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

Polarographic Study of the Effect of Gelatin on the Kinetics of Irreversible Electrode Processes

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The effect of gelatin on the kinetics of various irreversible electrode processes is interpreted quantitatively on the basis of a previously developed theory of irreversible polarographic waves. The presence of gelatin causes a decrease of the product αn_α (α transfer coefficient, n_a number of electrons involved in the rate-determining reaction), and this may result, in some cases, in the stabilization of an intermediate substance in an electrode process. The present interpretation is correlated to the conclusions of previous investigations on the effect of gelatin on the characteristics of polarographic waves. Experimental data are presented.

The effect of gelatin on the characteristics of polarographic waves has been the object of several investigations among which those of Meites and Meites are probably the most extensive.[1] It is generally observed that waves become flatter and are shifted toward more negative potentials (for cathodic waves) as the concentration of gelatin is increased. Sometimes, the split of a wave into two waves is also observed.[1] Two explanations have been advanced, which attribute these effects of gelatin either to adsorption of gelatin at the electrode surface or to the binding of the reducible substance with gelatin. In addition to these two interpretations, the possible influence of gelatin on the kinetics of the electrode process should not be overlooked. It was recently observed that the transfer coefficient for the reduction of iodate ion at the dropping mercury electrode is markedly decreased when gelatin is present in solution.[2] It could, of course, be argued that an interpretation solely based on the kinetics of the electrode process is misleading and that complexation with gelatin cannot be disregarded. It is in order to throw some light on this matter, that the present investigation was undertaken. In the course of this work a slightly modified form of the theory of irreversible waves previously developed[2,3] will be applied. This will be first discussed.

Variations of Rate Constant with Potential

In previous papers from this Laboratory[2,3] it was shown how one can determine from experimental waves, the relationship between the electrode potential and the rate constant for irreversible electrode processes. In the next step of the theory, the variations of the rate constant with the electrode potential are interpreted on the basis of the absolute rate theory. For this purpose, it is assumed that there is an equilibrium between the activated complex and the reducible or oxidizable substance in solution. In the writing of the corresponding equilibrium condition it is necessary to take into account the electrical work corresponding to the transfer of the number of electrons (n_a) involved in the rate-determining reaction. This electrical work is equal to the product of the electrical charge involved by the difference of electrical potential from the bulk of the solution to the activation position, and it can be written in the following two different forms: (1) As the product of $\alpha n_a F\eta$, where α is the transfer coefficient, n_a the number of electrons involved in the activation step, F the faraday and η the overvoltage. (2) As the product $\alpha\eta_a FE$, where E is the electrode potential referred to the normal hydrogen electrode. The former expression of the electrical work which is used in hydrogen overvoltage studies was applied in our previous paper.[2] However, by using such a relationship, it is implicitly assumed that only a fraction of the overvoltage helps to overcome the energy barrier. It seems more logical, however, to assume that it is a fraction of the total difference of potential from electrode to solution that is involved. The latter method will be applied here and the following equation will be used for the rate constant k[4]

$$k = \frac{\mathrm{k}T}{h}\,\delta \exp \frac{-\Delta G^{\ddagger} + \alpha n_a FE}{RT} \qquad (1)$$

where k is the Boltzmann constant, h the Planck constant, T the absolute temperature, δ the average distance between two molecules or ions of the substance reacting at the electrode, $\Delta G^{\ddagger}$ the free energy of activation for the electrode process, n_a the number of electrons involved in the rate-determining step, F the faraday, R the gas constant, E the potential *versus* the normal hydrogen electrode and α the transfer coefficient. Since the relationship between the rate constant k and potential E can be determined from experimental data,[5] it is possible to calculate $\Delta G^{\ddagger}$ and αn_a by application of equation (1). This procedure is applied in the present paper.

Experimental

Waves were determined either point by point with a Sargent polarograph Model III, or with a recording polarograph Sargent Model XXI. In the former case the potential of each point was measured with a Leeds and Northrup student potentiometer; in the latter case the potential axis was calibrated with the same student potentiometer. In all cases, results were corrected for the ohmic drop. An H-cell[6] was used throughout the work. Unless otherwise specified the concentration of reducible substance was 1 millimole per liter, and the temperature was 35 ± 0.1° The rate of flow of mercury and the drop time were as follows. In the study of *p*-nitroaniline and hexaquonickel ion, m was 2.04 mg. sec.$^{-1}$ at $E = -1.5$ volts (*vs.* S.C.E.). Drop times were measured at a potential corresponding to a point in the upper plateau of the wave. No single value

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(1) L. Meites and T. Meites, THIS JOURNAL, **73**, 177 (1951). References to other investigations on the effect of gelatin are given in this paper.

(2) P. Delahay and J. E. Strassner, *ibid.*, **73**, 5219 (1951).

(3) P. Delahay, *ibid.*, **73**, 4944 (1951).

(4) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 575-577.

(5) For a detailed discussion see ref. 2 and 3.

(6) J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem.*, *Anal. Ed.*, **11**, 504 (1939).

of t can be reported for each substance because the waves were shifted toward more negative potentials as the concentration of gelatin was increased, and this resulted in a variation of the drop time. Extreme values of t for the above substances were 2.02 and 3.01 sec. In the reduction of zinc tetrammine ion, m was 1.51 mg. sec.$^{-1}$ at $E = -1.6$ volts (*vs.* S.C.E.) and t varied from 2.89 to 3.18 sec. Waves were analyzed according to the method previously reported[2] and the values of $\Delta G^{\ddagger}$ and αn_a were calculated as indicated in the previous section.

Description and Discussion of Results

Data will be presented and discussed for the reduction of zinc tetrammine ion, hexaquonickel ion and *p*-nitroaniline.

Reduction of Zinc Tetrammine Ion.—The reduction of $Zn(NH_3)_4^{++}$ is irreversible, and it was found by oscillographic polarography (Sevcik method)[7] that the overvoltage for the reduction of this ion on mercury is sufficiently high to make it permissible to apply the theory of irreversible waves previously developed.[8] Linear log k *vs.* E plots were obtained and the free energies of activation and products αn_a (α transfer coefficient, n_a number of electrons in the rate-determining step) are listed in Table I. From these values of αn_a it is seen that there is a marked decrease in the value of αn_a as the concentration of gelatin is increased. If the electrode process is controlled by the rate of a single electrochemical reaction, n_a is an integer, and variations of αn_a are to be attributed to a change of α. On the other hand, if the rate of the over-all electrode process is controlled by the kinetics of simultaneous or consecutive electrochemical reactions, the value of n_a obtained from polarographic data represents an *apparent* number of electrons which is by no means a definite constant. Under these conditions, variations of αn_a can be caused by changes of α and n_a. In the present case, it is not possible to decide whether it is α or n_a or both parameters which vary when the concentration of gelatin is changed, but it can be concluded that the kinetics of the electrode process is affected by the presence of gelatin. Rather than to ascribe the effect to a change in one of the parameters α or n_a, it is safer to characterize the kinetics of the electrode process in terms of the product αn_a. Since the kinetics of an electrode process is determined by the conditions at the surface of the electrode, it is logical to assume that the adsorption of gelatin at the electrode surface is the primary cause of the effect of gelatin in the present case. In this connection it should be noted that Meites and Meites[1] questioned very seriously interpretations in which the effect of gelatin is explained on the basis of an adsorption effect. Their argument is that certain substances such as methyl red affect the polarographic characteristics of an electrode process in a range of potentials in which these substances are not surface-active. A possible answer to this point, however, is that methyl red may appear to be surface-inactive, but that actually it is sufficiently adsorbed at the electrode surface to influence the kinetics of the electrode process.

TABLE I

DEPENDENCE OF $\Delta G^{\ddagger}$ AND αn_a ON THE CONCENTRATION OF GELATIN

Solution	Concentration of gelatin, %	$\Delta G^{\ddagger}$, kcal.	αn_a
10^{-3} *M* zinc in 2 *M* NH_4OH 2 *M* NH_4Cl	0.001	41.6	1.07
	.01	37.0	0.93
	.1	37.9	.88
10^{-3} *M* nickel in 1 *M* KNO_3	.001	24.1	.56
	.005	21.8	.45
	.01	19.5	.32

Another possible interpretation is that zinc forms a complex with gelatin, but this can be discounted on the following ground. Zinc tetrammine ion is relatively stable since its unstability constant is $10^{-9.6}$ according to Charlot.[9] Furthermore, the concentration of gelatin is extremely small as compared to that of ammonia (2 molar). Since, as was pointed out by Meites and Meites,[1] in a 1 millimolar solution of a cation containing $5 \times 10^{-3}\%$ of gelatin there are approximately 17 moles of metal per equivalent of gelatin, it can be seen that complexation by gelatin can be disregarded at least for the 0.001 and 0.01% solutions and possibly for the 0.1% solution.

The present conclusion as to the influence of gelatin on the kinetics of electrode processes is to be correlated with investigations on the effect of adsorption corrosion inhibitors on the mechanism of hydronium ion discharge. Here also it is found that the overvoltage is increased because of adsorption of the inhibitor on the metallic surface.[10]

Reduction of Hexaquonickel Ion, $Ni(H_2O)_6^{++}$.—Data for the reduction of $Ni(H_2O)_6^{++}$ in presence of gelatin are presented in Table I. Note that there is a very large variation of αn_a as the concentration of gelatin is changed even in relatively narrow limits. The above discussion is applicable to the present case except for the possibility of complex formation between nickel (+2) and gelatin. Thus, the effect of gelatin could result from complexation and from a variation of αn_a. Notice that the change of αn_a for hexaquonickel ion is far more pronounced than that for zinc tetrammine ion (Table I).

Reduction of *p*-Nitroaniline.—The effect of gelatin on the polarographic behavior of *p*-nitroaniline is of special interest with regard to the ideas which are advanced in the present paper. Tanaka and Kobayashi recently reported[11] that the single wave observed in the reduction of *o*- or *p*-nitroaniline is split into two waves when gelatin is used as a maximum suppressor at concentrations higher than 0.01%. It was observed that the ratio of the limiting currents of the two waves varies with the concentration of gelatin, and this observation led the authors to the conclusion that the occurrence of two waves could not be accounted for by the formation of an intermediate product. This view is questioned in the present paper, and a new interpretation based on the kinetics of the electrode process is discussed.

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(7) A. Sevcik, *Collection Czechoslov. Chem. Communs.*, **13**, 349 (1948).

(8) See conditions of application of this theory in ref. 2.

(9) G. Charlot "Théorie et Méthode Nouvelle d'Analyse Quantitative," 3rd Ed., Masson et Compagnie, Paris, 1949, p. 195. The source of this datum is not quoted by the author.

(10) See for example J. O'M. Bockris and B. E. Conway, *J. Phys. Colloid Chem.*, **53**, 527 (1949); J. Elze and H. Fischer, *J. Electrochem. Soc.*, **99**, 259 (1952).

(11) N. Tanaka and Kobayashi, *Bull. Chem. Soc. Japan*, **24**, 132 (1951).

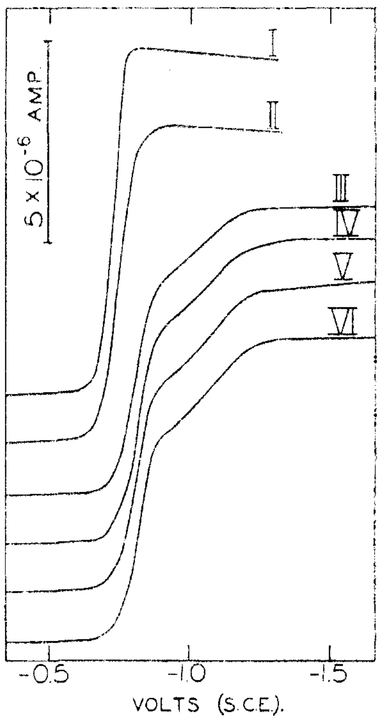

Fig. 1.—Waves of *p*-nitroaniline in universal buffer of *p*H 8.5 in presence of various concentrations of gelatin. Waves are shifted arbitrarily along vertical axis. Concentrations of gelatin: I, 0.005%; II, 0.01%; III, 0.05%; IV, 0.1%; V, 0.5%; VI, 1%.

Polarograms of *p*-nitroaniline for various concentrations of gelatin are shown in Fig. 1. These waves were recorded with a 0.5 millimolar solution of *p*-nitroaniline in the Britton and Robinson universal buffer[12] of *p*H 8.5. The buffer was made 0.5 molar in potassium nitrate in order to decrease the resistance of the cell. Log *k* *vs.* *E* diagrams are shown in Fig. 2 for various concentrations of gelatin. Notice that log *k* varies linearly with potential *E* at low concentrations of gelatin (curve I), but that a marked curvature is present at high concentrations of gelatin. Such a curvature is characteristic of kinetic complications (see below). From the linear segment of the log *k* *vs.* *E* curves of Fig. 2, one calculates the data of Table II.

TABLE II

$\Delta G^{\ddagger}$ AND αn_a FOR THE REDUCTION OF *p*-NITROANILINE AT *p*H 8.5

Concentration of gelatin, %	First wave		Second wave	
	$\Delta G^{\ddagger a}$	αn_a	$\Delta G^{\ddagger a}$	αn_a
0.05	25.8	1.08	..	..
.01	23.0	0.81	..	..
.05	23.0	.72	20.3	0.37
.1	22.4	.66	19.1	.30
.5	21.5	.60	19.6	.31
1.0	21.5	.60	19.3	.30

[a] In kcal.

From the value of $\Delta G^{\ddagger}$ and αn_a of Table II, it is possible to explain the effect of gelatin on the reduction of *p*-nitroaniline in the following manner.

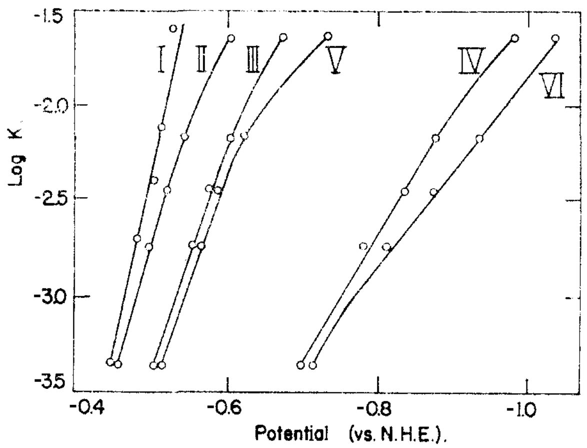

Fig. 2.—Variations of logarithm of rate constant with potential for the reduction of *p*-nitroaniline at *p*H 8.5. Concentrations of gelatin: I, 0.005%; II, 0.01%; III (1st wave) and IV (2nd wave), 0.05%; V and VI, 1%.

At concentrations of gelatin of the order of 0.01% or less, the activation step for the electrode process involves 2 electrons (αn_a between 0.8 and 1.1), and the over-all reduction of the nitro group goes to the amine. The rate determining step in the reduction of *p*-nitroaniline is probably the formation of the nitroso derivative, which corresponds to a two electron transfer. The subsequent reduction of the nitroso group to the amine would then proceed at a rate which is much larger than that of the reduction of the nitro to the nitroso group. As the concentration of gelatin is increased a step, subsequent to the formation of the nitroso derivative, becomes slower, and an intermediate product appears in solution. The reduction of this intermediate substance occurs at more cathodic potentials and, as a result, a second wave is observed. To this second wave corresponds the value αn_a = 0.3 which indicates a one electron transfer rate-determining step.

The appearance of a second wave in the reduction of *p*-nitroaniline can be explained by assuming that the kinetics of the electrode reaction is markedly affected by gelatin. Thus, the transfer coefficient and possibly the free energy of activation for the reduction of the intermediate compound corresponding to the plateau of the first wave are affected by the addition of gelatin in such a manner as to decrease the rate of reduction of this intermediate compound at a given potential. Therefore, the present interpretation follows the same lines as the discussion of the effect of gelatin on inorganic substances such as zinc tetrammine ion. It should be added that the effect of gelatin in the case of *p*-nitroaniline could also be interpreted by assuming that the intermediate product corresponding to the plateau of the first wave is bound very strongly to gelatin. The binding of various substances by protein was observed by Fiess and Klotz[13] for various compounds. In the present case, however, such a binding should be extremely strong to account for the large shift in potential. Actually, it is possible that the binding by gelatin favors the split of the wave although it should be

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(12) H. T. S. Britton, "Hydrogen Ions," Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1943, p. 313, Table 88 C.

(13) H. A. Fiess and I. M. Klotz, THIS JOURNAL, **74**, 887 (1952).

recalled that variations of αn_a are also observed when complexation with gelatin is very unlikely (see the case of zinc tetrammine ion).

Conclusion

The present investigation suggests that the presence of gelatin affects the kinetics of electrode processes at the dropping mercury electrode. Modification of the shape of irreversible waves can be interpreted on the basis of a variation of the product αn_a (α transfer coefficient, n_a number of electrons involved in the rate-determining step). This was shown in an experiment—the reduction of zinc tetrammine ion—in which the formation of a complex with gelatin was rather improbable. Thus, the adsorption of gelatin on the electrode can be interpreted quantitatively in terms of a variation of the product αn_a. The free energy of activation is affected to a lesser extent than αn_a.

It should be emphasized that it is not implied here that binding of gelatin with the substance reacting at the electrode is to be disregarded. There is substantial proof[14] that such binding may affect the polarographic characteristics for an electrode process. Such an effect of the binding by gelatin, however, should not be regarded as responsible for the effect of gelatin in all cases.

What has been said for irreversible electrode processes involving large overvoltages can be extended to quasi-reversible electrode reactions, since the present interpretation is valid regardless of the degree of irreversibility of the reaction. The method of interpreting the wave which was used here, however, is not applicable to quasi-reversible waves. The validity of the present interpretation in the case of quasi-reversible waves is strengthened by the interesting results obtained by Wiesner[15] in the reduction of 1,2-naphthoquinone-4 sulfonate in presence of eosin. Finally, it should be added that the present conclusions can be extended to other maximum suppressors. It was indeed observed by Meites and Meites[1] that various maximum suppressors cause effects similar to those obtained in presence of gelatin.

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[14] For a bibliography, see ref. 1.

[15] K. Wiesner, *Collection Czechoslov. Chem. Communs.*, **12**, 594 (1947).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, GLASGOW]

Aromatic Hydrocarbons. LXIII. Resonance Restriction and the Absorption Spectra of Aromatic Hydrocarbons[1]

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A systematic study has shown that in uniplanar aromatic hydrocarbons the ratio of the frequencies of the α- and β-bands is constant $\nu\alpha:\nu\beta = 1:1.35$. In the case of hydrocarbons with a high degree of overlapping of hydrogen atoms, the loss of resonance energy in the strained molecule becomes apparent by a decrease in this ratio.

The absorption bands of aromatic hydrocarbons have been classified into α-, β- and para-bands.[2]

(1) para-Bands are those which shift most strongly to the red with linear annulation, *i.e.*, fusion of benzene rings. They are, for example, the long wave bands in anthracene and the higher acenes, and the second group of bands in benzene and naphthalene. They shift to the red with falling temperature. The red shift, in going from the gaseous state to the solution in alcohol or hexane, amounts to -900 cm.$^{-1}$. (2) α-Bands, which are less intense, shift to the red on linear and angular annulation in the acene and phene series and are hidden, or partly hidden, by the more intense *p*-bands in the higher acenes, beginning with anthracene. These bands shift very little to the violet with falling temperature. The red shift, in going from the gaseous state to the solution in alcohol or hexane, amounts to -250 cm.$^{-1}$. The α-bands form the first group in the absorption spectra of benzene, naphthalene, phenanthrene and the higher phenes. (3) β-Bands, which are the most intense, show the same annulation effect as the α-bands and lie more in the ultraviolet. They shift considerably to the red with falling temperature. The difference between the gaseous state and the solution in alcohol or hexane amounts to -900 cm.$^{-1}$.

A systematic study has shown that in uniplanar aromatic hydrocarbons, the ratio of the frequencies of the α- and β-bands is constant: 1:1.35. This rule only applies if the hydrocarbons are uniplanar and there is no overlapping of H atoms, *e.g.*, in anthracene and pyrene. In diphenyl and in phenanthrene there is some degree of overlapping, but the loss of resonance energy in these cases is too small to be detected by the ratio $\nu\alpha:\nu\beta$. In these and similar cases low temperature absorption spectrography indicates deformation of the molecules.[3]

Owing to greatly increased overlapping (marked with X), a much higher degree of twisting, or another type of strain, can be assumed in 3,4-benzphenanthrene than in chrysene, Fig. 1) and the resulting loss of resonance energy becomes apparent in the ratio $\nu\alpha:\nu\beta$ which decreases to 1:1.324. In

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[1] Presented at the Diamond Jubilee of the American Chemical Society in New York, 1951.

[2] E. Clar, *J. Chem. Phys.*, **17**, 741 (1949); *Chem. Ber.*, **82**, 495 (1949); *Spectrochim. Acta*, **4**, 116 (1950).

[3] E. Clar, *ibid.*, **4**, 116 (1951).