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The Reduction of Weak Acids at the Dropping Mercury Cathode

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In the majority of cases the discharge of hydrogen - ions at a dropping mercury cathode from solutions of different acids is accompanied by the formation of well defined diffusion waves on the c.m.f. current intensity curves.

The diffusion current of hydrogen, I_d , depends on the rate of movement of hydrogen ions towards the electrode and also of undissociated molecules of acid which, on the surface of the cathode, are broken down into ions:

$$I_d = K_H \sqrt{[H^+]} + K_{HA} \sqrt{[HA]} \quad (1)$$

Here, $[H^+]$ and $[HA]$ are the concentrations of ions of hydrogen and acid respectively, in the solution, whilst K_H and K_{HA} are constants depending on the value of the diffusion coefficient of hydrogen and of molecules of the acid.

If solutions of strong acids undergo reduction, such acids being practically completely ionised, the component $K_{HA} \sqrt{[HA]}$ is small in comparison with $K_H \sqrt{[H^+]}$ and may be neglected. The diffusion current will then depend linearly on the concentration of hydrogen ions in the solution, or on the concentration of the corresponding acid.

For weak acids, the dissociation of which in polarographic solutions is substantially less than 100%, the second component of equation (1) is comparable in magnitude with the first and clearly cannot be discarded.

In the present investigations, the authors were concerned with the problem of preserving the linear relationship between the diffusion current and the total analytical concentration of acid in the solution. Furthermore, it was desirable to ascertain the dependence between the value of the diffusion current of any weak acid and the value of the dissociation constant of the latter.

In a number of organic acids, it is possible to observe the presence of such atomic groupings which can be reduced at the dropping mercury cathode and so give diffusion currents. For such acids, the appearance of two diffusion waves may be expected on polarograms, one corresponding to the reduction of hydrogen and the other being associated with the reduction of an acid anion.

The authors have examined the reduction of a comparatively large number of weak acids with a view, in doubtful cases, to having sufficient experimental data to decide which of the waves on the polarograms made refers to the reduction of hydrogen and which to an anion of the acid.

Experimental Method

For making the polarograms, a visual apparatus was used and a galvanometer with a current sensitivity of 0.58×10^{-9} A mm/M. All measurements were made at a temperature of $25 \pm 0.2^\circ$ C.

As anode, a saturated calomel half-element was employed, the potential of which was assumed to be zero.

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In the work different capillaries were required, but all the measured diffusion currents were converted for a capillary the characteristic of which was equal to $1 \text{ mg}^{2/3} \text{ sec}^{-1/2}$.

When investigating the reduction of acids soluble in water the authors used aqueous solutions. For acids with poor solubility in water, initial alcoholic solutions were prepared which, before polarographing, were mixed in the electrolyser with a solution of neutral electrolyte.

In the majority of cases it proved unnecessary to remove dissolved oxygen, since the reduction waves of hydrogen from acids were situated in the very much more negative region of potentials than the waves for oxygen reduction.

Results of experiments and their assessment

The reduction of aliphatic monobasic acids.

The authors submitted to polarography solutions of formic, acetic, isobutyric, isovaleric and chloroacetic acid in the presence of 0.1N HCl, 0.1N LiCl, and Li_2SO_4 , 0.1 N KOH and 0.05N $(\text{CH}_3)_4\text{NI}$. The hydrogen wave for all the acids was not discernible in hydrochloric acid and in a solution of potassium hydroxide.

In the first case, it is probable that hydrogen waves of weak acid are masked by the wave for the reduction of the base, and in the second case the concentration of hydrogen ions is diminished to a very small value as a consequence of neutralisation reaction.

In a base electrolyte comprising lithium chloride, lithium sulphate or tetramethylammonium iodide, formic, acetic, chloroacetic, isobutyric, and isovaleric acids, give well defined diffusion currents which are proportional to the content of acid in the solution provided that the concentration of acid is not too low.

The calculated values of the proportionality coefficient between the current and the concentration of the acid are shown in Table 1. The same Table gives the half-wave potentials of hydrogen reduction for solutions of the above-mentioned acids.

The half-wave potential depends fairly markedly on the concentration of the acids, being displaced by approximately 0.1 volt when the concentration of the acid is increased tenfold. The absence of diffusion currents in the reduction of formic, acetic, isobutyric, isovaleric and chloroacetic acids in alkaline and strongly acid media indicates that in neutral solutions the diffusion currents are associated with a discharge of hydrogen ions. In the case of trichloroacetic acid, it is possible to observe the appearance of a further diffusion wave at 0.90 - 0.95 volt in all probability not associated with hydrogen reduction. Anions of aliphatic acids, therefore, are not reduced at a dropping mercury cathode.

Table 1. Half-wave potentials and values of I_d/C for monobasic aliphatic acids with tetramethylammonium iodide as base electrolyte

No.	Name of acid	Dissociation Constant	Range of investigated concentrations in millimols per litre	I_d/C $\frac{\mu A}{m. mol}$	Limits of variation $-E_{1/2}V$
1	Formic	1.77×10^{-4}	1 - 10	2.42	1.74 - 1.85
2	Acetic Acid	1.75×10^{-5}	2 - 15	1.95	1.76 - 1.86
3	Isobutyric .	1.44×10^{-5}	3 - 25	1.64	1.81 - 1.87
4	Isovaleric .	1.7×10^{-5}	4 - 27	1.35	1.75 - 1.82
5	Chloroacetic	1.4×10^{-3}	1 - 10	3.14	1.65 - 1.71
6	Dichloroacetic ...	5.0×10^{-2}	1 - 5	4.25	1.55 - 1.64
7	Trichloroacetic	1.3×10^{-1}	1 - 8	4.55	1.57 - 1.68

Reduction of dicarboxylic acids

Winkel and Proake (1), investigating the reduction of oxalic acid, showed that, not only this acid, but all dicarboxylic saturated acids fail to reduce at a dropping mercury cathode. The authors mentioned discovered that oxalic acid neutralised by lithium hydroxide is not reduced and so does not enable diffusion waves to be obtained. In an 0.1N solution of hydrochloric acid, reduction takes place, but it ceases if a 0.01N solution is taken. The present authors carefully studied the behaviour of oxalic acid in solutions of hydrochloric acid, the concentration of which was varied from 0.01 - 0.1N, and did not obtain hydrogen diffusion currents of oxalic acid.

The absence of diffusion waves under these conditions is quite natural. Hydrogen ions from hydrochloric acid, present in considerable excess, cause the dissociation of the weaker oxalic acid and, becoming reduced on the mercury cathode, give on the polarograms only the current of the base electrolyte.

Clear diffusion currents were obtained by the authors - with a base electrolyte of lithium chloride and sulphate, and also of tetramethylammonium iodide. Similar reduction waves of hydrogen ions arising as a result of dissociation of molecules of the acids were obtained for solutions of malonic, succinic, adipic, tartaric, pyrotartaric, malic and citric acids.

For all these acids the hydrogen diffusion current is directly proportional to the concentration of molecules of acid in the solution.

For oxalic, malonic, tartaric, malic and citric acids, the reduction potentials are almost equal to one another and depend on the concentration of the acid. It is interesting to note that the half-wave potential of succinic acid does not depend on its concentration and amounts to -1.8 volts.

The experiments of the present authors on the reduction of a number of dicarboxylic acids lead to the conclusion that the diffusion currents of the latter are associated with the discharge of hydrogen ions present in the solution, owing to the electrolytic dissociation of molecules of the said acids.

Table 2. Half-wave potentials and values of I_p/C for dicarboxylic acids with tetramethylammonium iodide as base electrolyte

No.	Name of acid	Dissociation (Const) (first)	Range of concentrations studied in millimols per litre	I_p/C μA litre millimol	Limits of variation $- \pi_{1/2} V$
1	Oxalic	5.90×10^{-2}	1 - 8	4.45	1.66 - 1.80
2	Malonic	1.49×10^{-3}	2 - 13	2.70	1.69 - 1.74
3	Tartaric	1.04×10^{-3}	1 - 8	3.12	1.61 - 1.77
4	Citric	8.40×10^{-4}	1 - 6	3.30	1.64 - 1.77
5	Malic	3.88×10^{-4}	1.5 - 10	2.85	1.66 - 1.74
6	Pyrotartaric	8.7×10^{-5}	1 - 10	2.44	1.80 - 1.86
7	Succinic	6.89×10^{-5}	1 - 9	2.63	1.80
8	Adipic	3.7×10^{-5}	2 - 11	2.07	1.76 - 1.80

Reduction of aromatic acids

Benzoic, mandelic, gallic, salicylic and acetylsalicylic acids give well-pronounced diffusion waves from neutral solutions of lithium chloride and sulphate and of tetramethylammonium iodide. Phthalic acid gives polarograms with a double wave. With a tenfold increase in the concentration of the acid in the solution, the half-wave potential of the first stage is displaced by 0.1 volt and of the second by 0.15 volt in the direction of more negative values.

In strong acids, and in alkaline media, all these acids do not give diffusion currents.

Table 3 shows the numerical values of potentials of the acids mentioned above, and the diffusion current constants $K_d = \frac{I_d}{C}$

$\frac{I_d}{C}$

Table 3. Half-wave potentials and values of I_d/C for aromatic acids with tetramethylammonium iodide as base electrolyte

No.	Name of acid	Dissociation Const (first)	Range of investigated concentration in millimols per litre	I_d / C $\mu A / m. mol$	Limits of variation $-E_{1/2} V$
1	Benzoic	6.3×10^{-5}	0.9 - 6	1.90	1.56 - 1.72
2	Mandelic	1.1×10^{-4}	2 - 13	2.20	1.70 - 1.78
3	Gallic	3.8×10^{-5}	2 - 6	2.33	1.71 - 1.73
4	Phthalic	1.3×10^{-3}	1 - 11	3.22	1.60 - 1.85
5	Salicylic	1.01×10^{-3}	1 - 9	2.80	1.66 - 1.83
6	Acetylsalicylic	-	1 - 7	2.00	1.52 - 1.65
7	Anthranilic	1.07×10^{-5}	3 - 20	1.40	1.60 - 1.52
8	Sulphanilic	6.02×10^{-4}	2	-	1.54
9	Naphthionic	2×10^{-3}	2 - 10	-	1.42 - 1.52

Anthranilic ($C_6H_4NH_2COOH$), naphthionic ($C_{10}H_6NH_2SO_3H$) and sulphanilic ($C_6H_4NH_2SO_3H$) acids are not easily soluble in water, and for this reason the authors used alcoholic solutions. In the presence of tetramethylammonium iodide, all these acids give diffusion currents proportional to the concentration of the dissolved acid. It should be noted that, at a concentration of about 8 - 10 millimols/litre, higher maxima occur on the current intensity voltage curves which are not suppressed by gelatine and so render difficult the reliable measurement of the half-wave potential.

From Tables 1, 2 and 3 it will be seen that the numerical values of the diffusion current constants $K_d = \frac{I_d}{C}$ for acids differ. This difference is not associated with variation in the diffusion coefficient, since these differ only very slightly.

The value of the diffusion current constant of an acid is influenced by the dissociation constant of the acid: the greater the latter, the greater also K_d .

For the acids investigated, it was possible to discover a simple relationship between these two values, expressed by the equation:

$$\frac{I_d}{C} = a - bpK,$$

where pK is the decimal logarithm of the first dissociation constant of the acid with the sign reversed (for polybasic acids the subsequent dissociation constants were not taken into consideration since they are considerably less than the first); a and b are constants depending on the composition of the neutral electrolyte.

For 0.05N solutions of tetramethylammonium iodide, the equation has the form:

$$\frac{I_d}{C} = 5.25 - 0.725 \text{ pK}, \quad (2)$$

for a solution of 0.1 N Li_2SO_4 :

$$\frac{I_d}{C} = 4.65 - 0.642 \text{ pK}. \quad (3)$$

In Figure 3 the experimental data are shown graphically with the coordinates $\frac{I_d}{C}$ and pK.

It will be seen from the graph that acids for which the first dissociation is less than 5×10^{-8} should not give hydrogen reduction diffusion currents.

Table 4. Half-wave potentials and values of I_d/C for sulphamide compounds with tetramethylammonium iodide as base electrolyte

No.	Name of substance	K of dissociation	I_d/C $\frac{\mu\text{A.}}{\text{m.mol}}$	Potential volts $-\pi/2 \text{ V}$
1	n-acetylsulphanilamide	$4.2 \cdot 10^{-6}$	2.3 - 13.4	2.16 - 2.20
2	Sulphathiazole	$7.6 \cdot 10^{-8}$	2.0 - 10.4	1.66 - 1.74
3-	n-Sulphanilyl-sulphanilamide	$1.4 \cdot 10^{-8}$	2.00 - 7.9	1.70 - 1.86
4	Sulphadine	$3.7 \cdot 10^{-9}$	does not reduce	
5	Sulphanilamide	$3.7 \cdot 10^{-10}$	" " "	

Table 4 shows the experimental data for a number of sulphamide compounds characterised by low dissociation constants obtained by the present authors during the polarographic investigation of n-acetylsulphanilamide ($\text{NH}_2\text{C}_6\text{H}_4\text{SO}_2\text{NHCOCCH}_3$), sulphathiazole ($\text{NH}_2\text{C}_6\text{H}_4\text{SO}_2\text{NH} \cdot \text{C}_3\text{H}_4\text{SN}$), n-sulphanilyl-sulphanilamide ($\text{NH}_2 \cdot \text{C}_6\text{H}_4\text{SO}_2\text{NHC}_6\text{H}_4\text{SO}_2\text{NH}_2$), sulphadine ($\text{NH}_2\text{C}_6\text{H}_4\text{SO}_2 \cdot \text{NHC}_5\text{H}_4\text{N}$) and sulphanilamide ($\text{NH}_2\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2$).

It is only for the first compounds that it is possible to give the hydrogen diffusion currents.

The molecules of the remaining sulphamide compounds and also boric acid, the first dissociation constant of which is 5.7×10^{-10} , do not give hydrogen diffusion waves.

The empirical relationship obtained makes it possible to solve the problem of the reduction mechanism of a number of molecules possessing acid characteristics and having in addition reducible atomic groupings.

The diffusion current constant occurring at a potential of -1.6 to -1.8V during the discharge of hydrogen ions and absent in solutions of strong acids and alkalis, should agree with equation (2) or (3). It is clear that, in the reduction of the anion, the diffusion wave can be observed in acid and alkaline solutions. In addition, I_d/C , determined by the diffusion

coefficient of the anion and by the number of electrons participating in the process, should not depend on the dissociation constant of the acid.

Equations (2) or (3) can be used for the determination of the unknown dissociation constant of any acid.

For the value of the diffusion current constant we can write the equation:

$$\frac{I_d}{C} = 605. n D^{1/2} m^{2/3} t^{1/6} \quad (4)$$

on the condition that the diffusion current is measured in μA and the concentration in m mol/litre.

For the discharge of Hydrogen ions $n = 1$, and for our capillary $m^{2/3} t^{1/6} = 1$, whence

$$\frac{I_d}{C} = 605. n D^{1/2} \frac{1}{m \text{ mol}} \quad (5)$$

The diffusion coefficient of hydrogen ions in an aqueous solution calculated from the equivalent electrical conductivity equals $9.34 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$.

Consequently the diffusion current constant for hydrogen ions is $5.35 \frac{\mu \text{ ampere}}{m \text{ mol}}$

Comparison of this value with the values of I_d/C found for the acids investigated makes it possible to assess the approximate value of the separate components of equation (1). Thus, in acetic acid almost the whole of the hydrogen current is associated with the transport of undissociated molecules to the surface of the mercury cathode, in chloroacetic acid approximately 0.3 of the current is transported by hydrogen ions and 0.7 by undissociated molecules and in the case of dichloroacetic acid the corresponding figures are 0.6 and 0.4, etc. However, the change in the numerical values of the separate components of this equation does not destroy the linear relationship between the diffusion current and the analytical concentration of the acid.

Conclusions.

1. The reduction of a number of weak acids at a mercury cathode was investigated.
2. It was established that the reduction of hydrogen from solutions of weak acids with a neutral base of indifferent electrolyte proceeds at a half-wave potential varying from -1.6 to -1.3V.
3. An empirical relationship was found between the diffusion current of hydrogen and the dissociation constant of the acid.

Bibliography

1. A. Winkel and G. Proske. Ber., 1935, 68, 693, 1917.

Figures

Fig. 1: Polarogram of acids with 0.05N (CH₃)₂ as base electrolyte

- Curve 1 - Acetic acid, conc. 15.6 m mol/litre beginning from -1.4 V.
- Curve 2 - Oxalic acid, conc. 4.35 m mol/litre, beginning from -1.2 V.
- Curve 3 - Citric acid, conc. 7.55 m mol/litre, beginning from -1.2 V.
- Curve 4 - Phthalic acid, conc. 9.30 m mol/litre, beginning from -1.0 V.

Fig. 2: Graduated straight lines of weak acids.

1 - Oxalic; 2 - phthalic; 3 - adipic; 4 - acetic; 5 - anthranilic

Fig. 3: Relationship between $-\log K$ and $\frac{1}{C} \mu \frac{\text{litre}}{\text{m.mol}}$

0 - Experimental values for acids investigated.

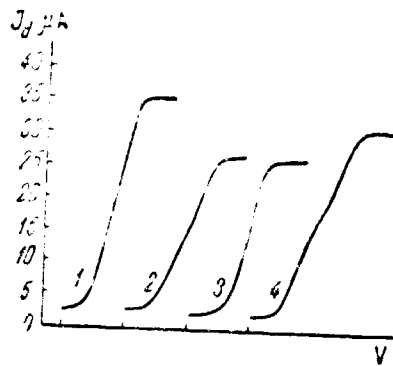


Рис. 1. Потенциометрический метод на фоне $0,05 \text{ M}$ Na_2SO_4

Кривая 1 — уксусная, конц. $15,6 \text{ ммоль/л}$, начало от $-1,4 \text{ В}$; 2 — щавелевая, конц. $4,0 \text{ ммоль/л}$, начало от $-1,2 \text{ В}$; 3 — лимонная, конц. $7,0 \text{ ммоль/л}$, начало от $-1,2 \text{ В}$; 4 — фталевая, конц. $0,30 \text{ ммоль/л}$, начало от $-1,0 \text{ В}$

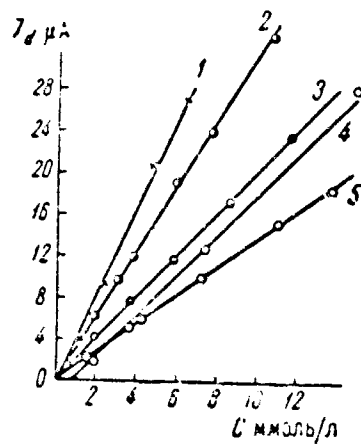


Рис. 2. Градуировочные прямые слабых кислот:

1 — щавелевая, 2 — фталевая, 3 — лимонная, 4 — уксусная, 5 — антрахионовая

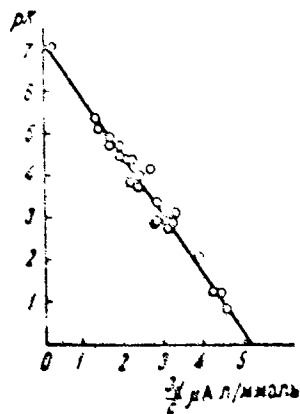


Рис. 3. Зависимость I/C от $\frac{I}{C}$

$$\frac{I}{C} \text{ на } \frac{I}{C}$$

○ — экспериментальные значения для исследованных кислот