*The Polarography of Terephthalaldehydic Acid**

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Holleck and Marsen[1] were the first to study the d. c. polarography of terephthalaldehydic acid. Their purpose was to investigate the effect of a substituted group on the polarographic behavior of benzaldehyde for eleven substituted benzaldehydes. Terephthalaldehydic acid has been investigated only qualitatively as one of these substituents.

In a previous paper[2] the present authors investigated the polarographic behavior of terephthalaldehydic acid in a sodium hydroxide solution; they reported a polarographic method for the rapid determination of a small amount of this acid in terephthalic acid, because terephthalic acid was well dissolved only in an alkaline solution.

In this paper, the authors will study in detail the d. c. and a. c. polarography of terephthalaldehydic acid in buffered solutions not containing ethanol over the pH region from 1 to 13.

The experimental results give some new information with respect to the polarographic reduction of terephthalaldehydic acid. The acid recombination and dissociation rate constants for this compound will be calculated, and a reduction scheme will be proposed.

Experimental

Apparatus.—A Yanagimoto AC/DC polarograph, model PA 102, was used for recording d. c. and a. c. polarograms. For the pH measurements, a Toa Dempa pH meter, model HM-5, was adopted. The dropping mercury electrode used had the following characteristics; $m=2.01$ mg./sec., $h=65$ cm., and $t=4.65$ sec. at an open circuit. The polarographic cells were of a modified H-type; the electrolytic compartment contained a mercury pool. When the a. c. polarograms were recorded, a "pool-condenser" of a 100 μF capacity was connected between the saturated calomel electrode and the mercury pool anode.[3]

All polarographic measurements were made at 25±0.5°C in a thermostat. Purified nitrogen gas was bubbled through the test solution for 10 min. to remove any dissolved oxygen.

Reagents. — The terephthalaldehydic acid* and other reagents used were of a guaranteed reagent grade.

Buffers and Test Solutions.—The Britton-Robinson buffers were mainly used to cover the pH range from 1 to 13. The other buffer systems used were as follows; 0.2 N potassium chloride - 0.2 N hydrochloric acid (pH 1.0~2.2), 0.2 N potassium biphthalate - 0.2 N hydrochloric acid (pH 2.2~3.8), 0.2 N potassium phosphate - 0.2 N sodium hydroxide (pH 4.0~6.2), 0.2 M potassium phosphate (monobasic) - 0.2 N sodium hydroxide (pH 6~8), 0.2 M boric acid - 0.1 N sodium hydroxide (pH 8~10), 0.1 M sodium citrate - 0.1 N hydrochloric acid (pH 1.1~5.8) and 0.2 N borax - 0.1 N sodium hydroxide (pH 9.5~12.0).

The test solution was prepared by taking 20 ml. of the buffer of the desired pH value and a given volume of a terephthalaldehydic acid standard solution[2] in a 25 ml. volumetric flask, adjusting the ionic strength to $\mu=0.13$ with 1.0 M potassium chloride, and then filling the flask up to the mark with water. No surface active substances were used. The pH value of the solution was again measured after the preparation of the test solution.

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* A summary of this work was presented at the 9th Symposium on Polarography held at Kyoto, October, 1962.

[1] L. Holleck and H. Marsen, *Z. Elektrochem.*, **57**, 944 (1953).

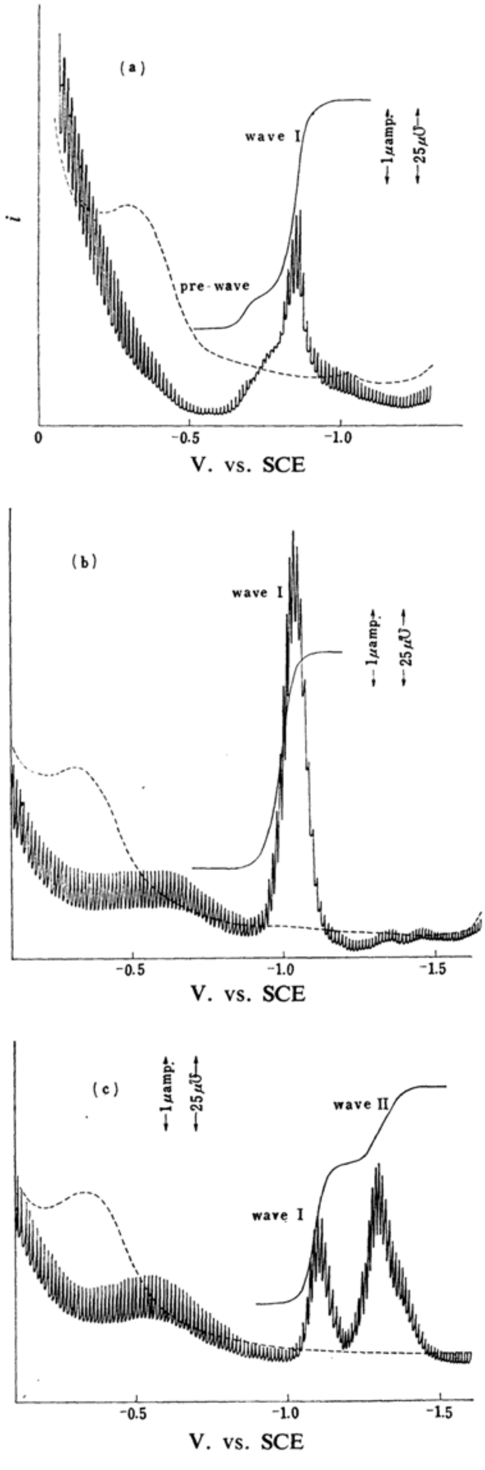
[2] M. Nishiyama, M. Maruyama and H. Hamaguchi, *Japan Analyst* (*Bunseki Kagaku*), **12**, 150 (1963).

[3] B. Breyer, F. Gutmann and S. Hacobian, *Australian J. Sci. Research*, **A4**, 595 (1951).

* Terephthalaldehydic acid was obtained from the Tokyo Kasei Co.; the analysis data gave a purity of 100±2% from the determination of the carboxyl group of this compound. The melting point was 257°C.

Results and Discussion

D. C. Polarography.—Figure 1 shows some typical d. c. and a. c. polarograms of 0.4 mM terephthalaldehydic acid in Britton-Robinson buffers over the pH range studied.



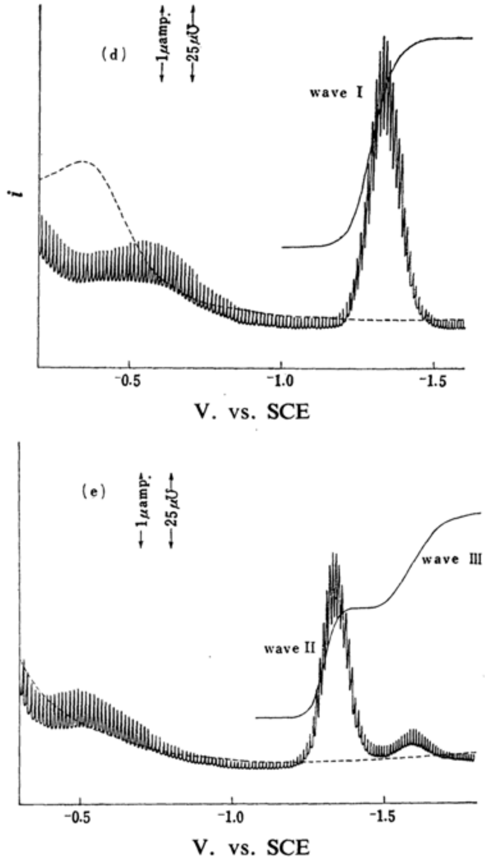


Fig. 1. D. c. and a. c. polarograms of 0.4 mM terephthalaldehydic acid in the Britton-Robinson buffers.
(a) pH 2.1, (b) pH 5.1, (c) pH 6.5,
(d) pH 8.0, (e) pH 13.2
——: d. c. polarogram (μamp.)
------: a. c. maximum base current (μ℧)
Oscillated curve: a. c. polarogram (μ℧)

The Effect of pH.—The variations in the wave height and the half-wave potential with variation in the pH are illustrated in Figs. 2 and 3 respectively. The reduction wave of terephthalaldehydic acid at a pH below 4.4 was accompanied by a pre-wave (Fig. 1-a). This pre-wave was not reported in the earlier investigation.[1] The behavior of terephthalaldehydic acid waves above pH 4.4 accorded approximately with the results of Holleck and Marsen; in the pH range from 4.4 to 5.5, a single wave (designated as wave I) was observed (Fig. 1-b); in the pH range from 5.5 to 7.5, two waves appeared—the height of the first wave, a positive one corresponding to wave I, decreased, and that of the second one, designated as wave II, increased with the increasing pH (Fig. 1-c). In the vicinity of pH 8, wave II alone was observed (Fig. 1-d), and as the pH increased from 8.2 to 11.5 the

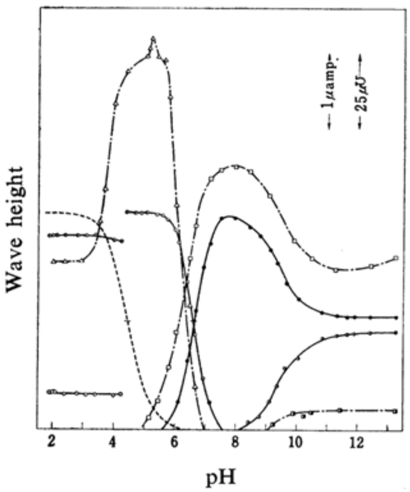


Fig. 2. Variation of the wave heights with pH.
At 0.4 mM terephthalaldehydic acid
—— d. c. waves (○ pre-, ⊙ I, ● II ◑ III)
— · — a. c. waves (△ I, □ II, ◨ III)
-------- theoretical dissociation curve

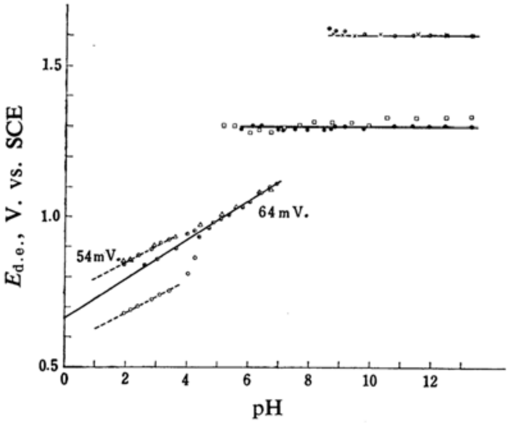


Fig. 3. The pH dependence of the half-wave and peak potentials.
At 0.4 mM terephthalaldehydic acid
——, ------: d. c. waves (○ pre-, ⊙ I, ● II, ◑ : III, ◑ I in biphthalate buffers)
a. c. wave (△ I, □ II × III)

height of wave II decreased while a third wave (wave III) appeared at a more negative potential, increasing with the ascending pH, both approaching about half of the sum of the wave heights (Fig. 1-e). The sum of the wave heights was kept approximately constant over the pH range from 4.4 to 13.2, but it increased slightly in the acidic pH region below 4.4 because of the occurrence of the pre-wave. The half-wave potential of wave I depended on the pH. In the pH range from 4.4 to 7.5 where the pre-wave disappeared, the plots of $E_{1/2}$ against pH gave a straight line with a slope of 64 mV./pH, and $E^0_{1/2}$, the half-wave potential extrapolated to pH 0, was -0.69 V. vs. SCE. The $E_{1/2}$-pH plot of wave I in the acidic pH range below 4.4 deviated from the $E_{1/2}$-pH relation line in the pH range from 4.4 to 7.5 and gave a slope of 54 mV./pH. It is an interesting fact, however, that in the biphthalate buffer the height of the pre-wave increased slightly and the $E_{1/2}$-pH plot of wave I, even in the pH range below 4.4, fitted on that straight line with a slope of 64 mV./pH (Figs. 2 and 3). The half-wave potentials for waves II and III under the conditions studied were about -1.30 and -1.60 V. vs. SCE respectively, and neither showed any pH-dependence.

The occurrence of the two waves* in the pH range from 5.5 to 7.5 and their pH-dependence can be explained reasonably by the acid dissociation-recombination mechanism; wave I is due to the reduction of the carbonyl group of the undissociated terephthalaldehydic acid, and wave II, to that of its anion. The pK_a of terephthalaldehydic acid, determined by the acid-base titration method, was 4.47±0.03 at 25°C**. On the other hand, pK'_a, which was obtained from the limiting current against the pH curve of wave I, was 6.60 at 25°C (Fig. 2). This result suggests the existence of an acid recombination kinetic current, as was pointed out by Holleck and Marsen1). Furthermore, the second occurrence of two-step waves, weves II and III, above pH 8.2 may be understood by applying the carbinolate-free radical dissociation theory.4,5) The "pK" for this dissociation equilibrium was about 9.5, which is the pH value corresponding to the increase in the height of wave III to one-fourth of the sum of the wave heights.

The Effect of the Ionic Strength on the Half-wave Potentials.—An investigation of the effect of the ionic strength on the half-wave potentials for waves I, II and III indicated the results given in Fig. 4. Figure 4 reveals that the half-wave potential of wave III is markedly affected by the ionic strength of the test solution. At pH 13.2 wave III was shifted to more positive potentials with the increasing ionic strength. Since wave II scarcely changed, the two waves were inclined to make a single wave. Similar phenomena were observed in

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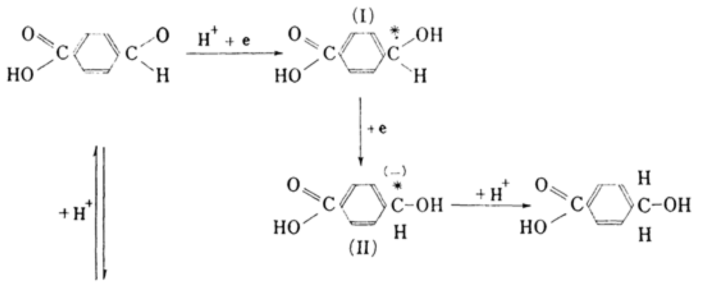
* The methyl ester of terephthalaldehydic acid gave a single wave over the pH range from 1 to 12.6)

** The dissociation constant of *o*-phthalaldehydic acid has been reported to be 3.6×10^{-5}.1)

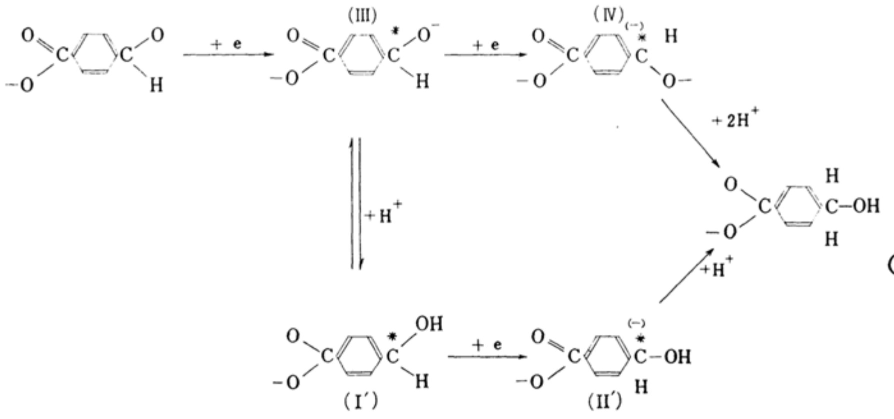
4) L. Holleck and H. Marsen, *Z. Elektrochem.*, **57**, 301 (1953).

5) P. J. Elving and J. T. Leone, *J. Am. Chem. Soc.*, **80**, 1020 (1958).

6) S. Ono and J. Nakaya, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **74**, 907 (1953).



(Scheme 1)



(Scheme 2)

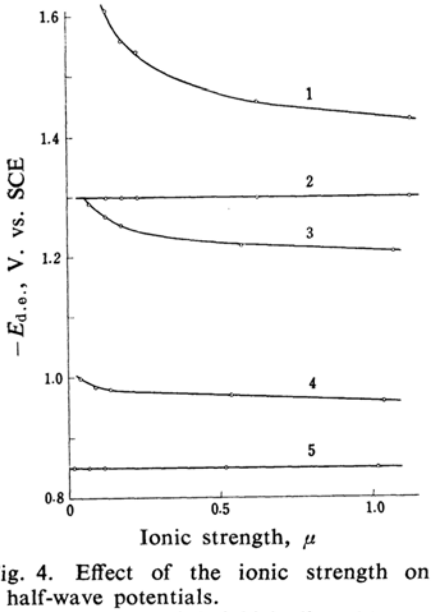


Fig. 4. Effect of the ionic strength on the half-wave potentials.
At 0.4 mM terephthalaldehydic acid
1) wave I at pH 2.1, 2) wave I at pH 5.1, 3) wave II at pH 7.9, 4) wave II at pH 13.2, 5) wave III at pH 13.2

the case of the increasing concentration of such a supporting electrolyte as sodium hydroxide.2) The positive shift of the half-wave potential of wave III is considered to be a key for elucidating the reduction mechanism for wave III.

The Dependence of the Limiting Current on the Mercury Pressure and the Temperature.—With respect to the mercury pressure-dependence, the plots of i_l against $h^{1/2}$ gave a straight line of a general expression, $i_l = ah^{1/2}+b$. If i_l is controlled exclusively by the diffusion, *b* should be equal to zero; if it is controlled completely by the reaction rate, *a* may be expected to be zero. On the other hand, the adsorption current is proportional to the mercury pressure. Table I shows the experimental data of the parameters *a* and *b*, and of the temperature coefficients at a proper pH value in five representative pH ranges. Table I reveals that wave I at pH 6.8 and the wave III at pH 13.2 are obviously of a kinetic nature, although both showed temperature coefficients of less than 1%. It is noticable that the temperature coefficient for wave I at pH 6.8 was practically zero.

The pre-wave appears to be the adsorption current, i_a, submitting to a general equation, $i_a = a'h$, where a' is a proportional constant (Table I). The single waves at pH 5.1 and 7.9, waves I and II respectively, seem to be controlled by the diffusion.

The Concentration-dependence and the Diffusion Current Constant.—Linear relationships between the sum of the wave heights and the concentration of terephthalaldehydic acid in the range from 1 to 0.04 mM were obtained over the pH range studied. The diffusion current constants for the single waves were calculated

TABLE I. THE MERCURY PRESSURE-DEPENDENCE AND THE TEMPERATURE COEFFICIENT (d. c. WAVES)

0.4 mM terephthalaldehydic acid in the Britton-Robinson buffers

pH	Wave	$i_l = ah^{1/2*} + b$		Temp. coeff. (20~30°C), %/deg.
		a	b	
2.1	Pre-wave	0.072**		Different
	I	0.28	+0.42	1.41
	Sum	0.39	0	1.36
5.1	I	0.36	0	1.48
6.8	I	0.05	+0.98	0
	II	0.31	−0.98	2.53
	Sum	0.36	0	1.32
7.9	II	0.33	+0.11	1.50
13.2	II	0.27	−0.65	1.49
	III	0.07	+0.65	1.00
	Sum	0.34	0	1.25

* $h = h_{\mathrm{exp}} - h_{\mathrm{back}}$

** The value was calculated as a', applying equation ; $i_a = a'h$.

by Ilkovič equation as 3.48±0.04 for wave I at pH 5.2 and 3.36±0.07 for wave II at pH 7.9. For wave II and the sum of the two waves at pH 13.2, 1.82±0.03 and 3.38±0.03 were obtained respectively.

The number of electrons, n, involved in the electrode process can be calculated by the equation, $I_D = 607\, n\, D^{1/2}$, where I_D is the diffusion current constant and D is the diffusion coefficient. If the diffusion coefficient for terephthalaldehydic acid is assumed to be 7.35×10^{-6} cm^2 sec^{-1}, that is, the value of the diffusion coefficient for phthalic acid as calculated by the Stokes-Einstein equation, $n = 2.12$, 2.04 and 2.05 are obtained for wave I at pH 5.2, for wave II at pH 7.9, and for the sum of the waves at pH 13.2 respectively. These values indicate that the sum of the wave heights for terephthalaldehydic acid, over the pH range studied, corresponds to a two-electron reduction of the carbonyl group.

Relationships between the heights of the pre-wave and of wave I at pH 2.1 and the concentration over the range from 0 to 0.4 mM of terephthalaldehydic acid are shown in Fig. 5. The height of the pre-wave reached a limiting value with the increasing concentration, substantiating the conclusion that the pre-wave is due to the adsorption of an organic substance, possibly the reduced form of undissociated terephthalaldehydic acid, at the dropping mercury electrode. Wave I at pH 2.1 could be distinguished, down to 0.08 mM of terephthalaldehydic acid, from the pre-wave (Fig. 5). Using the pK value of terephthalaldehydic acid, the bulk concentration of undissociated molecules at pH 2.1 is calculated as approximately equal to that of terephthalaldehydic acid, and at pH 5.16 the bulk concentration of undissociated molecules is calculated as 0.08 mM, when the analytical concentration of terephthalaldehydic acid is 0.4 mM. The pre-wave is still expected, therefore, to appear at pH 5.16, but experimentally it was observed at a pH lower than 4.4. To elucidate this fact, the effect of concentration of terephthalaldehydic acid on the half-wave potentials of the pre-wave and wave I at pH 4.0 was investigated (Table II). It was found that the pre-wave was shifted to a more negative potential with the decreasing concentration ; on the other hand, the main wave I shifted to more positive potentials. At 0.2 mM terephthalaldehydic acid, the pre-wave marged into wave I, and the half-wave potential for the coalesced wave remained unchanged with

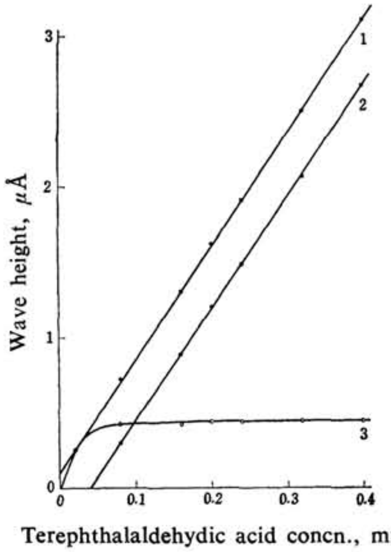


Fig. 5. Relationship between the terephthalaldehydic acid concentration and the d. c. wave heights at pH 2.1.
1) sum of wave heights, 2) wave I, 3) pre-wave

the decreasing concentration. It may be concluded that, since the equilibrium concentration of undissociated molecules in the bulk solution decreases visibly when the pH increases from 3 to 6, the difference in half-wave potentials between the pre-wave and wave I decreases, and the two waves coalesce.

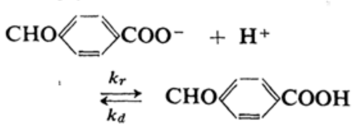
TABLE II. THE EFFECT OF TEREPHTHALALDEHYDIC ACID CONCENTRATION ON THE HALF-WAVE POTENTIALS AT pH 4.0

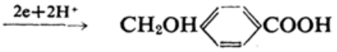
Concn. of terephthalaldehydic acid, mM	$-E_{1/2}$, V. vs. SCE		Difference between two half-wave potentials, V.
	Pre-wave	Wave I	
2.0	0.77	0.99	0.22
1.0	0.80	0.96	0.16
0.4	0.81	0.92	0.11
0.2	0.89		—
0.08	0.90		—
0.04	0.90		—

Log Plot.—For the study of the slopes and shapes of the terephthalaldehydic acid waves, the term $\log i/(i_d - i)$ was plotted against E, at 0.4 mM terephthalaldehydic acid. Wave I at pH 2.0 and 5.6 gave a linear log plot with a slope of about 43 mV., considerably greater than the theoretical value for the reversible two-electron reduction. In other media, the slopes of the log plot for wave I were in the range from 48 to 52 mV. Because wave II in the vicinity of pH 8 tended to show a maximum if a maximum suppresser such as gelatine was not added to the electrolytic solution, the log plot for wave II was slightly curved, even in 0.4 mM terephthalaldehydic acid, and the slopes were in the range from 62 to 78 mV. However, waves II and III at pH 13.2, the heights of which corresponded to a one-electron reduction, gave linear log plots with slopes of 43 and 98 mV. respectively. It seems that the abnormally large value of the slope for wave III indicates the irreversible nature of the electrode process involved.

Recombination and Dissociation Rate Constants.—The reduction current of terephthalaldehydic acid in the pH range from 5.5 to 7.5 well fits the theory of the kinetic recombination currents.[7]

The mechanism of the electrode process is given by;





(1)

where k_r and k_d are the recombination and dissociation rate constants respectively. The recombination rate constant can be calculated by the following equation;[8]

$$\log K_r = 2pK'_a - pk_a - 2\log 0.886 - \log t \qquad (2)$$

where t is the drop time. t was 4.48 sec. at -1.0 V. vs. SCE in the electrolytic solution studied. The k_r and k_d were calculated as follows; $k_r = 1.5 \times 10^8$ l. (mol. sec.)$^{-1}$, and $k_d = 5.2 \times 10^3$ sec^{-1}.

A. C. Polarography.—*The Behavior of A. C. Waves.*—A. C. polarograms in buffered solutions of various pH values are shown in Fig. 1. As compared with the d. c. wave heights, a. c. wave heights were greatly influenced by the change in the pH (Fig. 2). The peak potential for each a. c. wave agreed approximately with the half-wave potential for the corresponding d. c. waves (Fig. 3). In the acidic pH range below 4, a small "kink" was observed on the positive side of the a. c. first wave (a. c. wave I), where the pre-wave appeared on the d. c. polarogram. This "kink" is considered to be caused by the adsorption of the reduced form of undissociated molecules at the dropping mercury electrode. However, this "kink" differs from the adsorption peak of dyes;[9] riboflavin,[10] methylene blue,[11] flavinmononucleotide[12] and others[9] are known to give a d. c. pre-wave and a sharp, well-defined corresponding a. c. peak as a result of the adsorption of the reduced form in acidic solutions.

The height of a. c. wave I was strongly depressed in the pH range from 1 to 3. In the case of terephthalaldehydic acid, it seems that a strong adsorption of undissociated molecules was present in the potential region where the pre-wave and wave I were observed, resulting in the depression of the a. c. wave heights. (See the discussion of base current effects.) Although the concentration of undissociated terephthalaldehydic acid in equilibrium is considered to decrease rapidly when the pH is increased from 3 to 6, the height of a. c. wave I increased up to a maximum at pH 5.2, where the d. c. pre-wave merges into a

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[7] For review, R. Brdicka, *Collection Czechoslv. Chem. Communs.*, **19**, Suppl. 2, 41 (1954); R. Bridicka, *Z. Elektrochem.*, **64**, 16 (1960); M. Senda, *Rev. of Polarography*, **6**, 95 (1958).

[8] M. Takagi, ibid., **9**, 53 (1961).

[9] H. Hamaguchi, M. Maruyama and M. Nishiyama, unpublished. A summary of the work, however, was presented at the 14th Annual Meeting of the Chemical Society of Japan (1961).

[10] B. Breyer and T. Biegler, *Collection Czechoslv. Chem. Communs.*, **25**, 3348 (1960); *J. Electroanal. Chem.*, **1**, 453 (1960).

[11] S. L. Gupta and S. K. D. Agawal, *Kolloid-Z.*, **163**, 136 (1959).

[12] M. Senda, M. Senda and I. Tachi, *Rev. Polarography*, **10**, 142 (1962).

coalesced wave. It seems that the decreasing concentration of adsorbable species in the bulk solution weakens the depression of the a. c. wave height. However, the abnormal rise of the height of a. c. wave I in the pH range from 5.1 to 5.5 implies that the a. c. wave formation process in that pH range involves both the reduction of undissociated molecules and the adsorption of the reduced form. Furthermore, the deviation of the wave height against the pH curve of a. c. wave I from the theoretical dissociation curve reveals that it is necessary to take into account the a. c. kinetic current for the formation of a. c. waves. The pH values of the disappearance of a. c. wave I and of the appearance of a. c. wave II were shifted to a pH range more acidic by 0.5 pH unit than in the d. c. polarography (Fig. 2). It is considered that in this case the a. c. current is less affected by the kinetic reaction than are the d. c. kinetic currents.

The a. c. wave height-pH curve for a. c. wave II was found to have a shape analogous to that for d. c. wave II. On the other hand, a. c. wave III was ill-defined, and at pH 13.2 its height was as small as a tenth of the height of a. c. wave II (in the d. c. polarography, the ratio of the height of wave II to III was about unity). The reduction process for wave III is irreversible.

Base Current Effects.—In the pH region below 3, the base current was depressed on both the positive and the negative sides of a. c. wave I, indicating that the undissociated terephthalaldehydic acid and the reduced form were strongly adsorbed at the surface of the dropping mercury electrode (Fig. 1-a). As has been described above, this strong adsorption affects the a. c. pre-wave and wave I so as to depress the heights of these waves. As the pH increased from 3 to 5, the lowering of the base current was decreased, and the depression of a. c. wave I was weakened.

In the pH range from 5.1 to 5.5, where the abnormal rise of the height of a. c. wave I occurred, the base current between a. c. waves I and II was lowered.

Simultaneously, a new and small peak was observed on the negative side a. c. wave II, although there was no corresponding d. c. wave at this potential. This peak was shifted to more positive potentials with the increasing pH, and then it was merged into a. c. wave II. This fact suggests that the new peak is a kind of tensammetric one, because of the desorption of the reduced form of undissociated terephthalaldehydic acid. Further, above pH 5, a "hump" was observed at about —0.5 V. vs. SCE, probably due to the weak adsorption-desorption process for the dissociated terephthalaldehydic acid.

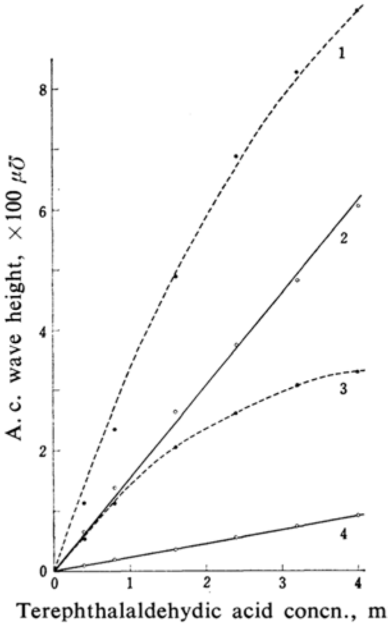

Fig. 6. Relationship between the terephthalaldehydic acid concentration and the a. c. wave heights.
1) wave I at pH 5.1, 2) wave II at pH 13.2, 3) wave I at pH 2.9, 4) wave III at pH 13.2
○, ●: experimental point
------: calculated curve

The Relation between A. C. Wave Height and the Concentration of Terephthalaldehydic Acid.—The plot of the a. c. wave heights at pH 2.1, 5.1 and 13.2 against the concentration of terephthalaldehydic acid are shown in Fig. 6. The plot for a. c. wave I at pH 2.1 and 5.1 were non-linear and fit the equation of the Langmiur adsorption isotherm, $i_p=abC/(1+bC)$, where i_p is the a. c. wave height, C is the molar concentration of terephthalaldehydic acid in the bulk solution, and a and b are the parameters with the following values; $a=$ 669.1 1./mol., $b=254.0\ \mu℧$ at pH 2.1 and $a=$ 2364.0, $b=163.0$ at pH 5.1. In strongly alkaline solutions, a. c. waves II and III each gave a straight line. These results may also substantiate the conclusion that the reduction of undissociated terephthalaldehydic acid includes the adsorption process, at least in the pH range below 5.1.

The Dependence of A. C. Wave Heights on the Mercury Pressure and the Temperature.—The a. c. wave heights of terephthalaldehydic acid change with the mercury pressure, as Table III shows, indicating that the d. c. polarographic electrode process in the reduction of terephthalaldehydic acid is irreversible.(13) The

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(13) M. Senda, *Kagaku no Ryoiki*, Suppl., No. 50, "Polarography I," p. 28 (1962).

temperature coefficients for a. c. waves gave considerably greater values than those usually observed for a. c. waves.

TABLE III. THE MERCURY PRESSURE-DEPENDENCE AND THE TEMPERATURE COEFFICIENT (A. C. WAVE)

0.4 mM terephthalaldehydic acid in Britton-Robinson buffers

A. c. wave height ($\mu\mho$)

h, cm.	Wave I			Wave II	Wave III
	pH 2.0	pH 5.1	pH 7.9	pH 13.2	
78.5	53.4	131.0	93.3	77.0	7.6
68.5	55.5	128.5	90.0	73.5	7.2
58.5	52.6	125.0	86.0	65.8	6.8
48.5	48.7	119.0	79.6	58.6	6.0
Temp. coeff., %/deg.	2.48	1.28	2.20	0.65	1.50

Reduction Mechanism.—From the d. c. and a. c. polarographic results and the discussion above, and from the similarity between the reduction of the carbonyl group of terephthalaldehydic acid and that of benzaldehyde,[14,15] the following mechanism is proposed; wave I is ascribed to the two-electron reduction of the carbonyl group of undissociated molecules following the adsorption at the electrode surface, and *p*-carboxyl benzyl alcohol is formed. Applying the reduction mechanism for benzaldehyde proposed first by Holleck and Marsen,[4] the process is written as Scheme 1. In this case, the electrode reaction via the intermediate carbinolate-free radical (I) and its radical ion (II) proceeds successively. The electrode reaction product, *p*-carboxyl benzyl alcohol, is adsorbed at the electrode surface, at least in the pH range below 4.4. Wave II is due to the reduction of anions; in the pH range below 8 the anion is reduced first to its radical ion (III), which combines rapidly with a proton, and then the electrode reaction proceeds successively to the formation of dissociated *p*-carboxyl benzyl alcohol. The whole reaction is a two-electron reduction (Scheme 2).

In the pH range from 5.5 to 7.5, the two waves, I and II, form a system of kinetic recombination currents in which the electrode process is given by Eq. 1. In view of the a. c. polarographic behavior in this pH range, it may be concluded the molecules of the undissociated terephthalaldehydic acid formed by the recombination in the reaction layer are first adsorbed at the electrode surface and then reduced. In the treatment of the acid-recombination kinetics of terephthalaldehydic acid, however, the adsorption was not taken into consideration.

The fact that the temperature coefficient of d. c. wave I at pH 6.8 was zero indicates that the dissociation equilibrium is shifted in favor of the anions with an increase in the temperature.

On the basis of their analysis of current-time curves in a drop life of the dropping mercury electrode, Kasening and Holleck[15] recently rejected the carbinolate-free radical dissociation theory for the reduction of benzaldehyde; instead, they proposed a new reduction scheme, in which a dissociation equilibrium of benzaldehyde was antecedent to the competitive reduction processes of the free molecule and the cation.

In the case of terephthalaldehydic acid, however, the polarographic behavior above pH 8.2 cannot be explained by the new theory, but only by the carbinolate-free radical dissociation theory. A dissociation equilibrium between radical ion III and radical I′ is established in the electrode reaction. Radical I′ is reduced at the same potential as the dissociated molecule, while radical ion III is reduced at more negative potentials than wave II, resulting in the appearance of wave III. In a strongly alkaline solution, wave II is due to the reduction to radical ion III, and wave III, to that from radical ion III to *p*-carboxyl benzyl alcohol, both corresponding to a one-electron reduction. The positive shift of the half-wave potential of wave III with the ionic strength or concentration of a supporting electrolyte is attributed to the unstability of radical ion III.

Summary

The d. c. and a. c. polarography of terephthalaldehydic acid has been investigated in buffered solutions containing no ethanol over the pH range from 1 to 13.

D.C. Polarography.—Terephthalaldehydic acid gives a pre-wave and three reduction waves. The pre-wave, which is due to the adsorption of the reduced form of undissociated molecules, is followed by wave I below pH 4.4. Our results above pH 4.4 accord approximately with Holleck and Marsen's. The half-wave potential for the wave I is pH-dependent, and the $E^0{}_{1/2}$ is -0.69 V. vs. SCE. The half-wave potentials of waves II and III, both pH-independent, are -1.30 and -1.60 V. vs. SCE under the conditions studied. The sum of the wave heights has been kept constant in

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[14] For review, Y. Nagata, *Rev. Polarography*, **7**, 12 (1959).

[15] B. Kasening and L. Holleck, *Z. Elektrochem.*, **63**, 166 (1959).

the pH range from 4.4 to 13.2, and it corresponds to the two-electron reduction of the carbonyl group. The two-step waves, in which wave I is due to the reduction of the undissociated molecule and wave II, to that of its anion, in the pH range from 5.5 to 7.5 form a system of kinetic recombination currents. The recombination and dissociation rate constants have been calculated as $k_r=1.5\times10^8$ l. (mol. sec.)$^{-1}$ and $k_d=5.2\times10^3$ sec^{-1}. The double waves above pH 8.2 have been explained by the carbinolate-free radical dissociation theory.

A. C. Polarography.—A. c. waves have been obtained to corresponding to the d. c. waves. The heights of the a. c. pre-wave and wave I are depressed below pH 5. This depression has been attributed to the strong adsorption of undissociated molecules at the dropping mercury electrode. The relationship between the a. c. wave height and concentration below pH 5 is non-linear. It has been noted that the a. c. kinetic current should be taken into account for the a. c. wave formation.

The electrode process for wave III is irreversible, and a. c. wave III is ill-defined.

A reduction mechanism over the pH range studied has been proposed.

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