diffusion of the EDTA liberated in the reduction of the bismuth-EDTA. The freed EDTA combines with the lead to form non-reducible lead-EDTA, thus decreasing its diffusion current. Direct proportionality of the diffusion current on the lead ion concentration may be achieved by obliterating the reduction wave of bismuth-EDTA by adding Triton X-100. This technique, known as *electrochemical masking*, is therefore useful in such cases. In amperometric titrations of two-component mixtures electrochemical masking also allows enhanced measurement sensitivity.[1]

Optimum Concentration of Maxima Suppressors

It should be realized that the concentration of surface active material which is recommended in textbooks for maxima suppression, *e.g.* 0.002% Triton X-100, is sufficient to produce a small distortion of the current–time curves for many depolarizers, especially when capillaries whose drop times exceed 4 seconds are employed. The optimum concentration will depend upon several factors such as the kinetics of the electrode process, the drop time of the capillary as well as the "activity" and diffusion coefficient of the surface active agent.

Acknowledgment.—We appreciate the help of Mr. H. L. Medford in the exploratory experiments. We thank the Rohm and Haas Company, Philadelphia, Pennsylvania, for samples of purified octylphenoxyethanols, and Doctors E. L. Stanley and Isador Rosenthal for their interest in this work. This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No AF 18(600)-1160. One of the authors (C.N.R.) wishes to thank the du Pont Company for a summer research grant (1956).

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

Adsorption Kinetics and Electrode Processes. II

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The effects of adsorption of non-reducible (non-oxidizable) foreign substances on kinetic parameters for electrode reactions and limiting currents are discussed. The decrease in effective area and the variations of kinetic parameters (the rate constant k_s at the standard potential and the transfer coefficient) resulting from adsorption can be separated when electrode coverages are determined. Coverages are obtained from measurements of the double layer differential capacity in the absence of the reducible (oxidizable) species. Application is made to the system Ti(IV)–Ti(III) in tartaric medium in presence of *n*-amyl alcohol, cyclohexanol or thymol. The rate constant k_s is essentially independent of coverage ($\theta < 0.4$) for the first two substances and decreases markedly for thymol. The effect of adsorption on limiting currents is studied by polarography, electrode coverages during drop life being determined from measurements of the double layer differential capacity. Variations of the limiting current with coverage at the end of drop life are studied for several systems and a tentative explanation is advanced. The interpretation of complete waves which are complicated by adsorption of a foreign substance is discussed, and application is made to the cadmium wave in presence of *n*-hexyl alcohol. Experimental methods are discussed in some detail, and an extrapolation method for minimization of contamination effects is discussed. It is recommended that the dropping mercury (or amalgam) electrode be used in kinetic studies rather than the stationary hanging mercury (or amalgam) drop. Values of k_s obtained with both electrodes are given for the Cd^{++}–Cd(Hg) system at 0°.

Introduction

Three groups of problems arise in the study of the effects of adsorption on electrode processes: (a) influence of adsorption in the absence of electrode reaction, *i.e.*, adsorption on ideally polarized electrodes; (b) influence of the adsorption of foreign substances (not reduced or oxidized) on the rate of electrode reactions; and (c) influence of adsorption of the reducible and/or reduced species on the characteristics of electrode reactions involving these substances. We shall be concerned primarily with the first two problems in this investigation.

The first group of problems includes two broad studies, namely, the investigation of adsorption equilibria and the kinetics of adsorption. Adsorption equilibria at electrodes were studied some thirty years ago by Frumkin[3] and Butler[4] and recently by Hansen and co-workers.[5] It is observed that the surface concentration exhibits a maximum in the neighborhood of the electrocapillary maximum and, in general, approaches zero at sufficiently anodic (displacement by anions) and cathodic (displacement by the solvent such as water) potentials. Adsorption kinetics with mass transfer control were studied in some detail in this Laboratory.[6] It was shown that adsorption equilibrium is reached slowly (after 15–30 min.) in unstirred dilute solutions for concentrations in the segment of the isotherm that can be linearized as a first approximation.

The second group of problems, namely, the effect of foreign substances on the rate of electrode processes, involves two major studies: the effect of adsorption on kinetic parameters for the electrode reaction and the influence of adsorption on electrode processes controlled by mass transfer (effect on limiting currents or transition times). Coverage of the electrode by a foreign substance increases the effective current density and, consequently, the overvoltage. Furthermore, the kinetic parameters for the electrode reaction also can be affected, and this effect also causes a variation of overvoltage.

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[1] Predoctoral fellow, 1955–1957; American Oil Company, Research Department, Texas City, Texas.

[2] A preliminary report on this work was presented at the National Meeting of the Electrochemical Society, San Francisco, April, 1956.

[3] A. N. Frumkin, *Z. Physik*, **35**, 792 (1926).

[4] J. A. V. Butler, *Proc. Roy. Soc.* (*London*), **122A**, 399 (1929).

[5] R. S. Hansen, R. E. Minturn and D. A. Hickson, *J. Phys. Chem.*, **60**, 1185 (1956).

[6] P. Delahay and I. Trachtenberg, THIS JOURNAL, **79**, 2355 (1957).

These two effects have not been separated, as far as we know, in the rather abundant literature pertaining to their study.[7,8]

The influence of adsorption of foreign substances on limiting currents and, to a lesser extent, on transition times has been the object of numerous papers in the polarographic literature.[7,8] Variations of limiting currents with the concentration of the adsorbed substance have generally been investigated but, to our knowledge, no attempt has been made to correlate the effect of adsorption with electrode coverage. This is not a simple matter, as we have shown,[6] since the electrode coverage varies during drop life.

Some of the questions raised above are answered, at least partially, in this investigation by the introduction of a novel approach, namely, that the kinetics of adsorption are taken into account and that electrode coverages are measured. A study is made of the variations of kinetic parameters and polarographic limiting currents with electrode coverage, and the influence of the structure of the adsorbed film is investigated. A method for minimization of the effect of electrode contamination also will be described.

Adsorption and Kinetic Parameters for Electrode Processes

We consider electrode reactions for which the reducible species (symbolized by O below) is soluble in solution and the reduced species (R) is soluble either in solution or in mercury (amalgam). These electrode reactions can be characterized by their *exchange current density*[9] provided

$$i_0 = nFk_sC_O^{(1-\alpha)}C_R^{\alpha} \tag{1}$$

that they proceed with a single rate-determining step involving n electrons. The notations in (1) are: F the faraday; k_s the *rate constant at the standard potential* for the couple O + ne = R; α the *transfer coefficient* for the cathodic process; and the C's the bulk concentrations. The parameters α and i_0 or k_s characterize the kinetics of the electrode reaction.

Electrode Coverage and Variations of the Rate Constant k_s.—The effect of electrode coverage by a foreign substance on the rate constant k_s of eq. 1 was studied for the reaction Ti(IV) + e = Ti(III) on mercury in tartaric acid. This electrode reaction was selected because k_s ($\approx 5 \times 10^{-3}$ cm. sec.$^{-1}$), as first measured by Randles and Somerton,[10] is well within the range of application of a.c. electrolysis. Furthermore, the formal potential ($\approx$ −0.42 volt *versus* S.C.E.) is in the neighborhood of the electrocapillary maximum, *i.e.*, in the range of maximum adsorption of polar organic substances.

The effect of three substances was studied: cyclohexanol, n-amyl alcohol and thymol. Electrode coverages (Table I) were determined from measurements of the differential capacity of the double layer in the absence of Ti(IV) and Ti(III) as in our previous study.[6] All measurements were made at the end of drop life just before the drop was dislodged from the capillary (see Experimental). Capillary characteristics: m = 2.70 mg. sec.$^{-1}$ and τ = 3.5 sec. (varied somewhat with concentration of adsorbed substance).

TABLE I

ELECTRODE COVERAGE AGAINST CONCENTRATION FOR ADSORPTION ON MERCURY AT 30° AND −0.41 VOLT (*vs.* S.C.E.) IN A SOLUTION 1 M IN TARTARIC ACID AND 0.1 M IN SODIUM CHLORIDE[a]

Cyclohexanol		n-Amyl alcohol		Thymol	
C, mmole $l.^{-1}$	θ	C, mmole 1.$^{-}$	θ	C, mmole 1.$^{-1}$	θ
0.5	0.10	0.1	0.11	0.04	0.17
1	.13	.2	.12	.08	.21
1.5	.15	.3	.12	.12	.26
1.9	.17	1.3	.29	.15	.30
2.4	.18	2.3	.42	.19	.36
3.3	.21				
4.5	.26				

[a] Capillary characteristics: m = 2.70 mg. sec.$^{-1}$, τ = 3.5 sec. (varied somewhat with adsorbed substance).

Variations of k_s with the coverage θ are shown in Fig. 1. Values of k_s for $\theta > 0$ were calculated for the uncovered area on the assumption that the exchange current density is equal to zero for a completely covered electrode. This approximation is quite satisfactory because it is known from the work of other investigators that i_0 decreases by several orders of magnitude when θ varies from 0 to 1. Actually, the uncertainty in the corrected value of k_s, which results from the error in θ, is larger than that corresponding to the assumption of $i_0 = 0$ for $\theta = 1$.

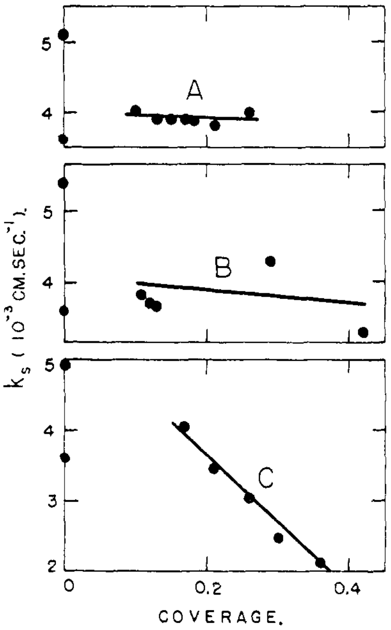

Fig. 1.—Variations of k_s of eq. 1 with electrode coverage for the reaction Ti(IV) + e = Ti(III) in a solution 6×10^{-3} M in Ti(IV), 6×10^{-3} M in Ti(III), 1 M in tartaric acid and 0.1 M in sodium chloride: (A) cyclohexanol; (B) n-amyl alcohol; (C) thymol. See text for discussion of values of k_s at $\theta = 0$.

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[7] See reviews by A. N. Frumkin, *Z. Elektrochem.*, **59**, 807 (1955); *Doklady Akad. Nauk SSSR*, **86**, 373 (1952). Translation of the latter paper was made available by the Naval Research Laboratory, Washington, D. C.

[8] See partial literature coverage in ref. 6; see also P. Delahay, *Ann. Rev. Phys. Chem.*, **8**, 229 (1957).

[9] For this particular form, see T. Berzins and P. Delahay, THIS JOURNAL, **77**, 6448 (1955), and some references therein.

[10] J. E. B. Randles and K. W. Somerton, *Trans. Faraday Soc.*, **48**, 937 (1952).

Data for *n*-amyl alcohol were less reproducible than for cyclohexanol and thymol. Values of k_s at $\theta = 0$ are the constants measured at the end of drop life (lower points) and the values extrapolated to $t = 0$. The former values are too low because no correction was made for partial coverage of the electrode by impurities. The extrapolated values of k_s are too high because of a pronounced decrease of k_s with increasing drop time (see below). Values of k_s for $0 < \theta < 0.1$ were not obtained because of electrode contamination by impurities (possibly traces of oil in nitrogen). Evidence of contamination without addition of an organic substance was provided by the decrease of a few per cent. in the differential capacity of the electrode in the supporting electrolyte when the drop time for a given capillary was varied from 2.5 to 6.6 sec. (the drop size was essentially constant).

If the range $0 < \theta < 0.1$ for which interpretation is uncertain is excluded, it is concluded from Fig. 1 that k_s is essentially independent of electrode coverage for cyclohexanol ($\theta < 0.3$) and possibly *n*-amyl alcohol ($\theta < 0.4$, scattering of points) whereas k_s decreases markedly with increasing coverage for thymol ($\theta < 0.4$). The increase in overvoltage caused by the addition of cyclohexanol or *n*-amyl alcohol primarily results from the decrease of effective area[11] whereas for thymol the decrease in k_s is also very significant. It is thus possible by coupling kinetic data determinations with electrode coverage measurements (by differential capacity measurements or other methods such as surface tension determinations) to separate the effect of electrode coverage from the variations of the parameter k_s. It would be premature to give a detailed model accounting for difference of behavior of cyclohexanol and thymol since further work is needed (*cf.* study of double layer, variations of the potential difference in the diffuse double layer).[7]

A similar study was undertaken to determine the variations of the transfer coefficient α with electrode coverage, but an unexpected difficulty arose: it was observed that k_s, as measured for a constant ratio Ti(IV)–Ti(III), varied somewhat with the total titanium concentration. Data were as follows: $k_s = 7.2 \times 10^{-3}$, 4.9×10^{-3} and 4.1×10^{-3} cm. sec.$^{-1}$ for total concentrations of titanium of 6×10^{-3}, 1.2×10^{-2} and 2.6×10^{-2} mole l.$^{-1}$, respectively, the ratio Ti(IV)–Ti(III) being equal to unity in all cases (values of k_s extrapolated to $t = 0$ during drop life). It was not possible under these conditions to determine α from the variations of the exchange current with the concentration of one reactant, the concentration of the other reactant being kept constant.[12] These variations of i_0 could be due to a change in the relative concentrations of several complexes or to a purely chemical step preceding electron transfer. They also could be caused by preferential adsorption of one of the titanium ions involved in the electrode reaction.[13] These two explanations are not incompatible but no further study of this effect was made. It should be noted that the exchange current density is independent of α at the standard potential (see eq. 1), and consequently the values of k_s reported above are not affected by the uncertainty in α *inasmuch as equation 1 is applicable.*

The adsorption of the reducible and/or reduced species may alter the values of θ in Fig. 1 since coverages were deduced from measurements with the supporting electrolyte alone. It is believed that the resulting error, if any, is not serious because the electrode potential was within 0.1 volt from the electrocapillary maximum, *i.e.*, in a range in which displacement of organic substances by ion adsorption is not very pronounced.

Minimization of the Effect of Electrode Contamination.—Adsorption with diffusion control is slow at low concentrations of adsorbate,[6] and consequently stationary electrodes become progressively contaminated upon exposure to a solution containing traces of adsorbable impurities. Since contamination may cause a serious error in the determination of i_0, k_s and α, it has been suggested[6] that these parameters be measured, whenever feasible, with a dropping mercury (or amalgam) electrode rather than with a stationary electrode. Stationary mercury or amalgam electrodes can be used provided that measurements are made within a few seconds of exposure to the solution (the adsorption rate decreases with the time of exposure), but a dropping electrode is more practical. It may even be useful to measure i_0, k_s and α for different drop times and extrapolate the data to time zero. Extrapolation of kinetic data with the square root of drop time is suggested because the electrode coverage for low concentrations of adsorbate and short times is approximately proportional[14] to $t^{1/2}$. This extrapolation, however, is not rigorous because the measured values of i_0, k_s and α are not necessarily linear functions of electrode coverage. Furthermore, this extrapolation is based on an equation which is rigorous (linearized isotherm) for the plane electrode but is only approximate for the dropping mercury electrode.

The effect of contamination was tested for the discharge of Cd^{++} on cadmium amalgam. The contamination effect is very pronounced for the cadmium electrode because the equilibrium potential (approximately -0.6 *versus* S.C.E.) is near the electrocapillary maximum, *i.e.*, in the range of maximum adsorption of neutral polar organic impurities. Cadmium ion discharge is quite fast and is almost beyond the range of a.c. electrolysis ($k_s < 0.1$ to 1 cm. sec.$^{-1}$ for equipment now available), and consequently measurements were made at 0°. The solution was prepared with bidistilled water and no impurity was added intentionally. Oxygen was removed by tank nitrogen, which probably contained traces of organic impurities (oil that could have been removed by combustion over copper oxide or by adsorption on charcoal at liquid air temperatures).

The rate constant k_s measured with the hanging amalgam electrode decreased markedly upon exposure until the limiting value 0.0038 cm. sec.$^{-1}$ was reached after 2 hr. Measurements also were made with a dropping amalgam electrode, and the *approximate* value $k_s \approx 0.2$ cm. sec.$^{-1}$ was obtained for three different drop times (5.34, 3.54 and 2.32 sec.). The value of k_s was independent of drop time at least for the relatively poor accuracy achieved for such a fast process. Note, however, that k_s obtained with the dropping amalgam electrode is about five times larger than the value measured with a hanging amalgam electrode after a 20 min. exposure[15] ($k_s = 0.037$ cm. sec.$^{-1}$).

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[11] This conclusion is essentially valid provided that the transfer coefficient does not decrease too markedly upon the addition of the organic substance.

[12] A plot of log i_0 against the logarithm of the varying concentration is a straight line whose slope yields α (see eq. 1). See H. Gerischer, *Z. Elektrochem.*, **57**, 604 (1953).

[13] Such adsorption processes in a.c. electrolysis were studied by H. A. Laitinen and J. E. B. Randles, *Trans. Faraday Soc.*, **51**, 54 (1955).

[14] The electrode coverage θ for the linearized isotherm ($\Gamma = KC$; Γ surface concentration, C volume concentration at the electrode) and for control by linear diffusion is $\theta = 1 - \exp(Dt/K^2)\operatorname{erfc}(D^{1/2}t^{1/2}/K)$, D being the diffusion coefficient of adsorbate. For $D^{1/2}t^{1/2}/K \ll 1$, one has $\exp(Dt/K^2) \approx 1$, $\operatorname{erfc}(D^{1/2}t^{1/2}/K) \approx 1 - 2D^{1/2}t^{1/2}/\pi^{1/2}K$ and $\theta = 2D^{1/2}t^{1/2}/\pi^{1/2}K$.

[15] The value $k_s \approx 0.04$ cm. sec.$^{-1}$ obtained at 25° in 1 *M* sodium sulfate with a hanging amalgam electrode by different investigators is probably too low on account of contamination: H. Gerischer, *Z. Elektrochem.*, **57**, 604 (1953); W. Vielstich and P. Delahay, THIS JOURNAL, **79**, 1874 (1957). See also ref. 9.

Effect of Adsorption on Current-Potential Curves and Limiting Currents

Method of Study.—The "blocking" of an electrode reaction by an adsorbed organic substance in the range of the limiting current can be regarded as a heterogeneous process preceding the electrochemical reaction. According to this simplified model, the reducible species must penetrate the film before reduction. One then could postulate that the penetration rate is a first-order process characterized by rate constants which could be measured, in principle, by methods of non-steady state electrolysis (potential-step and current-step methods). Unfortunately, such measurements appear difficult because the surface coverage for given conditions varies with potential,[3-5] and the application of non-steady state electrolysis would require a variation of potential of several tenths of a volt from a value at which there is virtually no reduction to a value in the range corresponding to the limiting current or the transition time. Likewise, polarography could not be applied easily because the electrode coverage varies continuously during drop life, and the resulting mathematical analysis would be very complex.

While these difficulties could be overcome in some cases, it is more fruitful to adopt a simpler approach, namely, to measure limiting currents in polarography for a known coverage of the mercury drop. Qualitative but interesting results on the effect of the adsorbed species and the nature of the reducible substance can be obtained as will now be shown. The experimental determination of coverage during drop life will be discussed first.

Coverage of Mercury Drop during Drop Life.—The mathematical treatment of adsorption kinetics with control by diffusion to a dropping mercury electrode is so complex as to require computer calculations.[6] Although such calculations[16] are of interest, it is much simpler to determine the electrode coverage during drop life from variations of the double layer differential capacity.

Capacities can be measured at different times during drop life by means of an a.c. bridge with a synchronization device, but the following method, although less accurate, is easier to apply. An a.c. signal of small amplitude (20 millivolts) was applied to a conventional polarographic cell containing the supporting electrolyte and the adsorbed species. The amplitude of the alternating current was recorded during drop life (Fig. 2) under conditions in which the current was proportional to the differential capacity of the double layer (see Experimental). The scale of current amplitudes was readily calibrated in capacities by substitution of a decade capacitance box for the dropping mercury electrode.

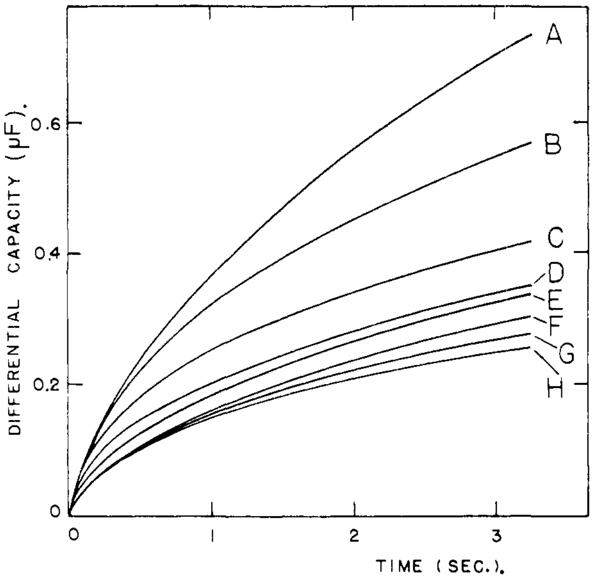

Fig. 2.—Variations of differential capacity of mercury drop during drop life at −0.72 volt (*versus* S.C.E.) and 30° for 0.5 *M* sodium citrate containing varying amounts of thymol; concentrations of thymol in 10^{-4} mole l.$^{-1}$: A (0); B (0.79); C (1.5); D (2.3); E (3.0); F (4.9); G (6.1); H (saturated, *i.e.*, 57).

The coverage θ was calculated by assuming that the differential capacity varies linearly with θ[17] (Fig. 3). Full coverage was assumed for curve H which was recorded with a saturated solution of thymol (5.7×10^{-3} *M*). At that concentration, adsorption equilibrium with respect to the bulk concentration is essentially achieved in an early stage of the drop,[6] and the differential capacity at the end of drop life is independent of drop time (constant drop size); this was indeed the case. Since the saturated solution corresponds to the plateau of the adsorption isotherm and the influence of mass transfer is minor, the assumption $\theta \approx 1$ for curve H is quite correct. Values of θ for $t < 0.5$ sec. were not calculated because of the uncertainty in the reading of Fig. 2.

It is seen from Fig. 3 that curves B, C and D approach a constant coverage and that a constant coverage is actually reached for curve E at least for $t > 0.5$ sec. Since for each bulk concentration of adsorbed substance there corresponds only a single equilibrium coverage, the results of Fig. 3 indicate that adsorption equilibrium, with respect to the bulk concentration, is approached for curves B, C and D and that equilibrium is reached for curve E. Curves F and G indicate a small decrease of coverage with increasing times but this effect probably results from the approximate evaluation of θ (see Experimental) and from experimental errors. The maximum value of θ cannot of course exceed the asymptotic value. It thus is a simple matter to determine whether or not adsorption equilibrium is reached at a D.M.E. It should be noted that the above method amounts to determining the differential capacity per unit area during drop life. This

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(16) Calculations are now being carried out in collaboration with the Oak Ridge Institute of Nuclear Studies.

(17) One has for the charge Q at the interface $Q = [c_{\theta=0}(1 - \theta) + c_{\theta=1}\theta](E - E_m)$ where the c's are the integral capacities, E is the electrode potential and E_m is the potential at the point of zero charge. By differentiation with respect to E there follows the differential capacity for the coverage θ

$$c_d = c_{\theta=0}(1 - \theta) + c_{\theta=1}\theta + \frac{\partial \theta}{\partial E}(c_{\theta=1} - c_{\theta=0})(E - E_m) + \left[\frac{\partial c_{\theta=0}}{\partial E}(1 - \theta) + \frac{\partial c_{\theta=1}}{\partial E}\theta\right](E - E_m)$$

It was assumed here (and also in our previous paper[6]) that the last two terms are negligible *in the vicinity of the point of zero charge*—not of course near the "peaks" in the c *versus* E curve in presence of an adsorbed substance. See A. Frumkin, V. S. Bagocky, Z. A. Iofa and B. N. Kabanov, "Kinetics of Electrode Reactions," Moscow University Press, Moscow, 1952, p. 41. Furthermore, one has from the definitions of integral (c_i) and differential (c_d) capacities

$$c_d = c_i + (E - E_m)\frac{\partial c_i}{\partial E}$$

and, consequently, $c_d \approx c_i$ when $E \approx E_m$. Hence, the differential capacity for coverage θ varies linearly with θ as a first approximation. Note that E_m is not the same for $\theta = 0$ and $\theta = 1$, and consequently the above equation for the charge Q and the corresponding model are open to question.

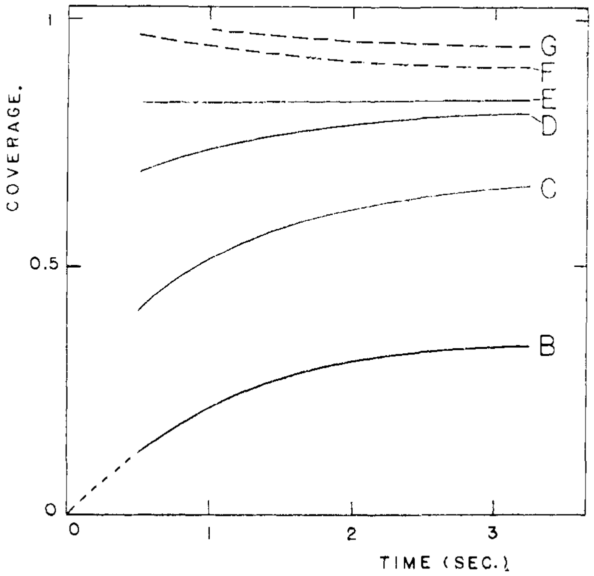

Fig. 3.—Surface coverage during drop life for the conditions of Fig. 2.

capacity is independent of time when adsorption equilibrium is reached.

Electrode Coverage and Limiting Current.—The addition of an organic substance which is adsorbed on the D. M. E. renders polarographic current–potential curves more irreversible and, in some cases, causes the division of a single wave into two waves. The first limiting current is caused by blocking of the electrode reaction by the adsorbed film. The second limiting current is reached when the blocking film is completely desorbed. The definition of the first wave varies from one system to another: for instance, excellent double waves are observed with the system corresponding to curve D of Fig. 4.

TABLE II

ELECTRODE COVERAGES AT THE END OF DROP LIFE[a] AT 30°

n-Hexyl alcohol		Quinoline		Thymol		
C, mmole l.$^{-1}$	θ^b	C, mmole l.$^{-1}$	θ^b	C, mmole l.$^{-1}$	θ^c	θ^d
0.12	0.039	0.039	0.25	0.15	0.50	0.66
.23	.089	.058	.32	.22	.65	.80
.34	.15	.077	.38	.30	.73	.83
.45	.27	.11	.42	.36	.81	–
.54	.44	.15	.44	.49	.86	.90
.64	.55	.18	.45			
.74	.60	.25	.51			
.94	.69	.30	.80			
1.26	.76	.63	.92			

[a] Capillary characteristics: $m = 2.70$ mg. sec.$^{-1}$, $\tau = 3.5$ sec. (varied somewhat from one medium to another). [b] In 1 *M* sodium citrate, 0.1 *M* sodium hydroxide at −0.72 volt (*versus* S.C.E.). [c] In 1 *M* potassium chloride at −0.70 volt (*versus* S.C.E.). [d] In 0.5 *M* sodium citrate at −0.70 volt (*versus* S.C.E.).

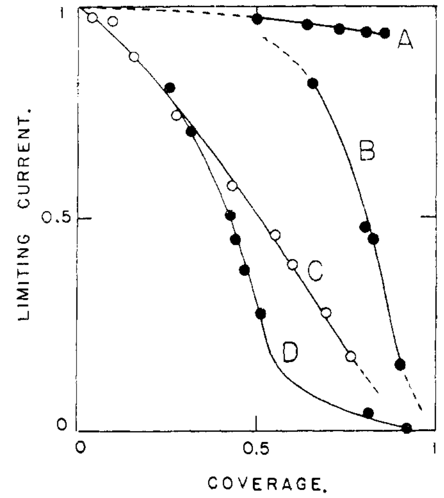

Fig. 4.—Variations of limiting current at the end of drop life with coverage. Currents expressed as the fraction of the diffusion current observed without adsorbed substance. Curve A, 2×10^{-3} Cd^{++} in 1 *M* KCl plus thymol; curve B, 2×10^{-3} *M* Cd^{++} in 0.5 *M* sodium citrate plus thymol; curve C, 4.0×10^{-3} *M* Cu^{++} in 1 *M* sodium citrate, 0.1 *M* sodium hydroxide, plus *n*-hexyl alcohol; curve D, same as C but with quinoline instead of *n*-hexyl alcohol. Potentials at which currents were measured: −0.72 (A and B) and −0.70 (C and D) volt *versus* S.C.E.

Two effects will be discussed: (a) the influence of the nature of the reduced species for a given adsorbed film (curves A and B in Fig. 4 and Table II) and (b) the effect of the nature of the adsorbed substance for a given reducible species (curves C and D). Curve A indicates only a very small effect of adsorption on the limiting current. There is little "blocking," and the diffusion process is not affected appreciably since the thickness of the diffusion layer is very large in comparison with the average distance between holes[18] in the film. The current density for the uncovered area is larger than in the absence of adsorbed film but there is no control by the kinetics of the electrochemical step because the rate of reduction of cadmium ions is high (the exchange current is large and $E < E^0$ in the limiting current range), and consequently the current for the uncovered area is still much smaller than the value which would be observed if there were no concentration polarization. These arguments have been advanced by Frumkin and others.[7] Of course, the positions of holes change continuously because of the dynamic character of the adsorption–desorption process, but this does not affect the argument.

Curve B of Fig. 4 for the reduction of cadmium citrate in presence of thymol indicates a strong blocking action. Several reasons can be invoked to account for the difference between this behavior and that of cadmium in chloride medium (curve A, Fig. 4): differences in the "size" of the ion, partial control by the electrochemical step, possibility of a chemical step preceding the electrochemical reaction proper, difference in charge for the ions of curves A and B and enhancement of the repulsion effect—as observed in the reduction of peroxydisulfate ion for instance[7]—resulting from partial coverage of the electrode. These different explanations cannot be ruled out entirely at this time, but it is believed that the "size" of the reducible species is the most important factor. Further work is now being planned to allow a definite choice between the

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(18) This does not imply necessarily that a partially covered surface is randomly covered.

above foregoing explanations: study of uncharged reducible species, measurement of exchange currents, detection of a possible chemical step.

Other cases also were studied: the limiting current for the reduction of the relatively small thallous ion (high diffusion coefficient in comparison with other ions) did not decrease appreciably upon the addition of *n*-hexyl alcohol (0.01 molar) or quinoline (0.005 molar). Likewise, *n*-hexyl alcohol (0.01 molar) or thymol (0.005 molar) had little effect on the limiting current for the reduction of cadmium in sulfate or chloride medium. Little effect on the limiting current was observed for cupric ion in nitrate medium upon the addition of *n*-hexyl alcohol (0.01 molar) whereas this substance (0.001 molar) completely suppressed the wave in a mixture of sodium citrate (1 *M*) and sodium hydroxide (0.1 *M*).

Further confirmation of the difference in behavior for curves A and B of Fig. 4 was obtained from current–time curves during drop life (Fig. 5). These curves were discussed in detail previously,[6] and it was pointed out that a maximum is obtained in the case of pronounced blocking. Thus, the drop grows very rapidly at the beginning of the drop life, and the coverage is relatively small (see also Fig. 3); the current then increases rapidly. However, the rate of growth decreases continuously during drop life, and the coverage increases thus causing a drop in current. Finally, further growth of the drop causes the current to increase. It is seen from Fig. 5 that the addition of thymol hardly affects the current–time curves for the reduction of cadmium ion in chloride medium whereas the characteristic maxima are observed in citrate medium. It should be noted that there was a rather small variation in coverage from one medium to another (Table II), but this difference cannot account for the results of Fig. 5.

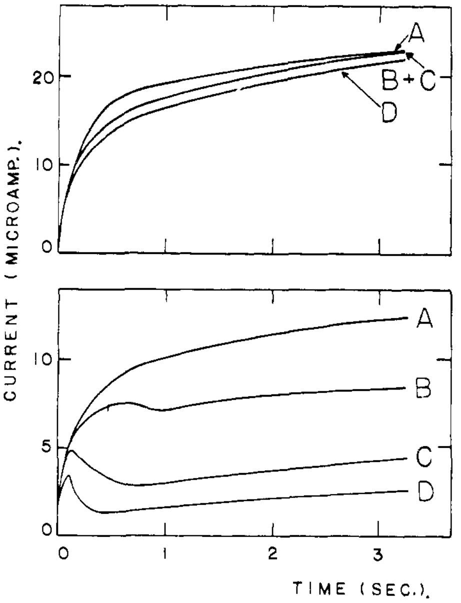

Fig. 5.—Current–time curves during drop life for 2×10^{-3} *M* Cd^{++} in 1 *M* potassium chloride (top) and 0.5 *M* sodium citrate for a varying concentration of thymol. Thymol concentrations in millimole l.$^{-1}$: A (0); B (0.22); C (0.36); D (0.49).

The effect of the nature of the adsorbed substance for a given reducible substance is apparent from curves C and D in Fig. 4. It is believed that it can be accounted for by differences in the structure of the adsorbed films and particularly differences in the "size" of the holes in the film.

Implication with Respect to Analysis of Polarographic Waves.—Adsorption of a foreign substance causes an increase in overvoltage[19] and renders current–potential curves more irreversible even when the limiting current is practically not affected (Fig. 6). An approximate analysis of such irreversible waves can be made by the method of Koutecky[20,21] provided that two conditions are fulfilled: (a) the equilibrium surface concentration of adsorbed species is practically independent of potential over the range of potentials being covered; (b) the bulk concentration of adsorbed species is so large that adsorption equilibrium with respect to the bulk concentration is essentially reached during the whole drop life. *In general, these conditions are not fulfilled.* For instance, it is obvious that current–time curves with a maximum (Fig. 5 bottom) do not correspond to the conditions of diffusion of the reducible and reduced species which are assumed in the absence of adsorption.

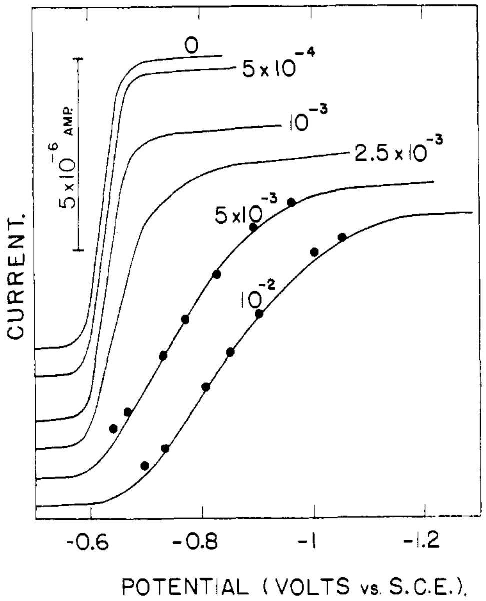

Fig. 6.—Polarographic waves for 10^{-3} *M* Cd^{++} in 1 *M* sodium sulfate with varying concentration of *n*-hexyl alcohol (number on each curve in mole l.$^{-1}$). Maximum currents during drop life are plotted: $m = 2.25$ mg. sec.$^{-1}$, $t = 3.68$ sec. Points are calculated values.

It is seen in Fig. 6 that experimental and currents calculated by Koutecky's method (maximum current during drop life) agree well for the cadmium wave in presence of *n*-hexyl alcohol for the two highest concentrations of *n*-hexyl alcohol. No agreement could be obtained for lower concentrations of *n*-hexyl alcohol, and discrepancies on the current in the ascending branch of the wave were as large as 30–100%. Kinetic data used in the calculations were as follows: values of *apparent* k_s (no correction for coverage), 1×10^{-4} and 2.2×10^{-4} cm. sec.$^{-1}$ for 10^{-2} and 5×10^{-3} molar *n*-hexyl alcohol solutions, respectively; $\alpha = 0.15$ and 0.17, respectively.

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[19] We do not consider the catalytic discharge of hydrogen caused by the adsorption of certain alkaloids and other substances.

[20] (a) J. Koutecky, *Collection Czechoslov. Chem. Communs.*, **18**, 597 (1953); (b) J. Koutecky and J. Cizek, *ibid.*, **21**, 836 (1956).

[21] See also H. Matsuda and Y. Avabe, *Bull. Chem. Soc. Japan*, **28**, 422 (1955); **29**, 134 (1956).

Significance of the Coverage as Deduced from Differential Capacity Measurements or Electrocapillary Curves

Coverage values obtained here are approximate as pointed out above (see note 17). More accurate values could have been obtained by the more tedious determination of electrocapillary curves. However, there is a much more important point than mere accuracy which requires comments, namely, the use of the statistical concept of coverage in the interpretation of processes at the molecular scale. Thus, the coverage is defined in terms of the effect of adsorbate on some properties of the electrode, *i.e.*, the differential capacity and the surface tension in the absence of an electrode reaction. Molecular and electrostatic interactions between the absorbate and the reactants of the electrode process must be considered for electrode reactions. The chief value of the determination of electrode coverages is precisely to give a method for the study of such interaction effects.

Experimental

Solutions and Cadmium Amalgam.—Bidistilled water was used in the preparation of all solutions. The titanium solutions were prepared from commercial 20% titanous chloride (W. H. Curtin Co., Houston) whose Ti(III) content was determined by titration with ferric chloride. Ti(IV) solutions were obtained by oxidation of Ti(III) by air in 1 *M* tartaric acid containing also 0.1 mole l.$^{-1}$ sodium chloride (to minimize the effect of chloride added as titanium chloride). To avoid oxidation of Ti(III), the supporting electrolyte containing the proper amount of Ti(IV) was deaerated before the addition of a small volume of concentrated Ti(III) solution. The concentrations of Ti(IV) and Ti(III) were controlled by polarography before each determination (prior to the addition of the organic substance). In experiments in which adsorbed substances were added, the solution was first deaerated in the cell, and the organic substance was added in the form of a small volume (perhaps 1 ml.) of a concentrated (often saturated) aqueous solution. In general, nitrogen was not bubbled through the cell after the addition of the organic substance to avoid losses by evaporation.

Cadmium amalgam was prepared by electrolysis from known weights of cadmium sulfate and mercury in 1 *M* sulfuric acid. After exhaustion of cadmium from solution (24-48 hr. with continuous moderate bubbling of nitrogen), the amalgam was kept in the electrolysis vessel, a small cathodic current (0.005 amp.) flowing continuously through the cell (hydrogen evolution). The amalgam was transferred and kept under nitrogen in the reservoir of the dropping amalgam electrode. The cadmium concentration in the amalgam was determined by polarographic analysis.

Determination of i_0 and k_s.—Exchange currents were determined by electrolysis with superimposed alternating voltage (0.005 volt amplitude). This method is by now classical and its theory and methodology need not be recalled.[22] Measurements were carried out with the bridge and cell previously used.[6] The cell impedance was balanced at the end of drop life against a resistance R_s and capacity C_s in series. The resistance R_e of the supporting electrolyte alone was measured in a separate experiment. The resistance R_p and capacity C_p in parallel that are equivalent to $R_s - R_e$ and C_s in series were calculated,[23] and linear plots of R_p against $\omega^{-1/2}$ ($\omega = 2\pi f$, f being the frequency of measurement) were prepared. The exchange current density was computed from the extrapolated value of R_p at $\omega^{-1/2} = 0$: $R_p = (RT/nF)(1/i_0A)$ where A is the electrode area. This method of calculation is inspired from the one applied by Gerischer.[24]

The rate constant k_s was computed readily from i_0 since $i_0 = nk_sFC$, C being the common value of C_O and C_R (see eq. 1). The transfer coefficient need not be known in the calculation of k_s from i_0 when $C_O = C_R$.

Electrode Coverage Measurements.—Electrode coverages were determined from differential capacity measurements with a bridge in the study of the effect of coverage on k_s. Direct measurements of the double layer differential capacity of the type discussed in connection with Fig. 2 and 3 were applied in all other cases. Conditions for approximately full coverage were achieved in both methods as indicated in the analysis of Fig. 2.

The technique for bridge measurements was the same as in a previous investigation[6] except that a dropping mercury electrode was utilized instead of a hanging mercury drop. The bridge was balanced at the end of drop life.

Capacity currents were determined with apparatus similar to one used in a.c. polarography.[25] An alternating voltage having an amplitude of 0.02 volt[26] was supplied by a General Radio isolation transformer (model 578-B) connected to a Hewlett-Packard oscillator (model 650A) which operated at 35 cycles per sec. This low frequency was selected so that the current through the cell was determined, for all practical purposes, by the impedance of the double layer capacity and not by the resistance of the other elements in series with the cell. For the same reason, a 47 ohm resistor of the radio type was connected across the output terminals of the secondary of the isolation transformer. The current—as measured by the ohmic drop across a 75 ohm resistor in series with the cell—was recorded with a Tektronix cathode-ray oscilloscope model 535 with preamplifier 53E (sensitivity of 50 microvolts per cm.). The potential of the dropping mercury electrode was adjusted against a saturated calomel electrode by means of a 100 ohm "Helipot" potentiometer. The latter was calibrated with a Leeds and Northrup student potentiometer.

Polarographic Measurements and Current-Time Curves.—These measurements which followed standard practice were made with a Sargent pen-and-ink recording polarograph model XXI. A fast Brown recorder (1.2 second for full scale deflection) was substituted for the recorder supplied by the manufacturer since fast recording is essential with solutions containing substances adsorbed on the dropping mercury electrode. Current-time curves during drop life were recorded with a Tektronix cathode-ray oscilloscope model 535 with 53D preamplifier. The polarographic cell was connected in series with a decade resistance box across which the preamplifier of the oscilloscope was connected.

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[22] See a review, for instance, H. Gerischer, *Z. Elektrochem.*, **59**, 604 (1955); also P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, New York, N. Y., 1954, pp. 146-178.

[23] $R_p = (R_s - R_e)\left(1 + \frac{1}{\omega^2(R_s - R_e)^2C_s^2}\right)$, $C_p = C_s \frac{1}{1 + \omega^2(R_s - R_e)^2C_s^2}$; see H. Gerischer, *Z. Elektrochem.*, **57**, 604 (1953).

[24] H. Gerischer, *Z. physik. Chem.*, **202**, 302 (1953); see discussion of the approximation being made on p. 306.

[25] See, for instance, P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, New York, N. Y., 1954, pp. 375-376.

[26] This relatively large amplitude could be used because measurements were made in a range of potentials in which the differential capacity varies slowly with potential.