

the same potentials on the polarogram of the diethyldithiocarbamate ion, bis-(diethylthiocarbamyl) disulfide is formed by oxidation at the interface. At potentials where the electrocapillary curve of the ion rises to the electrocapillary curve of the supporting electrolyte solution, the ion is no longer being oxidized to the disulfide. Again capillary activity, *i. e.*, adsorption, is manifested only in presence of the disulfide at the interface.

It may be seen from Fig. 6 that the change in unit interfacial tension, as indicated by drop time, decreases per unit change in concentration when the concentration increases. This indicates approaching saturation of the interface with adsorbed molecules. A similar effect is reflected in the current of the adsorption wave, Tables I and III. In his work with methylene blue, Brdicka observed that the adsorption wave was constant and independent of concentration.

(2) When the current, i_a , of the adsorption wave is equal to or greater than the current of the wave of the free molecules in solution, *i. e.*, $i_a > i_d - i_a$, only one wave is obtained and it appears at the potential of the adsorption wave, Table IV. When $i_a < i_d - i_a$, two waves appear. This effect was observed with methylene blue¹⁰ also.

(3) Brdicka¹⁰ showed that the adsorption current, i_a , is proportional to the time rate of change of surface of the mercury drop which in turn is proportional to the height of the mercury well. The mercury well height is inversely proportional to the drop time. Hence, the adsorption current should be inversely proportional to the drop time. This relation is realized as shown in Table IV.

TABLE IV

C, milli- molar	i_{ads} , ampere	t , sec./drop	$i_{ads} \times t$, coulomb
0.300	0.372×10^{-6}	4.04	1.50×10^{-6}
	$.332 \times 10^{-6}$	4.48	1.49×10^{-6}
	$.286 \times 10^{-6}$	5.30	1.51×10^{-6}

The resolution of the polarographic reduction wave of bis-(diethylthiocarbamyl) disulfide into two separate waves, an adsorption wave and a reduction wave of the free molecules in solution, and the fact that the sum of the waves must be measured to obtain the diffusion current, suggest that the single reduction wave of some organic compounds includes an adsorption wave. The reduction potential of the adsorption wave would not be sufficiently different from the reduction potential of the free molecules in solution to be resolved, but would be sufficiently different from the reduction potential of the free molecules in solution to cause the wave to appear irreversible by the criterion of the log plot. This principle is supported by the appearance of maxima in the middle of some reduction waves which could be explained on the premise that adsorption waves are present and that the maxima are occurring at the top of the waves of the free molecules in solution as in the case of the disulfide.

Acknowledgment.—The authors wish to thank Donald W. Beesing of this Laboratory for his analysis of sodium diethyldithiocarbamate for water of hydration.

Summary

The polarographic properties of the bis-(diethylthiocarbamyl) disulfide–diethyldithiocarbamate ion oxidation–reduction system have been presented. The standard oxidation–reduction potential has been measured as -0.33 volt *vs.* N.H.E. The two-step reduction wave of bis-(diethylthiocarbamyl) disulfide and the two-step oxidation wave of diethyldithiocarbamate ion have been demonstrated to be caused by adsorption of the disulfide at the mercury-solution interface. The ionization constant of the unstable diethyldithiocarbamic acid has been measured: $K_a = 2.9 \times 10^{-6}$ in 60% ethanol by volume at 25.0° .

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

Adsorption and Reduction of Tetrachloroplatinate(II) Ion at the Dropping Mercury Electrode

BY H. A. LAITINEN AND E. I. ONSTOTT¹

Tetrachloroplatinate (II) ion is reduced at the dropping mercury electrode at small values of the applied e.m.f. At more negative potentials, a pronounced decrease in the current is observed. Under certain experimental conditions, an ordinary polarographic wave is observed just before the discharge of the supporting electrolyte.

The early reduction process does not proceed in the presence of camphor at potentials where camphor is adsorbed at the electrode. Since an adsorbed film of camphor has previously been

observed to interfere with the adsorption and reduction of cystine² at the dropping mercury electrode, the early reduction process is best interpreted on the basis that adsorption is necessary for reduction and that desorption of the negatively charged complex ion is responsible for the decreasing current. The later reduction wave is interpreted as an irreversible reduction of the complex ion without adsorption.

Willis³ unsuccessfully attempted to find a

(2) Kolthoff and Barnum, *THIS JOURNAL*, **63**, 520 (1941).(3) Willis, *ibid.*, **67**, 547 (1945).

(1) Abstracted from the Doctorate Thesis of E. I. Onstott, 1950.

reduction wave for tetrachloroplatinate(II) ion, but did not fully describe the experimental conditions.

The influence of adsorption on the reduction of organic compounds has been considered in several publications⁴ but the present example is unusual in representing a negative ion, the desorption of which can be pictured as an electrostatic repulsion.

Experimental

Solutions for analysis were composed from weighed potassium tetrachloroplatinate(II) and from stock solutions of the other constituents. Potassium chloride was added as the weighed solid to the solutions requiring a high concentration of this constituent.

An H-cell having a 20-mm. fine sintered glass plug separating the two compartments was used to avoid traces of agar. In the cathode compartment was placed the solution for analysis, and in the anode compartment was placed a potassium chloride solution having the same concentration as the potassium chloride indifferent electrolyte of the test solution. The liquid level of the cathode compartment was kept about 1 cm. higher than that of the anode compartment in order that the flow of the test solution through the sintered glass plug would be in the desired direction. Actually, the levels of the two compartments did not equalize even after standing for one hour. The reference electrode employed was a bulb type saturated calomel electrode. The a.c. resistance of this type of cell was 720 ohms, using 0.1 N potassium chloride solution with the dropping mercury electrode as one electrode and the saturated calomel electrode as the other electrode.

A cell with a mercury anode in contact with the solution could not be used because the chlorocomplex is reduced to platinum metal by mercury. Because of this reaction, precautions were necessary to insure that the concentration of platinum in the solutions remained reasonably constant. The dropping mercury electrode was not inserted into the solution being freed of oxygen until just prior to recording the polarogram. After recording the polarogram, the solution was discarded.

Oxygen was removed from the solutions with oxygen-free nitrogen. The capillary had an m value of 1.467 mg. sec.⁻¹ for a mercury column height of 89.8 cm. The temperature of the solution at 25° did not deviate more than 0.1°, and the temperature of solutions other than 25° did not deviate more than 0.2°.

A Sargent Model XXI polarograph was used to record automatically the instantaneous current as the voltage changed continuously. For several of the solutions at 25°, average currents were recorded at several points along the polarographic wave by using maximum damping of the Brown recorder at a constant measured potential.

The desorption waves were analyzed by plotting $\log (i_d - i)/i$ vs. E . Currents were corrected for residual current and minimum current, the significance of which is explained in the discussion below. For the most part, maximum currents were used for obtaining the values of $(i_d - i)/i$. This procedure is applicable, since the maximum current of a diffusion controlled process is directly proportional to the average current. The desorption half-wave potentials were taken from the logarithmic plots. Corrections for iR drop of the cell were made. The half-wave potential calculated from maximum current data was generally about 10 mv. more negative than that calculated from average current data for the same solution, although slopes of the logarithmic plots for the two types of data did not differ appreciably. It was felt that data from the automatically recorded polarograms were sufficiently accurate for calculating the values of $(i_d - i)/i$. How-

ever, all diffusion current data reported are average current data.

Discussion

It was established that the current due to the reduction of tetrachloroplatinate(II) is controlled by diffusion. In Table I are listed data for diffusion currents obtained for solutions containing varying amounts of tetrachloroplatinate(II) ion at several temperatures. From the diffusion current constants, $i_d/Cm^{3/2}t^{1/2}$, it is apparent that the current is directly proportional to the concentration of the reducible ion in the bulk of the solution. The variation of the current with temperature, about 1.4% per degree, is evidence that the process is diffusion controlled, since the temperature coefficient for a rate controlled reaction is generally considerably larger. It was also found that the current varied approximately with the square root of the mercury column height, another criterion for concluding that the current is controlled by diffusion.

TABLE I
CONCENTRATION AND TEMPERATURE EFFECTS

Indifferent electrolyte 0.1 N KCl; i_d measured at about -0.7 volt; minimum current measured at -1.2 volt.

K ₂ -PtCl ₆ , millimolar	Slope of log plot	$-E_{1/2}$ vs. S. C. E.	min. i , μ amp.	i_d , μ amp.	$i_d/Cm^{3/2}t^{1/2}$, cm. ^{3/2} /s. ^{1/2}
0.20 ^a	.094	.895	0.08	1.13	3.38
1.00 ^a	.096	.894	.85	5.75	3.42
0.10 ^b	.098	.891	.06	0.66	3.92
.20 ^b	.096	.896	.26	1.35	4.00
.40 ^b	.099	.897	.38	2.76	4.10
1.01 ^c	.100	.894	.82	6.87	4.03
2.02 ^c	.099	.898	1.53	14.00	4.11
0.10 ^b	.095 ^f	.890 ^f	0.06	0.66	3.92
.20 ^b	.098 ^f	.884 ^f	.26	1.35	4.00
.40 ^b	.096 ^f	.887 ^f	.38	2.76	4.10
1.01 ^b	.097 ^f	.887 ^f	.82	6.87	4.03
2.02 ^b	.099 ^f	.883 ^f	1.53	14.00	4.11
0.20 ^a	.103	.889	0.25	1.50	4.46
1.00 ^a	.104	.895	1.48	7.55	4.50
0.20 ^d	.105	.896	0.26	1.60	4.78
1.00 ^d	.106	.895	1.53	8.04	4.80
0.20 ^e	.113	.897	0.37	1.77	5.30

^a 15°. ^b 25°. ^c 35°. ^d 45°. ^e 55°. ^f Calculated from average current data.

The decrease in diffusion current as the potential is increased (Fig. 1) is best explained by assuming that a desorption process occurs, adsorption of the reducible ion being a necessary condition for reduction to occur. In the region of decreasing current, only part of the complex ions reaching the electrode are adsorbed and reduced. At potentials where the current is decreasing, a state of adsorption equilibrium exists, the amount of adsorbed tetrachloroplatinate(II) ion decreasing with increasing potential until all of it is finally desorbed.

In order to predict how the amount of adsorbed reducible ion changes with potential, the

(4) (a) Brdicka, *Coll. Czech. Chem. Comm.*, **12**, 522 (1947); *Chem. Listy*, **38**, 252 (1944); *Z. Elektrochem.*, **48**, 278 (1942); **46**, 686 (1942); (b) Kolthoff and Lehmicke, *This Journal*, **70**, 1879 (1948); (c) Stock, *J. Chem. Soc.*, 586, 783 (1949).

thermodynamics of adsorption equilibrium must be considered. Suppose that a surface phase A at an electrical potential ψ_a having a surface concentration C_a of adsorbed negative ions with a charge z is in contact with a solution phase B at an electrical potential ψ_b having a concentration C_b of unadsorbed ions.

At equilibrium, the electrochemical potential of tetrachloroplatinate(II) ion the two phases will be equal

$$\mu_a + zF\psi_a = \mu_b + zF\psi_b \quad (1)$$

In the solution phase, the chemical potential may be expressed in terms of surface concentration

$$\mu_b = k_b + RT \ln C_b f_b \quad (2)$$

where f_b is the activity coefficient of ions at concentration C_b .

According to Fowler and Guggenheim⁵ the free energy of a non-localized monolayer of adsorbed molecules on a surface is

$$F_{ads} = kTN \ln (JN/A) - kTN \quad (3)$$

where k is the Boltzmann constant, T is the temperature, N the number of molecules adsorbed on surface area A , and J is a constant depending on the nature of the adsorbed molecules, the nature of the surface and the temperature. In their derivation of this equation, Fowler and Guggenheim assumed that the adsorbed molecules do not interact. If this equation holds for adsorbed ions, then an expression for the chemical potential is obtained by taking the derivative of F_{ads} with respect to N

$$\mu_a = dF_{ads}/dN = kT \ln (JN/A) \quad (4)$$

By depicting N in terms of surface concentration, the above equation may be written

$$\mu_a = k_a - RT \ln A + RT \ln C_a f_a \quad (5)$$

where k_a includes a constant for converting N to molar surface concentration, and f_a the activity coefficient of the adsorbed ion, is used to account for deviations from ideality. By combining equations (1), (2) and (5), and setting $(\psi_a - \psi_b)$ equal to E , the following equation is obtained

$$E = (k_b - k_a)/zF + RT/zF \ln(f_b/f_a) + RT/zF \ln A + RT/zF \ln (C_b/C_a) \quad (6)$$

In order to use this equation for the interpretation of polarographic data, it is necessary to express the concentrations of the adsorbed ion and the ion in the solution phase in terms of current. The concentration of the adsorbed reducible ion will be directly proportional to the current, assuming for tetrachloroplatinate(II) ion that the platinum metal and chloride ions liberated on reduction do not influence the adsorption equilibrium. The concentration of reducible ion at the electrode surface will be proportional to $(i_d - i)$. Putting these relations into equation (6) and setting z equal to minus two for the charge of the

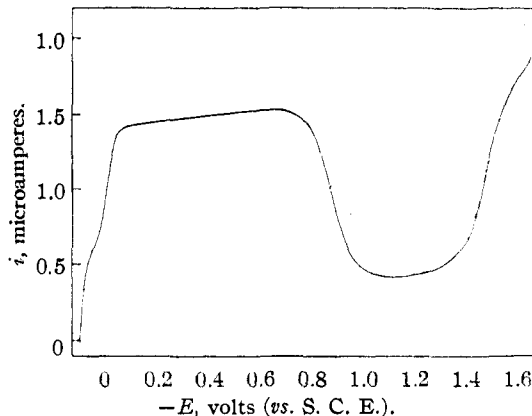


Fig. 1.—Polarogram of $2 \times 10^{-4} M K_2PtCl_4$, $0.1 M KCl$.

tetrachloroplatinate(II) ion, and changing to logarithms to the base ten, the following equation is obtained for a temperature of 25°

$$E = K - 0.0296 \log(f_b/f_a) - 0.0296 \log A - 0.0296 \log(i_d - i)k_1/ik_2 \quad (7)$$

The constant k_2 is a proportionality constant related to the Ilkovic equation, as the concentration of unadsorbed reducible ion at the electrode surface is determined by diffusion of the reducible ion, but the constant k_1 does not have the same sense. It is a proportionality constant relating surface concentration and current. By combining constant terms, equation (7) may be written in terms of a "desorption half-wave potential"

$$E = E_{1/2}^d - 0.0296 \log(i_d - i)/i \quad (8)$$

This equation, which is the same as the expression describing the shape of the wave for the reduction of a divalent metal ion soluble in mercury except for the sign on the last term, can be used to predict the shape of the desorption wave and to test the reversibility of the electrode reaction. A plot of $\log(i_d - i)/i$ vs. E should give a straight line plot having a slope of 0.0296, and the desorption half-wave potential should be independent of the concentration of tetrachloroplatinate(II) ion.

In choosing experiments to test equation (8), it was decided to use potassium chloride as the indifferent electrolyte in order to make the complex ion more stable and to keep the concentration of chloride ion at the electrode surface constant, since chloride ion is liberated in the reduction process. The concentration of tetrachloroplatinate(II) ion was varied, and the temperature also was varied. In Table I are data collected from these experiments. To obtain a straight line plot in testing equation (8), it was necessary to correct the current values for the minimum current which is produced in the region of the flat portion of the polarographic curve after desorption has taken place. The fact that the concentration of reducible ion at the electrode does not

(5) Fowler and Guggenheim, "Statistical Thermodynamics," Cambridge University Press, London, 1939.

become equal to that in the bulk of the solution probably means that a normal reduction process is going on; that is, a certain percentage of tetrachloroplatinate(II) ions diffusing to the electrode are reduced without being adsorbed. It will be shown later that this complex ion actually is reduced irreversibly at more negative potentials, and this minimum current may be the tail end of the normal reduction wave. In making this correction, however, it must be assumed that the minimum current remains reasonably constant from the potential where the diffusion current is measured to the potential where the minimum current is measured.

The slopes of the logarithmic plots were constant for one temperature, and varied with temperature approximately as would be expected, but their values were higher than would be predicted. Such deviations usually are attributed to non-reversibility of the electrode reaction, and a similar interpretation here may be in order.

The desorption half-wave potential appeared to be independent of the tetrachloroplatinate(II) ion concentration and of temperature in the temperature range studied, provided the chloride ion concentration was held constant. An increase in the chloride ion concentration had the effect of making the desorption wave occur at more negative potentials. Increasing the chloride ion concentration also caused the normal irreversible reduction of tetrachloroplatinate(II) ion to occur at more positive potentials. With 0.1 *N* potassium chloride, the normal reduction wave blended with the potassium ion discharge wave so that a diffusion current region was not readily discernible (Fig. 1), but when the potassium chloride concentration was increased to one molar, a distinct diffusion current region was observed (Fig. 2), and the desorption wave blended with the normal reduction wave before the desorption process was complete. A further increase in the potassium chloride concentration to 4 molar had the effect

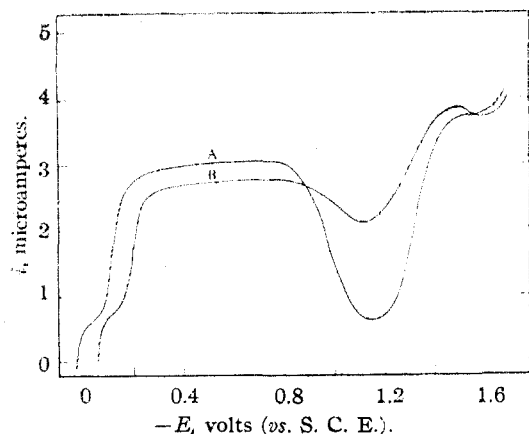


Fig. 2.—Polarograms of $4 \times 10^{-4} M K_2PtCl_4$: curve A, in 1.0 *M* KCl; curve B, in 4.0 *M* KCl.

of making the diffusion current of the desorption wave almost continuous with that of the normal reduction wave (Fig. 2). However, the current of the wave following the desorption wave was higher than would be expected for the reduction of tetrachloroplatinate(II) ion. The additional current undoubtedly was caused by the anomalous reduction of water, a phenomenon which has been observed by Orlemann and Kolthoff⁶ quite generally in solutions containing a very high concentration of indifferent electrolyte in the presence of substances which undergo reduction at more positive potentials.

The effect of chloride ion concentration on the desorption half-wave potential may be qualitatively accounted for by the fact that the overvoltage for the "normal" reduction is decreased by increasing chloride concentration. If the overvoltage is pictured in terms of an energy barrier for reduction, the effect of adsorption of the complex is to decrease the activation energy. With increasing chloride concentration a smaller net free energy of adsorption suffices to overcome the energy barrier for reduction, and therefore the adsorption reduction can proceed at more negative potentials. A complicating factor is the adsorption of chloride ion itself, and its desorption in the same potential range at which the diminishing current is observed. The abnormal slopes of the desorption waves may in part be caused by changes in free energy of adsorption due to desorption of chloride ion.

There appears in equation (7) a term containing the symbol *A* which denotes the area available for adsorption. In equation (8) this term is combined with the other constants to give a single term expressing the desorption half-wave potential, but it can be conveniently segregated in order to predict the effect of changing the area available for adsorption by adding a material which is strongly adsorbed on the dropping mercury electrode. By writing

$$E = E_{1/2}^0 - 0.0296 \log A - 0.0296 \log (i_d - i)/i \quad (9)$$

and taking *A* to be unity in the absence of the strongly adsorbable material, the change in the desorption half-wave potential with a change in *A* can be qualitatively explained. A quantitative interpretation should not be attempted, as the adsorption process was not shown to be reversible. The addition of a material which is strongly adsorbed should shift the desorption wave to more positive potentials by reducing the average area available for adsorption of reducible tetrachloroplatinate(II) ion.⁷

Results of experiments carried out to test equation (9) are summarized in Table II. A

(6) Orlemann and Kolthoff, *This Journal*, **64**, 833 (1942).

(7) The presence of an adsorbed layer might also be expected to diminish the rate of adsorption of the complex ion per unit area of uncovered surface, and to decrease the free energy of adsorption. These effects likewise would cause a shift of the desorption wave to more positive potentials.

saturated solution of camphor had a large effect, shifting the desorption wave in the positive direction as is shown in Fig. 3. The magnitude of the current after desorption occurred was the same as the residual current (Fig. 3) until the camphor was desorbed at a potential of about -1.3 volt, where the current suddenly jumped to the value it would have if no camphor were present. This effect of saturated camphor preventing a reduction process from proceeding until it is desorbed was observed by Kolthoff and Barnum² in studying the reduction of cystine at the dropping mercury electrode. As the camphor concentration was decreased, the shift in the desorption half-wave potential became less pronounced, and the potential at which camphor was desorbed became more positive. In curve C is shown a striking example of adsorption phenomena. Here the presence of camphor caused tetrachloroplatinatate(II) ion to be partially desorbed, but the desorption of camphor itself occurred at a potential positive enough so that re-adsorption and subsequent desorption of the complex ion could occur. At the more negative potential the normal reduction wave of tetrachloroplatinatate(II) ion was observed.

TABLE II

Temperature 25° ; i_d measured at about 0.2 volt more positive than the desorption half-wave potential; minimum current measured at -1.2 volt.

K ₂ PtCl ₆ , milli- molar	Added adsorbent	Slope of log plot	$-E^{d/2}$ vs. S. C.		i_d , μ amp.	i_d , μ amp.	i_d / $t^{1/2}$, cm. ² /s
			E	min. i , μ amp.			
0.40 ^a	None	0.099	0.897	0.38	2.76	4.10	
.99 ^b	None98 ^d	..	6.78	4.06	
.40 ^b	None98 ^d	..	2.71	4.06	
.40 ^b	0.01% gel	.118 ^c	.915 ^c	.15	2.73	4.09	
.99 ^a	.01% gel	.098	.907	.49	6.89	4.09	
.99 ^a	.01% gel	.101 ^c	.894 ^c	.49	6.89	4.09	
.40 ^a	.01% agar	.099	.834	.16	2.70	4.01	
.40 ^b	.01% agar	.137	.892	.19	2.69	4.00	
1.01 ^a	Satd. octyl alc.	.077	.400	0	6.78	4.02	
0.99 ^b	Satd. octyl alc.42 ^c	
.10 ^b	Satd. camphor33 ^c	
.40 ^a	0.01% camphor	.087	.495	0	2.68	3.99	
.40 ^b	.01% camphor	.115	.545	0	2.73	4.07	
.20 ^b	.004% camphor	.097	.553	

^a 0.1 N KCl in different electrolyte. ^b 1.0 N KCl in different electrolyte. ^c Calculated from average current data. ^d Approximated from polarograms.

The potentials at which camphor is adsorbed and desorbed are readily ascertained from the residual current curve shown in Fig. 5. Before the camphor is adsorbed, the residual current has the same value it would have if camphor were not present, but at the potential camphor is adsorbed, the current suddenly increases. Desorption of the camphor also causes the current to increase suddenly to the value it shows when camphor is absent. In the potential range where camphor is adsorbed the residual current is almost constant, as the capacity of the double layer is greatly decreased by the adsorption of camphor. The slope of the residual current curve is pro-

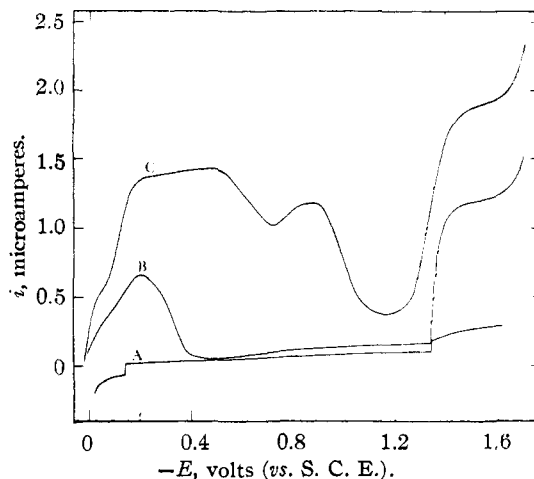


Fig. 3.—Polarograms in 1.0 M KCl: curve A, blank, saturated with camphor; curve B, 1×10^{-4} M K_2PtCl_6 , saturated with camphor; curve C, 2×10^{-4} M K_2PtCl_6 , 0.002% camphor.

portional to the capacity of the double layer. Decreasing the camphor concentration has the effect of making the surge in current less abrupt, and diminishing the range of potential in which the camphor is adsorbed. Shikata and Watanabe⁸ and Taschi⁹ have previously observed the effect of camphor on the residual current. A similar adsorption phenomenon was observed by Heyrovsky and co-workers,¹⁰ who found that the desorption of pyridine from a dropping or streaming mercury electrode brings about a sudden increase in the residual current.

Saturated octyl alcohol also shifted the desorption half-wave potential markedly in the positive direction. Agar (0.01%) had a similar but less pronounced effect. Gelatin (0.01%) however, shifted the desorption half-wave potential about 10 millivolts in the negative direction when the chloride ion concentration was 0.1 molar. With one molar chloride ion the desorption half-wave potential was shifted by gelatin in the expected direction.

Organic compounds adsorbed on the dropping mercury electrode decrease the surface tension of the mercury drops, and the drop time becomes shorter than it would be in the absence of an adsorbed compound. Adsorbed ions have a similar but less pronounced effect. Tetrachloroplatinatate(II) ion, however, did not appear to change the drop times by appreciable amounts. The concentrations used in the polarographic experiments probably were not great enough to effect a measurable change in the drop time. Even at best this method of detecting adsorption phenomena is not a sensitive one.

(8) Shikata and Watanabe, *J. Agric. Chem. Soc. Japan*, **5**, 904 (1929).

(9) Taschi, *Mem. College of Agric., Kyoto Imp. Univ.*, No. 22, 4-2 (1938).

(10) Heyrovsky, Sorm and Forjet, *Coll. Czech. Chem. Comm.*, **12**, 11 (1947).

Little attention was given to the adsorption reduction wave occurring at the more positive potential or to the normal reduction wave occurring at the more negative potential, as the main interest was in the desorption wave. It was noted, however, that the potential where the adsorption reduction wave starts shifted to more negative values as the chloride ion concentration was increased, while the potential of the "normal" reduction process changed in the positive direction.

The effect of increasing concentration of chloride ion on the half wave potential for the normal reduction is opposite to the expected behavior for a reversible reduction process. For the irreversible reduction of chloro complexes, the effect of increasing chloride ion concentration is often to diminish the overvoltage, as has been previously observed by Lingane¹¹ in his study of the chloro complexes of tin and by Lingane and Nishida¹² in their work on the chloro complexes of antimony.

That the normal reduction process is highly irreversible is shown by the fact that the reciprocal slope of the linear plot of $\log(i_{dl} - i)/i$ for a solution containing 0.4 millimolar tetrachloroplatinate(II) ion, one molar potassium chloride and 0.01% agar was 0.102. The large overvoltage, shown by the half-wave potential of -1.35 volts, is itself evidence for an irreversible

process. In fact, if the overvoltage were not so large, the phenomenon of the adsorption reduction wave undoubtedly could not have been observed.

Summary

1. It is shown that tetrachloroplatinate(II) ion must be adsorbed on the dropping mercury electrode to be reduced at potentials more positive than about one volt (*vs.* S.C.E.).

2. The desorption wave is described, and an equation expressing the desorption half-wave potential is derived. The desorption process does not appear to be reversible, although the desorption half-wave potential is independent of the solution tetrachloroplatinate(II) ion concentration.

3. Added adsorbents shift the desorption half-wave potential to more positive values by decreasing the effective area available for adsorption of tetrachloroplatinate(II) ion, and perhaps by changing the free energy and kinetics of adsorption.

4. Tetrachloroplatinate(II) ion in potassium chloride indifferent electrolyte shows a normal irreversible reduction wave which has a half-wave potential of -1.35 volt (*vs.* S.C.E.) for one molar potassium chloride. The half-wave potential shifts to more positive values as the chloride ion concentration is increased.

(11) Lingane, *THIS JOURNAL*, **67**, 919 (1945).

(12) Lingane and Nishida, *ibid.*, **69**, 530 (1947).

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE DEPARTMENT OF GEOLOGY, UNIVERSITY OF CHICAGO]

Immiscibility in the System $H_2O-Na_2O-SiO_2$ ¹

BY IRVING FRIEDMAN²

Introduction

A previous paper³ dealing with this system showed that liquid immiscibility existed from about 225° up to the highest temperature investigated, 350°. The unusual character of this system as compared to the $H_2O-K_2O-SiO_2$ system, plus the fact that an understanding of the relationships in this system is basic to the study of the petrologically important $H_2O-Na_2O-SiO_2-Al_2O_3$ system, prompted a continuation of this work to temperatures above the critical temperature of water.

Experimental

All of the mixtures used in this research were made from the same materials that were used in the previous

work. The experimental procedures were also quite similar. In order to secure more rapid quenching than had previously been possible, a quenching apparatus was constructed consisting of a coil of $1/2$ " copper tubing, the i. d. of the coil being a little greater than the o. d. of the bombs. The tubing has numerous small holes bored facing the inside of the coil. Both ends of the copper tubing are connected through a valve to the cold water supply. The hot bombs are dropped into the coil and the cold water turned on. The numerous water jets cool the bomb from 450° to below 100° in about fifteen seconds.

The bombs previously used developed cracks, usually longitudinal in direction, when used at the higher temperatures with these alkaline solutions. Most of the cracks were through the thickest part of the bombs, and were not due to pressure failure. In all about 24 stainless steel (303) bombs leaked through material failure. That the alkaline solutions were responsible is shown by the fact that several bombs used by Bowen and Tuttle on the $MgO-SiO_2-H_2O$ system have withstood years of use, while other bombs constructed from the same bar of steel and used on the $H_2O-Na_2O-SiO_2$ system by Morey have shown cracks after several hours or days of use. Recently, another worker⁴ noticed the same failure. It has been suggested that slag inclusions, leached out by the alkaline solutions, has caused the failures.

To overcome the above difficulty, bomb bottoms were

(1) This work was supported by the Office of Naval Research under contract N6 o. r. i. 20, T. O. 21. For detailed material supplementary to this article order Document 2814 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting \$0.50 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or \$0.70 for photocopies (6 × 8 inches) readable without optical aid.

(2) Institute for Nuclear Studies, University of Chicago, Chicago, Ill.

(3) O. F. Tuttle and I. I. Friedman, *THIS JOURNAL*, **70**, 919 (1948).

(4) J. W. Gruner, University of Minnesota, personal communication.