substance; (II) determination of the fractional surface coverage θ from the charge on the electrode; and (III) determination of θ from differential capacities. Results are compared for adsorption of *n*-amyl alcohol on mercury in a 1 *M* sodium perchlorate and 0.001 *M* perchloric acid solution. Interfacial tensions are measured by the drop time method, and differential capacities are measured with a dropping mercury electrode. Special precautions are discussed. Coverages from methods I and II are in fairly good agreement, and it is concluded that the model on which method II is based is essentially correct. Methods II and III complement each other and give compatible sets of coverage. Extrapolation of differential capacities to zero frequency is essential in the computation of the charge but not in the direct evaluation of θ from differential capacities in the range of potentials well within the desorption peaks.

Adsorption of a neutral substance on electrodes can be characterized in three different ways: (a) by the surface excess Γ at a given potential E and a given activity a in solution for the absorbed substance; (b) by the ratio $\theta = \Gamma/\Gamma_{\max}$ for given potential and activity, $\Gamma_{\max}$ being the maximum of all values over the whole range of potentials for $a \rightarrow \infty$; and (c) by the ratio $\Gamma/\Gamma'_{\max}$ at given potential and activity where $\Gamma'_{\max}$ is the maximum value of Γ *at potential E* for $a \rightarrow \infty$. The ratio θ is called the "fractional surface coverage"— a convenient but somewhat misleading expression because of possible solvent adsorption even for $\theta = 1$. The ratio $\Gamma/\Gamma'_{\max}$ does not particularly characterize the coverage because this ratio varies between 0 and 1 for any value of the coverage $\theta (0 \leqslant \theta < 1)$. The ratio $\Gamma/\Gamma'_{\max}$ will not be discussed any further here.

Correlation at constant temperature between Γ, $\Gamma_{\max}$, θ, E and a is generally presented in plots of $\Gamma = f(a)$ or $\theta = f(a)$ at constant E (isotherm) and plots of $\Gamma = f(E)$ or $\theta = f(E)$ at constant a. One can assume, as a first approximation, that the activity coefficient of neutral substances in electrolyte solutions is equal to unity.

The surface excess Γ is a thermodynamic quantity which can be determined from electrocapillary curves. Thus, $\Gamma = -\partial\gamma/\partial\mu$, where γ is the electrode–solution interfacial tension and μ is the chemical potential in solution for the adsorbed substance. Since $\mu = \mu_0 + RT \ln a$, μ_0 being the standard chemical potential, Γ is directly obtained from a plot of γ against $\ln a$. This approach is classical.[2] Determination of Γ and $\Gamma_{\max}$ suffices for the calculation of θ.

Another approach, which is not a thermodynamic one, was developed by Frumkin[3] from a model of the Helmholtz double layer composed of two capacities in parallel for the covered and uncovered area of the electrode, respectively. Thus

$$q = \theta q_{\theta=1} + (1-\theta) q_{\theta=0} \qquad (1)$$

where the q's are the charges on the electrode for the coverages 0, θ and 1, respectively. By differentiation of eq. 1 there follows

$$c = \theta c_{\theta=1} + (1-\theta) c_{\theta=0} + (q_{\theta=1} - q_{\theta=0}) \frac{\partial\theta}{\partial E} \qquad (2)$$

where the c's are the differential capacities for the coverages 0, θ and 1, respectively. The capacity c varies linearly with θ when the term in $\partial\theta/\partial E$ is quite negligible.

The purposes of this investigation are as follows. (a) Determination of the validity of eq. 1 by comparison of values of θ directly obtained from surface excesses or from the charge q. (b) Evaluation of the error resulting from deletion of the term in $\partial\theta/\partial E$ in eq. 2. In addition, the computation of q by integration of c–E curves, which is now classical in double layer studies,[4] will be extended to adsorption of neutral substances. See also the fundamental papers by Frumkin and Gaikazyan[5] and related papers.[6]

This study was made for the adsorption of *n*-amyl alcohol on mercury in 1 *M* sodium perchlorate (also 0.001 *M* in perchloric acid). This alcohol was selected because it does not form a multilayer on mercury electrodes as was shown by Melik-Gaikazyan.[5c] Interfacial tensions were measured by the drop time method and differential capacities were determined with the same dropping mercury electrode (drop times of 50–70 sec.; see Experimental). The Lippmann electrometer, which gives more accurate results than the drop time method, was not used to achieve conditions as nearly identical in the measurement of surface tension and differential capacity. Differential capacities could, of course, have been obtained by double differentiation of the electrocapillary curves, but this procedure was not applied because of its inherent uncertainties.

Experimental

An H-cell with a fritted disk separator of fine porosity was utilized. Both compartments of the cell were filled with the electrolyte with *n*-amyl alcohol. One compartment, without electrode, was connected with a bridge of large cross section to a hydrogen electrode. The bridge

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(1) Research Associate, 1957–1958; on leave from the Technical University, Munich.

(2) (a) N. K. Adams, "The Physics and Chemistry of Surfaces," 3rd Ed., Oxford University Press, New York, N. Y., 1941, p. 347; (b) R. Parsons, in "Modern Aspects of Electrochemistry," J. O'M. Bockris, Editor, Butterworths, London, 1954, pp. 103–179.

(3) (a) A. N. Frumkin, *Z. Physik*, **35**, 792 (1926); (b) A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa and B. N. Kabanov, "Kinetics of Electrode Processes," Moscow University Press, Moscow, 1952, p. 41.

(4) D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947); *Ann. Rev. Phys. Chem.*, **6**, 337 (1955); see also ref. 2b.

(5) (a) A. N. Frumkin and V. I. Melik-Gaikazyan, *Doklady Akad. Nauk SSSR*, **77**, 855 (1951); (b) V. I. Melik-Gaikazyan, *Zhur. fiz. Khim.*, **26**, 560 (1952); (c) **26**, 1184 (1952). Translations kindly made available by Prof. D. C. Grahame, Amherst College.

(6) (a) T. Berzins and P. Delahay, *J. Phys. Chem.*, **59**, 906 (1955); (b) W. Lorenz and F. Möckel, *Z. Elektrochem.*, **60**, 507 (1956).

and the vessel with the hydrogen electrode were filled with the electrolyte without *n*-amyl alcohol to avoid poisoning of the hydrogen electrode. This was the reference electrode, and potentials given below are all referred to it. The behavior of the hydrogen electrode was entirely reliable at the very low current densities involved in this study. Polarization was avoided (a) by the use of an electrode of sufficient area (about 5 cm.^{2}), and (b) by selection of an electrolyte which was 0.001 M in perchloric acid to avoid variations of pH.

Hydrogen was bubbled continuously over the hydrogen electrode and for 20 min. through the two compartments of the H-cell to remove oxygen. The hydrogen gas used for oxygen removal was bubbled through towers containing the electrolyte at the same concentration of *n*-amyl alcohol as in the cell. Evaporation of *n*-amyl alcohol was thus avoided.[5b] The electrolyte solution was prepared from analytical grade reagents and from twice distilled water. The *n*-amyl alcohol was redistilled before use.

Interfacial tensions were deduced from the drop time of a dropping mercury (triply distilled) electrode. A conventional polarographic capillary (Sargent) was drawn out in its middle section to increase the drop time to 50–70 sec. for a 100 cm. head of mercury. Such long drop times are necessary for near achievement of adsorption equilibrium. Adsorption kinetics with diffusion control is indeed quite slow at the dropping mercury electrode,[7] and adsorption equilibrium with respect to the bulk concentration is only reached for sufficient concentrations and/or long drop times. Longer drop times than the usual 3–6 sec. were also adopted by Laitinen and Mosier.[8] According to standard practice two corrections were made (a) for the back pressure (Kucera) and (b) for dislodging of the drop not exactly at the capillary tip (Harkins). Equations for corrections are summarized by Corbusier and Gierst.[9] The radius of the capillary tip, which was needed in these corrections, was determined by calibration with a solution of known interfacial tension, *e.g.*, 0.1 M sodium nitrate.

Differential capacities were measured at the end of drop life with the same capillary that was used in the interfacial tension determinations. Measurements were made with the previously described bridge[10] except that the inductance in the polarization circuit was increased to approximately 5000 henries to avoid correction for this inductance at low frequencies. The dropping mercury electrode and a platinum foil cylinder (1 cm. diameter), used as counter electrode, were connected to the bridge.[11] The capillary tip was ground in the shape of an elongated cone with a base at the tip of approximately 1.5 mm. diameter to avoid frequency dispersion due to shielding; see Grahame.[11] Errors on capacity did not exceed 1% except at 50 c.p.s. at which errors were as large as 2–3%. The potential of the dropping mercury electrode was adjusted against the hydrogen electrode.

All data were obtained at 30 ± 0.2°.

Description and Discussion of Results

Electrocapillary curves and differential capacity–potential curves are plotted in Fig. 1 and 2. Except for the pure electrolyte, capacities are the values exptrapolated with the square root of frequencies to zero frequency from data at 50, 100 and 200 c.p.s. No extrapolation was necessary for the pure electrolyte, and capacities were only measured at 1000 c.p.s. This extrapolation holds for adsorption with diffusion control.[5,6]

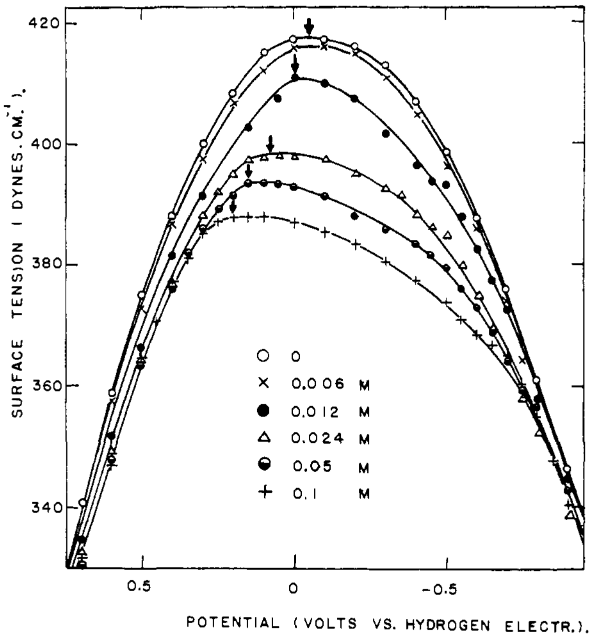

Fig. 1.—Electrocapillary curves for *n*-amyl alcohol at different molar concentrations in 1 M sodium perchlorate and 0.001 M perchloric acid. Potentials are referred to the hydrogen electrode in the electrolyte without alcohol. Arrows indicate points of zero charge. The curve for 0.003 M alcohol (not shown) coincides within experimental errors with the curve for the pure electrolyte.

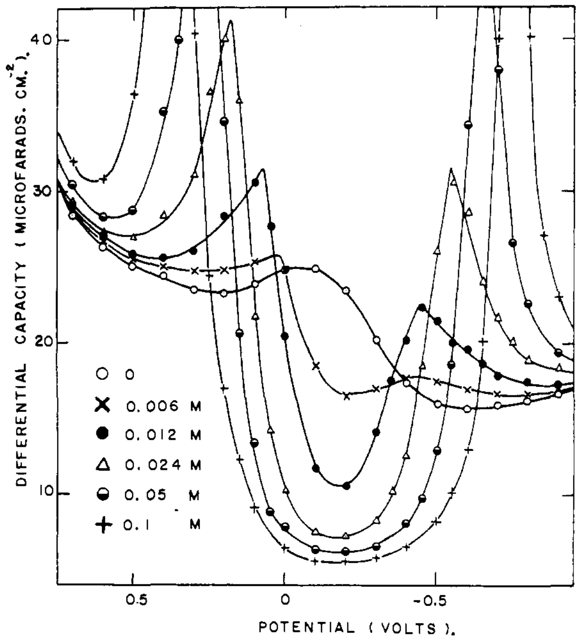

Fig. 2.—Differential capacity *versus* potential curves for the solutions of Fig. 1. Capacities extrapolated to zero frequency except for the pure electrolyte. Same reference electrode as in Fig. 1. Capacities in microfarads.cm.$^{-2}$ at the desorption peaks and not shown are: for 0.05 M alcohol 56 at E = 0.27 volt and 46 at E = −0.66; for 0.1 M alcohol 63 at E = 0.38 and 60 at E = −0.75.

Surface Excess.—Interfacial tension values are plotted against the logarithm of alcohol concentration in Fig. 3 from data taken from Fig. 1. The surface excess Γ is proportional to $-\partial\gamma/\partial \ln C$ (see Introduction) if the activity coefficient of *n*-amyl alcohol can be assumed constant over the concentration range being considered. This assumption will be made here. Diagrams of the

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(7) P. Delahay and C. T. Fike, THIS JOURNAL, **80**, 2628 (1958); see ref. therein.

(8) H. A. Laitinen and B. Mosier, *ibid.*, **80**, 2363 (1958).

(9) P. Corbusier and L. Gierst, *Anal. Chim. Acta*, **15**, 254 (1956).

(10) P. Delahay and I. Trachtenberg, THIS JOURNAL, **79**, 2355 (1957).

(11) D. C. Grahame, *ibid.*, **68**, 301 (1946); **71**, 2975 (1949).

type in Fig. 3 are classical. For recent results see ref. 12 and 13.

From the curves of Fig. 3 and similar curves for other potentials one can now compute the ratio of Γ at a given potential to the maximum surface excess $\Gamma_{\max}$ over the who e range of potentials for the 0.1 M solution (Fig. 4). Since Γ is virtually constant for $C > 0.024$ M for the precision achieved here, one can assume that the maximum value of Γ deduced from Fig. 3 for $C = 0.1$ M is $\Gamma_{\max}$, *e.g.*, that the ordinate of Fig. 4 is the coverage $\theta = \Gamma/\Gamma_{\max}$.

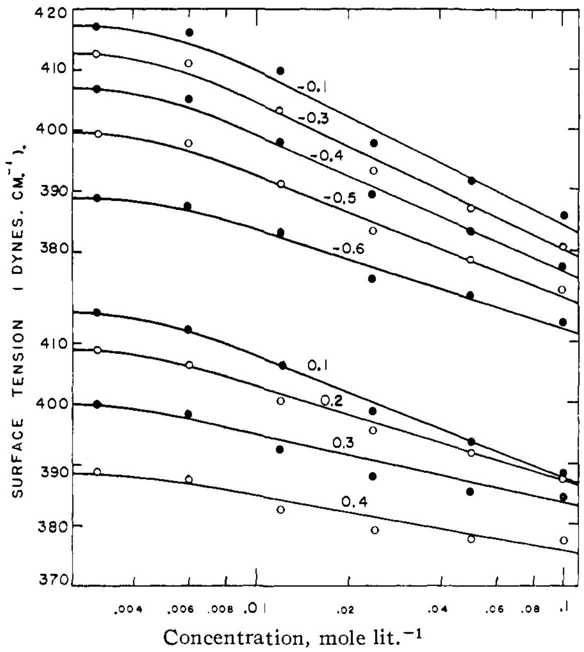

Fig. 3.—Variations of interfacial tension with the concentration (logarithmic scale of abscissa) of *n*-amyl alcohol for different potentials and for the same electrolyte as in Fig. 1. Same reference electrode as for Fig. 1.

Theories for the interpretation of Fig. 4 were developed by Frumkin[3a,14] and Butler.[15] The treatment of Butler was improved by Lorenz and Möckel[6b] who considered surface saturation. These theories will not be examined in detail here but one point will be made about the Butler and Lorenz-Möckel treatments. According to these authors the maximum value of Γ for a given solution activity should be observed at the apex of the electrocapillary curve. Comparison of Figs. 1 and 4 shows that this is not the case. Examination of the data of Melik-Gaikazyan[5b] also confirms this discrepancy between theory and experiment.

Coverage from the Charge on the Electrode.—The results of Fig. 4 will now be compared with the coverage deduced from eq. 1. The charge q needed for this comparison was computed by graphical integration (interval of 0.05 volt) of the curves of Fig. 2. The potentials of zero charge needed in this integration were determined from electrocapillary curves. Tangents to these curves were constructed at different potentials in the vicinity of the point of zero charge; the slope $q = -\partial\gamma/\partial E$ to these tangents was plotted against potential, and the intersection at $q = 0$ was determined. This method is more accurate than direct determination of the apex of the electrocapillary curves. It should be noted that differentiation of electrocapillary curves with respect to E yields q just as integration of the differential capacity–potential curves. The latter method was chosen here for self consistency with coverage data directly obtained from differential capacities (see below).

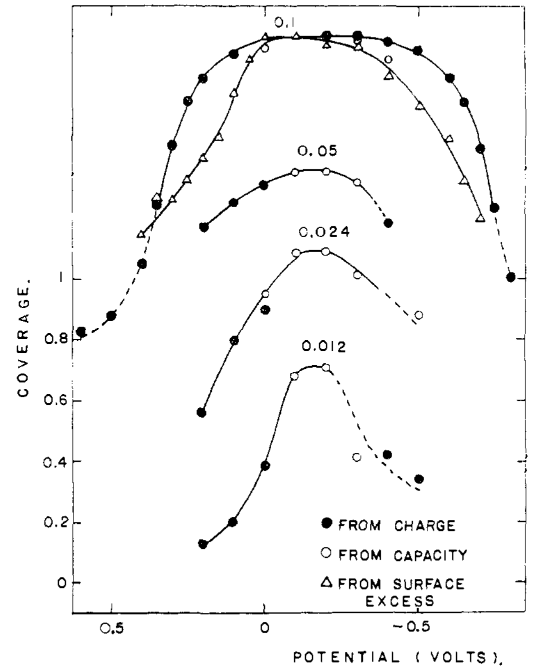

Fig. 4.—Variations of coverage θ with potential for the solutions of Fig. 1. Same reference electrode as in Fig. 1. Curves for 0.024, 0.05 and 0.1 M *n*-amyl alcohol are shifted upward by 0.2, 0.4 and 0.8 unit of θ, respectively.

It is essential in the computation of q by integration of differential capacities to utilize capacities extrapolated at zero frequency as was pointed out by Frumkin and Melik-Gaikazian.[5a] This is important because the height of desorption peaks is strongly frequency dependent.[5,6] Recent work by Hansen[14] in which capacities were obtained at 1000 c.p.s. and not extrapolated to zero frequency should be re-examined in this respect.[16] (However, this remark does not necessarily imply invalidation of his conclusions.)

Charge–potential curves are plotted in Fig. 5. The q–E curve for the electrolyte alone has the same general shape as the curves reported by Grahame.[4] The curves for solutions with *n*-amyl alcohol

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(12) L. Gierst, thèse d'agrégation, University of Brussels, 1958.

(13) E. Blomgren and J. O'M. Bockris, paper presented at the symposium on charge transfer, Toronto, 1958.

(14) See also R. S. Hansen, R. E. Minturn and D. A. Hickson, *J. Phys. Chem.*, **60**, 1185 (1956); **61**, 953 (1957).

(15) J. A. V. Butler, *Proc. Roy. Soc.* (*London*), **A122**, 399 (1929).

(16) Likewise, differential capacities obtained directly from the oscillographic recording of the capacity current for a fast sweep of potential cannot easily be interpreted because of the diffusion component. This remark also applies to the charge–potential curves obtained by electrical integration of the capacity current–potential curves. See J. W. Loveland and P. J. Elving, *J. Phys. Chem.*, **56**, 250, 255, 935, 941, 945 (1952).

tend to coincide with the curve without alcohol at sufficiently positive potentials. This indicates that desorption is nearly complete for $E > +0.7$ volt and also that calculations of q are sufficiently accurate. The coincidence of q–E curves is not as satisfactory on the negative side and, in particular, two curves intersect the q–E curve obtained in the absence of n-amyl alcohol. This discrepancy possibly results from computation uncertainties and experimental errors.

Application of eq. 1 requires the knowledge of the charge $q_{\theta=1}$ that would be determined at any potential if there were no desorption. This charge is not known but it can be evaluated according to a suggestion of Frumkin[3] on the assumption[5d] that $q_{\theta=1}$ varies linearly with potential. Variations of $q_{\theta=1}$ with E are thus obtained by extension of the nearly linear segment ($-0.4 < E < 0$ volt) of the q–E curve (Fig. 5) for $C = 0.1$ M. This assumption is supported by the following experimental evidence. The q–E curves for the upper concentrations of alcohol have a nearly linear common segment whose length increases with the alcohol concentration (see Fig. 5 and Melik-Gaikazyan).[5b]

Values of θ calculated from eq. 1 are plotted in Fig. 4 and compared with the θ's obtained from surface excess. The two sets of θ's are comparable, but the values deduced from eq. 1 are generally larger than the θ's obtained from the surface excess. This discrepancy may entirely result from experimental and computation errors, or it may be due to approximations resulting (a) from the nature of eq. 1 and (b) from the assumption of a linear dependence of $q_{\theta=1}$ on potential. At any rate, the approximations are quite satisfactory in view of the fair agreement between the two curves of Fig. 4 for the 0.1 M n-amyl alcohol.

Coverage from Differential Capacities.—Application of eq. 2 requires the value of $c_{\theta=1}$. This capacity can be taken as the minimum capacity observed with a sufficiently high concentration of adsorbed substance, *e.g.*, for a concentration at which the capacity curve is hardly changed by variation of concentration. In our case $c_{\theta=1} = 5.6$ microfarads. cm.$^{-2}$. (Note that the potential range for minimum capacity for the 0.1 M alcohol solution in Fig. 2 and for $\theta \approx 1$ in Fig. 4 coincide.) It is further assumed that $c_{\theta=1}$ is independent of potential. This is a direct implication of the linearity between $q_{\theta=1}$ and potential assumed above.

Values of θ computed from eq. 2 without the term in $\partial\theta/\partial E$ are plotted in Fig. 4 *for potentials well within the desorption peaks.* Values of θ's computed from eq. 1 are also plotted in this diagram for potentials for which the necessary values of q can be read on Fig. 5 with reasonable accuracy. The two sets of θ's are compatible and complement each other.

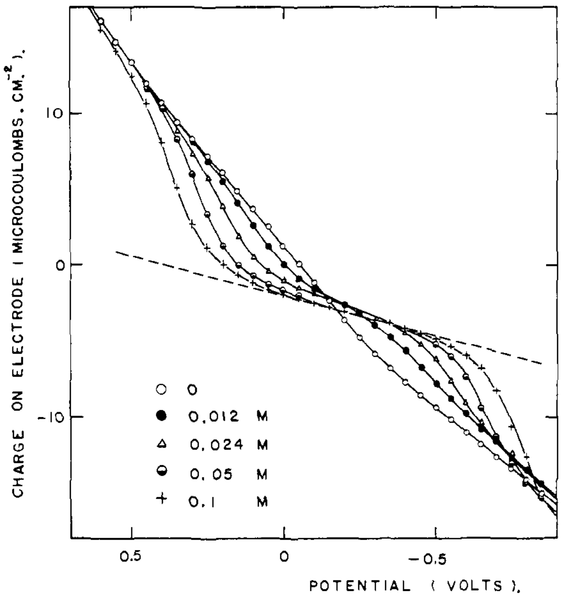

Fig. 5.—Variations of charge on the electrode with potential for the solutions of Fig. 1. Same reference electrode as in Fig. 1. The curves for 0.003 and 0.006 M n-amyl alcohol are not shown to simplify the diagram.

The use of capacities not extrapolated to zero frequency was also examined for the computation of θ. Values of θ computed at 1000 c.p.s. for potentials well within the desorption peaks agree within experimental errors with the values calculated from capacities extrapolated to zero frequency. This is not surprising since the capacity in the range of maximum adsorption is hardly frequency dependent. Extrapolation is thus not necessary in this case.[17]

Conclusions

The determination of the surface excess Γ has the great advantage of being based on thermodynamics, *e.g.*, of not depending on a model. However, very precise data on surface tension (perhaps, errors of the order of 0.1%) are needed to allow the calculation of θ with reasonable accuracy in the lower part of the concentration (activity) range. This disadvantage results from the determination of Γ and $\Gamma_{\max}$ from the slope of γ *versus* log a curves (Fig. 3). However, the determination of $\Gamma_{\max}$ generally does not require *very* precise measurement of γ.

The methods based on eq. 1 and 2 (without the term in $\partial\theta/\partial E$) are not thermodynamic in character. Their validity depends on the model used for the double layer and on the assumption of linear dependence of $q_{\theta=1}$ with potential. This assumption and the model from which eq. 1 is derived seem quite satisfactory in view of the agreement between coverages deduced from the surface excess and from the charge. The two methods for the evaluation of θ from the charge and differential capacities complement each other, *e.g.*, one method can be applied in the range of potentials in which the other becomes very uncertain. Extrapolation of differential capacities to zero frequency is essential in the computation of the charge but not in the evaluation of θ from differential capacities well within the desorption peaks.

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(17) For applications see refs. 8 and 10; also P. Delahay and I. Trachtenberg, THIS JOURNAL, **80**, 2094 (1958).