

attention to such details as sample history and time-schedule of measurements when working with pressed specimens. Thus our results provide a point of departure for future work with Ag_2HgI_4 and in particular indicate quite clearly that, both in the approach to order and the approach to disorder, two nucleation steps are involved, *cf.* Fig. 4 (lower part). This conclusion is supported by the fact that a small bump is observed in conductivity curves both for T -increasing and T -decreasing. The bump is real; it occurs in all samples, both pressed and cast. That it has not been noted in previous conductivity studies is indicative of measurements made too rapidly.

The two transitions implied by the two nucleations may be designated (for T -increasing) as $\beta \rightarrow \beta'$ and $\beta' \rightarrow \alpha$. We suggest that in the $\beta \rightarrow \beta'$ transition Ag-ions become disordered occupying at random $2/3$ of the face center positions of the unit cube and in the $\beta' \rightarrow \alpha$ transitions Ag and Hg-ions become further disordered occupying at random $3/4$ of the corners plus face centers of the unit cube. This picture, however, leads to some difficulty in interpretation of the relative sizes of the conductivity changes. It is usually said, following Kete-

laar,¹ that the large increase in conductivity near 52° is the result of one mole of lattice vacancies becoming available to the conduction process. Thus since transference number measurements for the α -modification⁸ show that Hg-ions account for only 6% of the current, one would expect the $\beta \rightarrow \beta'$ transition to exhibit the largest conductivity effect. An alternative assignment would let the $\beta \rightarrow \beta'$ transition involve mixing of Ag and Hg-ions, and the $\beta' \rightarrow \alpha$ transition the extension of the disorder to the normally unoccupied top and bottom face centers of the unit cube. X-Ray diffraction and transference experiments would be fruitful in deciding between these possibilities provided suitable single crystals can be prepared and adequate attention is paid to details of sample history.

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CHICAGO 16, ILLINOIS

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Effect of Adsorbed Films on Kinetics of Electrode Reactions¹

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The transfer coefficient and electron transfer rate constant for a totally irreversible electrode reaction can be measured by determining the dependence between the current and potential at the foot of the polarographic wave. This method was used to study the effect of the adsorption of such surface active agents as n -octyl alcohol, β -naphthol and camphor upon the reduction of nickel(II) ions in sodium perchlorate medium, iodate ions in basic and acidic media, the reduction of the chloro complexes of tin(IV) and tin(II), the reduction of the ammonia and some amine complexes of copper(II), and the reduction and oxidation of the ammonia complexes of copper(I). The effect of high concentrations of sodium perchlorate upon the reduction of nickel(II) also was studied.

During recent years, many observations have been made on adsorption and its effect upon electrochemical reactions. No attempt will be made here to survey the field,² but mention should be made of the extensive work of Loshkarev and Kryukova³ on the effect of organic compounds on electrode systems, the observations of Meites and Meites⁴ on the effects of gelatin upon the characteristics of polarographic waves, the work of Berzins and Delahay⁵ on the kinetics of adsorption, and that of Strassner and Delahay⁶ on the effect of gelatin upon the kinetics of irreversible electrode reactions.

Two quantities, the transfer coefficient and the electron transfer rate constant, are usually used to describe the kinetics of electrode reactions. These

two quantities can be determined by polarographic methods,⁷⁻¹⁰ by chronopotentiometry,¹¹ by a.c. impedance measurements¹² or by determining the relationship between current and electrode potential.¹³ The latter method is particularly simple for totally irreversible electrode reactions under conditions such that the rates of mass transfer are very large in comparison to the rate of electron transfer.

This condition is readily fulfilled by measuring the current at the foot of a polarographic wave.⁹ By increasing the concentration to a relatively high value (*ca.* 0.01 M), the currents at the lower 10 to 15% of the polarographic wave are increased to readily measured magnitudes. If the rate of the

(1) This work was supported by grants G-750 and G-2420 of the National Science Foundation, and a fellowship donated by the U. S. Rubber Co.

(2) For references, see W. J. Subcasky, Ph.D. thesis, University of Illinois, 1957.

(3) M. Loshkarev and A. Kryukova, *Doklady Akad. Nauk. S.S.S.R.*, **62**, 97 (1948); **72**, 729, 919 (1950); **107**, 432 (1956).

(4) L. Meites and T. Meites, *THIS JOURNAL*, **73**, 177 (1951).

(5) T. Berzins and P. Delahay, *J. Phys. Chem.*, **59**, 906 (1955); *Z. Elektrochem.*, **59**, 792 (1955).

(6) J. E. Strassner and P. Delahay, *THIS JOURNAL*, **74**, 6232 (1952).

(7) (a) P. Delahay, *ibid.*, **73**, 4944 (1951); (b) P. Delahay and J. E. Strassner, *ibid.*, **73**, 5219 (1951); (c) P. Delahay, *ibid.*, **75**, 1430 (1953).

(8) D. M. H. Kern, *ibid.*, **76**, 4243 (1954).

(9) P. Kivalo, K. B. Oldham and H. A. Laitinen, *ibid.*, **75**, 4148 (1953).

(10) J. Koutecky, *Chem. Listy*, **47**, 323 (1953); *Collection Czechoslov. Chem. Commun.*, **18**, 597 (1953).

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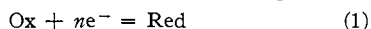
(12) J. E. B. Randles, *Faraday Soc. Disc.*, **1**, 11 (1947).

(13) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, (a) pages 40-41; (b) page 34.

process is determined by electron transfer, the current is proportional to instantaneous electrode area, and is determined conveniently by measuring the current at the instant of drop detachment. By mechanical detachment of the mercury drops at various time intervals, the constancy of current density with time at a given potential can conveniently be tested.

This procedure is advantageous in avoiding the complications due to the interaction of electron transfer and diffusion rates,¹⁰ and is especially so if a polarographic maximum, indicative of stirring at the electrode surface, is present. This stirring process introduces complications which cannot be taken into account by theories based on diffusion calculations. Maximum suppressors are often added to eliminate the stirring, but such suppressors are quite generally surface active, and the results would therefore not be characteristic of a clean electrode. At the foot of the wave, stirring has no effect unless it is so pronounced that the shape and area of the electrode are affected. Indeed, a slight amount of stirring is helpful for it tends to decrease the concentration gradient and permits a larger portion of the wave to be used for determining the kinetic constants.

Under conditions such that the back reaction can be neglected,¹⁴ the cathodic current for a process



is given by^{13b}

$$i_c = nFA C_{\text{Ox}} k^0 \exp\left[-\frac{\alpha n_a F}{RT} (E - E^0)\right] \quad (2)$$

where n and n_a are, respectively, the number of electrons involved in the over-all reaction and the rate-determining step. A is the electrode area, C_{Ox} is the concentration of oxidized species, k^0 is the formal heterogeneous electron transfer rate constant, α is the transfer coefficient, E is the applied potential, and E^0 is the formal potential of the couple. Taking the logarithm of equation 2

$$\log \frac{i_c}{nFA C_{\text{Ox}}} = \log k^0 - \frac{1}{2.3} \frac{\alpha n_a F}{RT} (E - E^0) \quad (3)$$

If the quantity on the left hand side of eq. 3 is plotted against $(E - E^0)$, the resulting straight line has a slope determined by αn_a and an intercept of $\log k^0$.

Experimental

Instantaneous currents were measured at the instant of drop fall with either a Sargent Model XXI Polarograph or a Leeds and Northrup Electrochemograph, Type E. The currents were measured at constant potentials at five or ten millivolt intervals along the foot of the wave. The potential also was measured at the instant of drop fall with an L and N student potentiometer. All currents were corrected for residual current and the potential corrected for ohmic drop within the cell. The a.c. resistance of the dropping mercury electrode (DME), the solution and the reference electrode was measured at the instant of drop fall. To eliminate variations of drop time and, hence, electrode area, with potential, a mechanical drop detacher was used to give a constant drop time. The drop times used were 4.972 and 9.970 seconds. By measurements of double layer capacity as a function of time and concentration, it was established that adsorption equilibrium had been reached

(14) The back reaction contributes less than 1% if $-(E - E^0)$ exceeds $0.06/n_a \alpha$ volts at 25°. For $C_{\text{Ox}} = C_{\text{Red}} = 10^{-3}$ mole cm.⁻³, $n = 1$, $A = 10^{-2}$ cm.², $i = 10^{-7}$ amp., this corresponds to $k^0 = 10^{-4}$ cm. sec.⁻¹.

before the end of drop life, and that the concentration of surface active agent corresponded to a saturation of the electrode surface.

The reference electrode was made with a saturated solution of sodium chloride instead of potassium chloride. The potential of this modified saturated calomel electrode (referred to as SCE*) was -5.0 millivolts vs. SCE at 25°. The salt bridge (saturated NaCl) was closed with a sintered glass frit; no agar plug was used. Oxygen was removed from the solutions with oxygen-free nitrogen.

The maximum drop area was calculated from the flow rate and drop times. Experimental data were plotted as the $\log(i/nFA C_{\text{Ox}})$ vs. $(E - E^0)$. The value of the formal heterogeneous rate constant and product, αn_a , were calculated from the logarithmic plots by the method of least squares.

Nickel perchlorate was prepared by dissolving an excess of C.P. nickel(II) oxide in perchloric acid. The resulting salt was recrystallized twice from distilled water. A concentrated stock solution was prepared and quantitatively diluted. The concentration of this stock solution was determined by adding an excess of EDTA in $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer and back-titrating with a standard zinc solution using Erichrome Black T as the indicator.¹⁵ Concentrated sodium perchlorate was prepared by neutralizing perchloric acid with sodium hydroxide to pH 3.5. The concentration of the stock solution of NaClO_4 was determined by passing a sample through a cation exchange resin in the hydrogen form and titrating the liberated hydrogen ions to an end-point pH of 3.5. A sample of anhydrous cuprous chloride was prepared by C. H. Liu of this Laboratory by reduction of copper(II) chloride with sulfur dioxide. β -Naphthol was purified by repeated extraction with small amounts of ethanol, followed by dissolution in a minimum of ethanol and precipitation with distilled water. Camphor was added as a 2.5 M solution in ethanol. The organic amines and n -octyl alcohol were purified by distillation. All other solids were purified by recrystallization from distilled water. Weighed quantities of the dried solids were added to the supporting electrolyte.

Results and Discussions

Aquated Nickel Ion.—The reduction of nickel(II) in a perchlorate medium is irreversible as shown by the fact that the half wave potential is about 0.5 volt more negative than the reversible standard potential for the nickel couple.¹⁶ Figure 1 illustrates the effect of a strongly adsorbed material upon an irreversible polarographic wave. The rate constant k^0 was decreased so markedly by an adsorbed layer of camphor that the foot of the reduction wave was barely discernible before the desorption potential of camphor was reached. The sudden rise of current due to nickel reduction occurs at the same potential (-1.32 v. vs. SCE* for a 5 millimolar solution of camphor) as does the desorption of camphor, as shown by a sudden increase in residual current. The same sudden rise is evident in the logarithmic plot (curve D, Fig. 2). Table I gives the values of the heterogeneous rate constant, k^0 , and the product αn_a (α transfer coefficient, n_a number of electrons in the rate-determining step) for the reduction of aquated nickel ion in the presence of several surface active agents. The logarithmic plots are shown in Fig. 2. Two straight line portions were found in the plot of $\log i/nFA C_{\text{Ox}}$ for each solution with the exception of the one containing n -octyl alcohol. Similar variation in the product αn_a with potential have been noted for the reduction of nickel in a nitrate medium⁹ and for the reduction of iodate in a basic medium.^{7b}

(15) W. F. Harris and T. R. Sweet, *Anal. Chem.*, **26**, 1648 (1954).

(16) I. M. Kolthoff and J. J. Lingane, "Polarography," Second Edition, Interscience Publishers, Inc., New York, N. Y., 1952, p. 486.

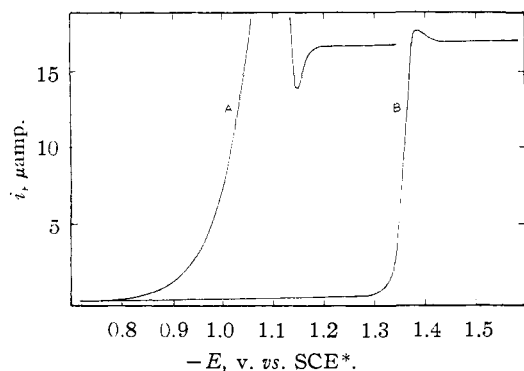


Fig. 1.—Effect of camphor on the reduction of aquated nickel ion. Current-voltage curves of $2.54 \times 10^{-3} M$ $Ni(ClO_4)_2$ in $0.10 M$ $NaClO_4$: curve A, no camphor; curve B, $5 mM$ camphor.

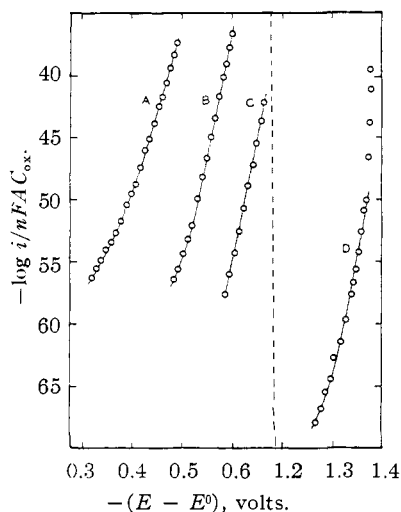


Fig. 2.—Effect of surface active agents on the kinetics of the reduction of aquated nickel ion. Logarithmic plots of $0.0254 M$ $Ni(ClO_4)_2$ in $0.10 M$ $NaClO_4$. (a) No surface active agent; (b) solution saturated with β -naphthol; (c) solution contained $2 \times 10^{-3} M$ n -octyl alcohol (potential axis shifted 0.10 volt in a negative direction); (d) solution saturated with camphor.

The effects of the concentration of $NaClO_4$ upon the kinetics of the nickel reduction are shown in Table II and Fig. 3. Since the standard potential of the nickel(II)–nickel amalgam couple is not known, the values of the rate constants were referred to the reversible potential of the nickel(II)–

TABLE I
EFFECT OF SURFACE ACTIVE AGENTS UPON THE REDUCTION OF $Ni(H_2O)_6^{++}$

Supporting electrolyte	Potential range, v. vs. SCE*	αn_a	k^0 , cm. sec. ⁻¹
$0.50 M$ $NaClO_4$	-0.75 to -0.86	0.50	5.14×10^{-9}
	-0.86 to -0.99	0.73	7.61×10^{-10}
$0.50 M$ $NaClO_4$ with $2.0 \times 10^{-3} M$ n -octyl alcohol	-0.98 to -1.06	1.15	6.06×10^{-10}
$0.10 M$ $NaClO_4$	-0.75 to -0.86	0.63	1.22×10^{-9}
	-0.86 to -0.98	$.77$	3.02×10^{-9}
$0.10 M$ $NaClO_4$ satd. with β -naphthol	-0.97 to -1.01	$.67$	7.17×10^{-10}
	-1.01 to -1.09	1.18	2.92×10^{-10}
$0.10 M$ $NaClO_4$ satd. with camphor	-1.26 to -1.30	0.70	1.09×10^{-10}
	-1.31 to -1.35	1.20	1.18×10^{-10}

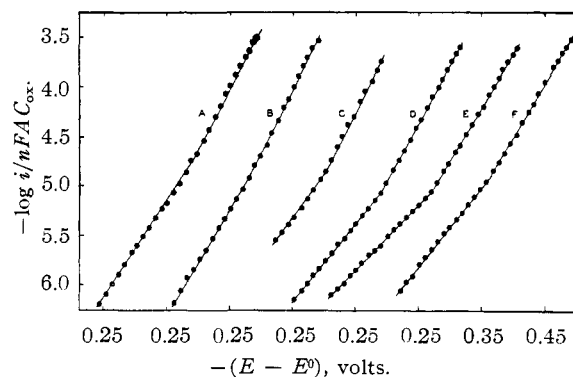


Fig. 3.—Effect of $NaClO_4$ upon the kinetics of the reduction of $Ni(H_2O)_6^{++}$. Logarithmic plots for $0.0254 M$ $Ni(ClO_4)_2$ in various concentrations of $NaClO_4$: (a) $0.0 M$ $NaClO_4$; (b) $0.1 M$ $NaClO_4$; (c) $0.5 M$ $NaClO_4$; (d) $1.0 M$ $NaClO_4$; (e) $2.0 M$ $NaClO_4$; (f) $3.0 M$ $NaClO_4$. Potential axis shifted for each curve.

nickel metal couple, which serves as a convenient reference point. The values of αn_a of course are independent of the reference potential.

TABLE II
EFFECT OF $NaClO_4$ UPON THE REDUCTION OF $0.0254 M$ $Ni(ClO_4)_2$

$NaClO_4$ concn., M	Potential range, v. vs. SCE*	αn_a	k^0 , cm. sec. ⁻¹
0.00	0.730 to 0.86	0.57	3.18×10^{-9}
	$.86$ to $.98$	$.73$	3.44×10^{-10}
.10	$.75$ to $.86$	$.63$	1.22×10^{-9}
	$.86$ to $.98$	$.77$	3.02×10^{-9}
.50	$.75$ to $.86$	$.50$	5.14×10^{-9}
	$.86$ to $.99$	$.73$	7.61×10^{-10}
1.00	$.74$ to $.86$	$.46$	8.05×10^{-9}
	$.86$ to 1.00	$.70$	2.41×10^{-10}
2.00	$.74$ to 0.86	$.39$	3.53×10^{-8}
	$.86$ to $.99$	$.64$	1.03×10^{-9}
3.00	$.71$ to $.86$	$.47$	1.69×10^{-8}
	$.86$ to $.98$	$.64$	1.56×10^{-9}

* Referred to standard potential rather than standard amalgam potential. See text.

According to Sanborn and Orlemann,¹⁷ nickel(II) shows two reduction steps at high salt concentrations, the product at the top of the first wave being nickel(I). Since the values of the kinetic constants show no appreciable change with concentration of $NaClO_4$, it is plausible to assume that the addition of the first electron is the rate-determining step at all electrolyte concentrations. The rate of addition of the second electron, however, decreases with increasing salt concentration until at the highest concentration it occurs so slowly that nickel(I) becomes the reaction product.

The effect of surface active agents is to decrease the rate constant, the magnitude of the effect being much greater for camphor than for octyl alcohol or β -naphthol presumably because of the more compact nature of the adsorbed film. The value of αn_a was nearly the same for all three surface active agents (1.15 to 1.20). Evidently two electrons must be involved in the rate-determining step.

(17) R. H. Sanborn and E. F. Orlemann, THIS JOURNAL, **78**, 4852 (1956).

The Copper(II)-Copper(I)-Ammonia System.—In an ammoniacal medium copper is reduced in two reversible one-electron steps. In Fig. 4 is shown the effect of a saturated solution of camphor upon the reduction of 0.020 *M* CuSO₄ in 1 *M* NH₃–1 *M* NH₄NO₃. As shown by residual current curves, camphor is adsorbed at a potential more positive than that at which the reduction of copper begins. In a 1 *M* NH₃–1 *M* NH₄Cl solution, adsorption occurs at a more negative potential so that the current due to reduction begins to rise until the potential of adsorption is reached. After this potential the current decreases to a value slightly greater than that of the residual current.

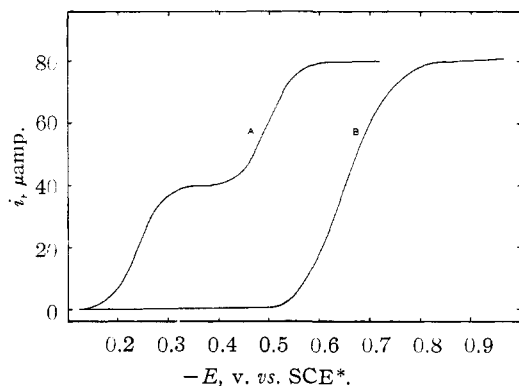


Fig. 4.—Effect of camphor upon the reduction of copper (II). Current voltage curve of 0.02 *M* CuSO₄ in 1 *M* NH₄OH–1 *M* NH₄NO₃: curve A, no camphor; curve B, saturated with camphor.

In either supporting electrolyte, when the solution is saturated with camphor a single wave with a height equal to that of the total double wave is obtained. The kinetic values for this wave are given in Table III.

TABLE III
KINETIC PARAMETERS FOR THE COPPER(II)-COPPER(I)
SYSTEM
All solutions saturated with camphor

Solution	αn_a	k^0 , cm. sec. ⁻¹
0.010 <i>M</i> CuSO ₄ –1 <i>M</i> NH ₄ OH–1 <i>M</i> NH ₄ Cl	0.27	1.03×10^{-9}
0.025 <i>M</i> CuSO ₄ –1 <i>M</i> NH ₄ OH–1 <i>M</i> NH ₄ NO ₃	.37	2.28×10^{-9}
0.026 <i>M</i> CuCl–1 <i>M</i> NH ₄ OH–1 <i>M</i> NH ₄ NO ₃	.55	9.75×10^{-10}
0.035 <i>M</i> CuCl–1 <i>M</i> NH ₄ OH–1 <i>M</i> NH ₄ NO ₃	.10	3.64×10^{-10}
0.047 <i>M</i> CuSO ₄ –1 <i>M</i> KNO ₃ –1.0 <i>M</i> ethylenediamine	.92	1.12×10^{-9}
0.046 <i>M</i> CuSO ₄ –1 <i>M</i> KNO ₃ –0.95 <i>M</i> propylenediamine	.93	9.44×10^{-9}
0.046 <i>M</i> CuSO ₄ –0.10 <i>M</i> KCl–0.10 <i>M</i> EDTA	.43	1.43×10^{-9}
0.045 <i>M</i> CuSO ₄ –1 <i>M</i> NH ₄ OH–1 <i>M</i> NH ₄ NO ₃ –0.71 <i>M</i> EDTA	.47	8.75×10^{-9}

^a Reduction on Cu(I) to Cu(Hg). ^b Oxidation of Cu(I) to Cu(II).

The low value of αn_a for the reduction of Cu(NH₃)₄⁺⁺ suggested that there was only one electron involved in the rate-determining step, *i.e.*,

the rate-determining step was the reduction of Cu(II) to copper(I). Using the standard potential for this reduction as the reference point, the value of the rate constant in the chloride medium was 1.03×10^{-6} cm. sec. ⁻¹ and in the nitrate medium it was 2.28×10^{-6} cm. sec. ⁻¹ referred to the reversible formal potential of the Cu(II)–Cu(I) couple. Even at the foot of the wave the reduction product was metallic copper and not copper(I). Analysis of a mercury sample which had been used for electrolysis at a current level of approximately 15% of the limiting current value showed copper to be present. At this same current density in the absence of camphor the product of reduction was copper(I).

Table III also shows the kinetic constants for the reduction and oxidation of 0.0263 *M* CuCl in 1 *M* NH₃–1 *M* NH₄NO₃. By use of the equations relating the rate constant to the potential it can be shown that the two potential dependent rate constants, for the reduction of Cu(II) to Cu(I) and for the reduction of Cu(I) to Cu(Hg), are equal at –0.566 volt (SCE*). At potentials more cathodic than this value the reduction of Cu(I) is faster than the reduction of Cu(II) to Cu(I). This supports the conclusion that in the reduction of Cu(II) it is the addition of the first electron which is the rate determining step. Once this first electron has been added the second electron adds immediately. This also explains the formation of metallic copper as the reduction product even at low current densities.

The value of αn_a was found to vary from 0.27 to 0.37 as the supporting electrolyte was changed from 1 *M* nitrate to 1 *M* chloride (Table III). This variation cannot be ascribed to complexation in the bulk of the solution, because the formation constants of the ammine and chloro complexes are such that the predominant species in both solutions are Cu(NH₃)₄⁺⁺ and Cu(NH₃)₂⁺. However, considering the surface active character of chloride, it is possible that mixed ammine-chloro complexes are involved at the electrode surface. On the other hand, the effect of chloride in altering the shape of the potential-distance curve near the electrode surface, and hence the shape of the potential barrier, may be decisive.

The value of αn_a as determined from the oxidation of copper(I) is 0.10, in contrast to the value of 0.37 as determined from the reduction of copper(II). From the reversible behavior of the system copper(II), (I), (0) in the absence of camphor it may be inferred that the rate of attainment of complexation equilibrium in the bulk of the solution is rapid. However, it may be that at the electrode surface the adsorbed camphor layer impedes the attainment of equilibrium. Added to this is the complication that the effect of the camphor film at the two potentials may not be the same.

Copper(II) Amine Complexes.—The kinetic parameters for the ethylenediamine, propylenediamine (1,2-diaminopropane) and ethylenediamine tetraacetate complexes of copper(II) in the presence of a saturated solution of camphor are given in Table III. Figure 5 illustrates the striking effect of the presence of a surface active agent upon the polarogram of 1.930×10^{-3} *M* CuSO₄ in 0.1 *M* KCl–0.10 *M* EDTA. The rate constants given in Table III

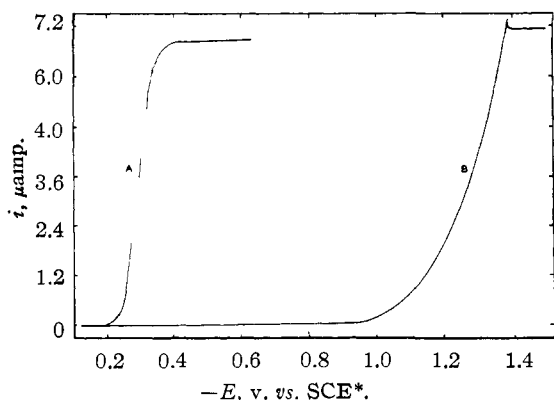


Fig. 5.—Effect of camphor upon the reduction of the EDTA complex of copper(II). Current-voltage curves for the reduction of $1.93 \times 10^{-3} M$ CuSO_4 in $0.10 M$ KCl – $0.10 M$ EDTA : curve A, no camphor; curve B, saturated with camphor.

are referred to the formal potential of the particular complex. This formal potential takes into consideration the amount of complexing agent present and the pH of the solution.

From the similarity of constants for the simpler amine complexes it can be assumed that these two ions are reduced by the same mechanism. The great difference of constants for the EDTA complex illustrates the effect of size and charge of ions undergoing a reduction retarded by an adsorbed film. The value of αn_a for the simpler amines is approximately double that of the EDTA complex. This suggests that the transfer coefficient for each reduction is approximately 0.45 and that the difference between the values of αn_a for the two types of complexes lies in the number of electrons involved in the rate-determining step.

Chloro Complexes of Tin(IV) and Tin(II).—The effect of varying concentrations of camphor upon the reduction of $1.51 \times 10^{-3} M$ stannic chloride in $1 M$ HCl – $4 M$ NH_4Cl is shown in Fig. 6. As the camphor concentration increased or the potential approached the electrocapillary maximum the inhibiting effect became more pronounced, presumably because of the more compact nature of the film. The second wave corresponding to the reduction from tin(IV) to tin(0) was affected to a greater extent because it occurred closer to the electrocapillary maximum and because four electrons were involved.

Non-linear plots of log current density versus electrode potential obtained for the first portion of the wave for SnCl_4 in $1 M$ HCl – $4 M$ NH_4Cl in the presence or absence of camphor were indicative of kinetic complications in the reduction of tin(IV) to tin(II). The height and shape of this wave is dependent upon the total chloride ion concentration.¹⁸ This effect was postulated to be due to the slow reduction of mixed aquo and chloro complexes of tin(IV). The non-linear logarithmic plots indicate that even in high chloride concentration the current is limited not only by the rate of electron transfer but also by the rate of a chemical reaction probably involving the formation of the species which undergoes reduction.

(18) J. J. Lingane, *THIS JOURNAL*, **67**, 919 (1945).

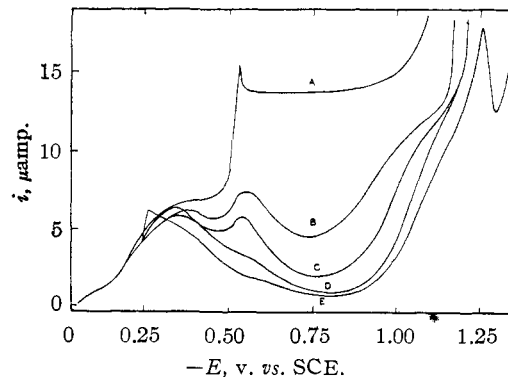


Fig. 6.—Effect of camphor upon the reduction of $1.51 \times 10^{-3} M$ SnCl_4 in $1 M$ HCl – $4 M$ NH_4Cl : curve A, no camphor; curve B, $1 mM$ camphor; curve C, $2 mM$ camphor; curve D, $4 mM$ camphor; curve E, saturated with camphor.

The final current rise starting at about -0.8 volt (SCE*) is due to a mixed reduction of tin(IV) to tin(II) and of hydrogen ions of the supporting electrolyte. The maximum found just before the desorption of camphor (approx. -1.30 volt for a saturated solution) is characteristic of hydrogen discharge. A similar effect was found for residual current curves in the presence of greater than 4 millimolar camphor. This mixed reduction process was also shown by the fact that the current at the peak was greater than the current for total double wave in the absence of camphor. A spectrogram with a d.c. arc showed no metallic tin in a sample of mercury electrolyzed at -1.23 volt (SCE*). The lack of formation of metallic tin as a reduction product of tin(IV), even at potentials beyond the reversible tin(II), tin(0) potential was an indication that the species of tin(II) formed by the electroreduction of tin(IV) was not identical with that present at equilibrium in a tin(II) solution. A partial aquo complexation of tin(IV) would account for this behavior, if the equilibrium between aquo and chloro complexes of tin(II) is not instantaneous. This same reason would account for the kinetic complication found in the first portion of the wave.

Kinetic constants for the reduction of tin(II) in $1 M$ HCl – $4 M$ NH_4Cl saturated with camphor could not be determined because the wave was not completely irreversible. Even at the foot of the wave the current was diffusion controlled. The time dependence of the current was determined by measuring the current as a function of drop time with a constant flow rate of mercury. The current was found to follow an equation of the form

$$i = at^{0.15}$$

The value of the exponent for a diffusion controlled current is 0.167.

Iodate Ion.—The reduction of $0.010 M$ iodate in $0.10 M$ KCl – $0.10 M$ phthalate buffer at pH 3.2 and in a $0.10 M$ KCl – $0.05 M$ borate buffer at pH 9.2 was studied in the presence and absence of camphor and β -naphthol. The results will not be presented in detail,¹⁹ because it was not found possible to make a straightforward interpretation. A few observations, however, are noteworthy.

(19) W. J. Subcasey, Ph.D. thesis, University of Illinois, 1957.

In the acidic buffer, the current density and kinetic parameters were found to vary with time, as might have been anticipated from the fact that iodide, the reduction product of iodate, reacts with iodate to form iodine at pH 3.2. A catalytic cycle, involving iodine as an intermediate, is therefore operative. Moderate stirring caused a decrease in current at a given potential, due to partial removal of iodide. In the alkaline buffer, the current density was essentially independent of time. However, in the presence of camphor, time variations were noted. Also, when enough potassium iodide was added to the borate buffer to make the iodide

concentration 0.10 *M*, variations of current density with time were noted both in the presence and absence of camphor.

Several linear portions were found in each plot of $\log i_c/nFAC_{ox}$ versus electrode potential. The effect of camphor was to increase markedly the apparent value of n_a and to decrease the value of k^0 . From the present results it does not appear possible to assign a single value of n_a , and therefore a single-rate determining reduction step over a wide range of potentials.

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[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY, AND THE OAK RIDGE INSTITUTE OF NUCLEAR STUDIES]

Adsorption Kinetics with Diffusion Control—The Plane and the Expanding Sphere

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Adsorption kinetics with control by diffusion toward a plane and an expanding sphere (dropping mercury electrode) are discussed from computer solutions of the corresponding boundary value problems. The kinetics are characterized by two quantities: D/Γ_m and C^0/a , D being the diffusion coefficient of the adsorbate, Γ_m the surface concentration for full coverage, C^0 the bulk concentration of adsorbate, and a the adsorbate volume concentration for full coverage when the isotherm is identified with its tangent at $C^0 = 0$ (linearized isotherm). It is shown that adsorption equilibrium is practically reached within less than 1 sec. when $C^0 \geq 10a$ (an order of magnitude for values of D and Γ_m generally encountered). The process is somewhat slower for the expanding sphere than for the plane. Coverage for a given C^0 varies fairly linearly with $t^{1/2}$ at the beginning of the adsorption process.

Adsorption kinetics with diffusion control were discussed in previous papers¹ for the simplified cases of either a linearized isotherm or a large volume concentration of adsorbate. It was concluded from theory and experiment that adsorption equilibrium (with respect to the bulk concentration) for concentrations in the segment of the isotherm which can reasonably be linearized is practically reached only after 15–30 minutes. Significant implications in electrochemical kinetics, polarography, surface tension measurements were discussed. Implications in radiotracer techniques also should be mentioned.

An analytical solution for the complete isotherm was not reported and, in fact, would be very difficult to obtain.² However, it was possible to carry out calculations for the complete isotherm with the ORACLE computer at Oak Ridge for diffusion at a plane and an expanding sphere (dropping mercury electrode). These results are summarized below.

Adsorption on a Plane

Influence of Concentration.—In this case which was previously stated^{1a} we consider adsorption on a plane with control by semi-infinite linear diffusion. Conditions for a surface initially free of adsorbate are

$$\begin{aligned} C &= C^0 \text{ for } x > 0 \text{ and } t = 0 \\ C &\longrightarrow C^0 \text{ for } x \longrightarrow \infty \text{ and } t \geq 0 \\ \frac{D}{\Gamma_m} \int_0^t \left(\frac{\partial C}{\partial x} \right)_{x=0} dt &= \frac{C_{x=0}/a}{1 + C_{x=0}/a} \end{aligned} \quad (1)$$

(1) (a) P. Delahay and I. Trachtenberg, *THIS JOURNAL*, **79**, 2355 (1957); (b) **80**, 2094 (1958). A detailed bibliography is given in these papers.

(2) Dr. F. J. Pellicciaro of the University of Delaware investigated this problem at Oak Ridge during the Summer of 1957.

where x is the distance from the interface solid-solution, t the time elapsed since the beginning of the adsorption process, C the volume concentration of adsorbate, C^0 the volume concentration of adsorbate in the bulk of solution (maintained constant for $x \rightarrow \infty$), D the diffusion coefficient of adsorbate (assumed to be independent of C), Γ_m the surface concentration of adsorbate for full coverage and a the parameter of the Langmuir isotherm. Note that a is the concentration for which the surface concentration Γ is equal to Γ_m when the isotherm is identified with its tangent at $C^0 = 0$ (linearized isotherm).

The influence of the quantities C^0/a and D/Γ_m which characterize adsorption kinetics in this case will be studied separately. Results will be expressed as the ratio Γ_t/Γ_e of the surface concentration Γ_t at time t to the surface concentration Γ_e when equilibrium is reached ($\Gamma_t/\Gamma_e \rightarrow 1$ for $t \rightarrow \infty$).

Variations of Γ_t/Γ_e with time for different bulk concentrations are shown in Fig. 1 for the value $D/\Gamma_m = 10^4 \text{ cm.}^4 \text{ sec.}^{-1} \text{ mol.}^{-1}$. This value is quite representative: $D = 5 \times 10^{-6} \text{ cm.}^2 \text{ sec.}^{-1}$; $\Gamma_m = 5 \times 10^{-10} \text{ mole cm.}^{-2}$, *i.e.*, a coverage of approximately 30 sq. ångströms per molecule.

The following conclusions can be drawn from Fig. 1. (a) The rate of attainment of equilibrium coverage (with respect to the bulk concentration) increases with concentration. (b) At very low concentrations, variations of Γ_t/Γ_e with time are hardly dependent on the bulk concentration of adsorbate.³ It was pointed out previously^{1a} that Γ_t/Γ_e , at any time, is independent of the bulk con-

(3) Computations were not made for $C^0/a < 0.01$ because major changes in coding would have been required.