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Zh. anal. Khim., 6 (2), 96 - 100, 1951, U.S.S.R.

In the electrolysis of solutions of different acids with the dropping mercury cathode, in most cases the discharge of the hydrogen ions is accompanied by the formation of diffusion waves. For weak acids in which the dissociation is less than 100% the movement of the ions of hydrogen to the surface of the cathode occurs because of the diffusion of the actual hydrogen ions and of the diffusion of undissociated molecules of the acid already undergoing dissociation on the surface of the cathode.

For strong acids, for example hydrochloric acid, practically the whole current depends on the diffusion of hydrogen ions, as a result of which direct proportionality is maintained between the current and the concentration of the acid. For weak acids both components of the diffusion current may be commensurate and therefore it is necessary first of all to determine whether a linear relationship is maintained between the concentration of the acid and the diffusion current. The authors examined the reduction of a number of saturated mono- and dibasic acids, aromatic acids, amino-acids and certain sulphamide compounds possessing acid properties. The solutions tested as base electrolyte were 0.1N and 1.0N hydrochloric acid, 0.1N and 1.0N solutions of potassium hydroxide, 0.1N solutions lithium sulphate and chloride, 0.1N potassium chloride and 0.05N and 0.1N solutions of tetramethylammonium iodide. In those cases where the acids examined were soluble with difficulty in water, alcoholic solutions were initially prepared and introduced into an electrolyzer containing one or another compound as base electrolyte. The concentrations of the acids examined varied from 1 to 30 m M/l. All measurements were made in a thermostat at a temperature of $25 \pm 0.2^\circ\text{C}$. The potentials were measured with reference to the saturated calomel electrode. Dissolved oxygen, in cases where it interfered with the measurements, was removed by blowing a current of electrolytic hydrogen through the solution being analysed for 15 to 20 minutes.

All diffusion currents were measured with a capillary for which $m^{2/3} t^{1/6} = 1$.

As a result of the experiments carried out it was established that hydrogen waves in the weak acids tested are not present when solutions of hydrochloric acid and potassium hydroxide are used as indifferent electrolyte.

In the presence of a considerable excess of hydrochloric acid the dissociation of the weak acid decreases to a negligibly small value and the hydrogen wave of the latter is covered by the diffusion wave of the base electrolyte.

In alkaline solutions, owing to neutralization the concentration of the hydrogen ions and also of the free acid diminishes to a very small value.

Here it should be noted that some anions of organic acids can be reduced at the dropping mercury cathode in acid and alkaline solutions. However, the half-wave potential of the anion as a rule differs from the half-wave potential of hydrogen of this acid. In addition, as will be shown later, the proportionality coefficient in the equation relating the diffusion current and the concentration during the reduction of the anion does not depend upon the dissociation constant of the acid being reduced.

According to the experiments carried out by the authors the half-wave potential of hydrogen reduction depends to some extent on the chemical nature of the acid and the concentration of the latter. At the same time the half-wave potential of hydrogen in all the acids examined is displaced towards more negative values by 10-15 mV for a 15-20 fold increase in the concentration of the acid. Only in the case of succinic acid does the half-wave potential of hydrogen reduction remain constant and equal to - 1.80 V, irrespective of the acid content in the solution investigated.

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Using solutions of neutral lithium and potassium salts and also tetramethyl-ammonium iodide as base electrolyte the direct proportionality between the hydrogen current and the concentration of certain acids is maintained, provided that the concentration of the latter is not less than 10^{-3} - 10^{-4} M/l.

Furthermore, the authors did not observe any hydrogen diffusion currents. For very weak acids of which the first dissociation constant is less than 10^{-8} .

Better shaped waves are observed when using solutions of tetrasubstituted salts as indifferent electrolyte.

Figs. 1 and 2 give some of the plotted polarograms.

Table 1 gives a summary of the acids investigated, the half-wave potentials measured for the reduction of hydrogen and the diffusion current coefficients calculated by graphs.

Figs. 3 and 4 show the straight lines for some of the acids investigated.

On examining the plotted polarograms and the graduated straight lines drawn according to these polarograms, it was noted that the diffusion current coefficient K_d in the equation:

$$i_d = K_d c,$$

where i_d is the diffusion current in microamperes and c , the concentration of the acid in millimols per litre, depends on the first dissociation constant of the acid.

TABLE 1
Half-wave potentials of hydrogen and values for weak
acids in 0.05 N(CH₃)₄NI as base electrolyte

Acid	Range of Concentr. examined in mM/l	Range of variation $E_{1/2}$ V	K_d	First dissociation constant of the acid
Formic	1-10	1,74-1,85	2,42	$1,77 \cdot 10^{-4}$
Acetic	2-15	1,76-1,86	1,95	$1,75 \cdot 10^{-5}$
Isobutyric	3-25	1,81-1,87	1,64	$1,44 \cdot 10^{-5}$
Isovaleric	4-27	1,75-1,82	1,35	$1,7 \cdot 10^{-5}$
Chloroacetic	1-10	1,65-1,71	3,14	$1,4 \cdot 10^{-3}$
Dichloroacetic	1-5	1,55-1,64	4,25	$5,0 \cdot 10^{-2}$
Trichloroacetic	1-8	1,57-1,68	4,55	$1,3 \cdot 10^{-1}$
Oxalic	1-8	1,66-1,80	4,45	$5,9 \cdot 10^{-2}$
Malonic	2-13	1,69-1,74	2,70	$1,49 \cdot 10^{-3}$
Tartaric	1-8	1,64-1,77	3,12	$1,04 \cdot 10^{-3}$
Citric	1-6	1,64-1,77	3,30	$8,4 \cdot 10^{-4}$
Malic	1,5-10	1,66-1,74	2,85	$3,88 \cdot 10^{-4}$
Pyrotartaric	1-10	1,80-1,86	2,44	$8,70 \cdot 10^{-5}$
Succinic	1-9	1,80	2,63	$6,89 \cdot 10^{-5}$
Adipic	2-11	1,76-1,80	2,07	$3,7 \cdot 10^{-5}$
Benzoic	0,9-6	1,56-1,72	1,90	$6,3 \cdot 10^{-5}$
Mandelic	2-13	1,70-1,78	2,20	$1,4 \cdot 10^{-4}$
Gallic	2-6	1,71-1,73	2,33	$3,8 \cdot 10^{-5}$
Phthalic	1-11	1,60-1,85	3,22	$1,3 \cdot 10^{-3}$
Salicylic	1-9	1,66-1,83	2,80	$1,06 \cdot 10^{-3}$
Acetylsalicylic	1-7	1,52-1,65	2,00	-
Anthranilic	3-20	1,52-1,60	1,40	$1,07 \cdot 10^{-5}$
Sulphanilic	1	1,54	-	$6,02 \cdot 10^{-4}$
Naphthionic	2	1,42-1,52	-	$2 \cdot 10^{-3}$
Cinnamic	1,8-7,2	1,96-2,05	1,92	-
N-acetylsulphanilamide	2,3-13,3	2,16-2,20	1,30	$4,2 \cdot 10^{-6}$
Sulphathiazole	2,04-14,7	1,66-1,74	0,21	$7,6 \cdot 10^{-8}$
Sulphazole	1,4-4,5	1,73-1,66	0,10	$1,6 \cdot 10^{-8}$
N-sulphanilyl-sulphanilamide	2,05-7,9	1,70-1,86	0,20	$1,4 \cdot 10^{-8}$
Sulphidin	1-2	non-reducible	-	$3,7 \cdot 10^{-9}$
Sulphanilamide	1-4	"	-	$3,7 \cdot 10^{-10}$
Boric Acid	1-10	"	-	$5,7 \cdot 10^{-11}$

The larger the dissociation constant the larger the diffusion current coefficient. This difference cannot be explained by the change of the diffusion coefficients since the latter do not differ significantly.

Probably, the increase in the diffusion current with increasing strength of the acid is linked with an increase in the concentration of the hydrogen ions, the latter having a greater mobility than the undissociated molecules. For solutions of tetramethylammonium iodide a simple relationship exists between the diffusion current coefficient (K_d) and the logarithm of the first dissociation constant of the acid taken with the opposite sign (pK) and is expressed by the equation:

$$K_d = 5.25 - 0.725 pK$$

This relationship is shown graphically in fig. 5 with K_d and pK as co-ordinates. Separate experimental values obtained by the authors are marked by small circles.

It can be seen from the equation and the diagram that the polarographic determination of the concentration of acids the dissociation constants of which are less than 10^{-7} - 10^{-8} is difficult. For such acids the hydrogen ion concentration in the solution is so small that the polarographic method becomes insufficiently sensitive.

The empirical relationship obtained permits a solution of the problem of the mechanism of the reduction of molecules possessing an acid character and reducible atomic groupings.

When the diffusion current has a half-wave potential of about -1.6, -1.8V and is in conformity with equation (1) the reduction of hydrogen can be assumed. Obviously this diffusion wave must be absent when solutions of strong acids and alkalis are used as base electrolyte.

It is evident that in the reduction of the anion a diffusion wave may be observed in acid or alkali media and should not depend on the dissociation constant of the acid.

According to the experiments of Neuman and Riabov (1) the anions of some halogen-acetic acids give diffusion currents of reduction even in alkaline solutions. However, the half-wave potentials of anions have a somewhat smaller value than the half-wave potential of the cathode current of hydrogen in these acids.

The authors used a polarographic method of analysis for quantitative determination of the concentration of a number of medicinal sulphamide compounds.

The results of a number of quantitative determinations of disulphane, sulphazole and sulphathiazole are shown in Table 2.

TABLE 2
Results of quantitative determination of
sulphamide compounds

Substance	Concentration in the solution in mM/l	Determined polarograph- ically in mM/l	Relative error in %
Disulphane	2.05	2.20	-2.5
	3.10	3.05	-1.7
	4.20	4.15	-1.2
	4.80	4.74	-1.3
Sulphazole	2.1	2.15	+2.4
	2.7	2.73	+1.1
	4.0	3.89	-2.7
	4.5	4.40	-2.2
Sulphathiazole	3.92	3.98	+1.5
	5.85	5.80	-0.9
	7.45	7.55	+1.3
	9.00	9.05	+0.6

Mean $\pm$ 2.5

For their determination the authors used calibration curves constructed by means of standard solutions. In addition, the diffusion coefficient can be calculated from equation (1) if sufficiently reliable data on the dissociation constant of the acid are available.

Equation (1) is also suitable for the determination of the first dissociation constant of a compound possessing acid properties.

Conclusions

1. It was found that weak acids produce diffusion currents of hydrogen with potentials of about -1.6, -1.8 V only in a background solution of indifferent electrolytes.
2. Between the diffusion current constant of hydrogen and the dissociation constant of weak acid there is a relationship of the form $K_d^n = a + b \log K_a$, which may be used to calculate the dissociation constant of the acid.
3. It was established that a linear relationship is maintained between the diffusion current and the concentration of the acid.

Bibliography

1. M. B. Neuman & A. V. Riabov, Scientific Reports of Gorkov State University, Edition 14, (1948).

Figures

- Fig. 1 Polarograms of solutions of acids in a base electrolyte 0.05N $(CH_3)_4NI$:
- 1) - acetic acid, concentr. 15.6 mM/l, starting from 1.4 V;
 - 2) - oxalic acid, concentr. 4.95 mM/l, starting from 1.2 V;
 - 3) - citric acid, concentr. 7.5 mM/l, starting from 1.2 V;
 - 4) - phthalic acid, concentr. 9.3 mM/l, starting from 1.0 V;

- Fig. 2 Polarograms of solutions of N-acetylsulphanilamide:
- 1) - base electrolyte 0.1N $(CH_3)_4NI$;
 - 2) - concentr. of N-acetylsulphanilamide 2.3 mM/l;
 - 3) - 3.6 mM/l;
 - 4) - 4.5 mM/l;
 - 5) - 7.2 mM/l;
 - 6) - 13.4 mM/l;

- Fig. 3 Calibration graphs for solutions of some acids:

- Line 1) - Oxalic acid;
 2) - phthalic;
 3) - adipic;
 4) - acetic;
 5) - anthranilic.

- Fig. 4 Calibration graph for N-acetylsulphanilamide in 0.05N $(CH_3)_4NI$ as base electrolyte.

- Fig. 5 Relationship between the diffusion current coefficient K_d and pK for weak acids.

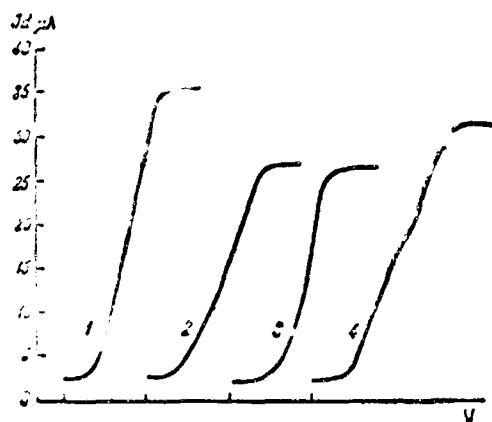


Рис. 1. Полярограммы растворов кислот на фоне $0,05\text{ N } (\text{CH}_3)_4\text{NJ}$:
кривая 1 — уксусная кислота, конц. $15,6\text{ mM/l}$, начало от $1,4\text{ V}$; 2 — щавелевая кислота, конц. $4,05\text{ mM/l}$, начало от $1,2\text{ V}$; 3 — лимонная кислота, конц. $7,55\text{ mM/l}$, начало от $1,2\text{ V}$; 4 — фталевая кислота, конц. $9,3\text{ mM/l}$, начало от $1,0\text{ V}$

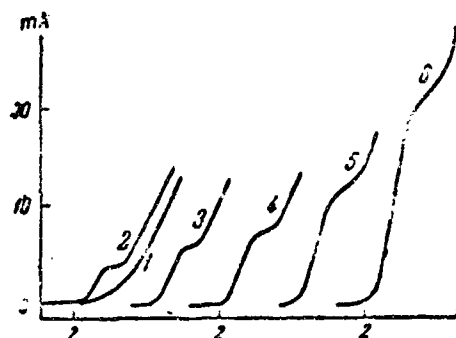


Рис. 2. Полярограммы растворов N-ацетилсульфаниламида:
кривая 1 — фон $0,1\text{ N } (\text{CH}_3)_4\text{NJ}$; 2 — конц. N-ацетилсульфаниламида $2,3\text{ mM/l}$; 3 — $3,6\text{ mM/l}$; 4 — $4,5\text{ mM/l}$; 5 — $7,2\text{ mM/l}$; 6 — $13,4\text{ mM/l}$

Рис. 3. Градуировочные графики для растворов некоторых кислот:
прямая 1 — щавелевая кислота; 2 — фталевая; 3 — адипиновая; 4 — уксусная; 5 — антрахионовая

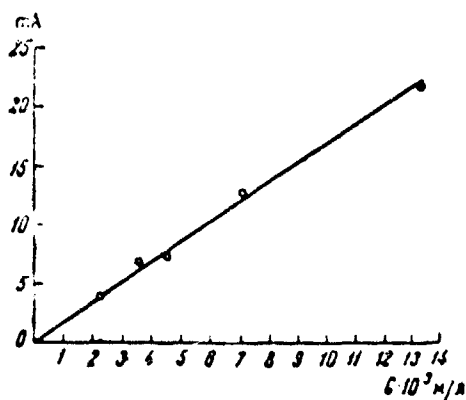
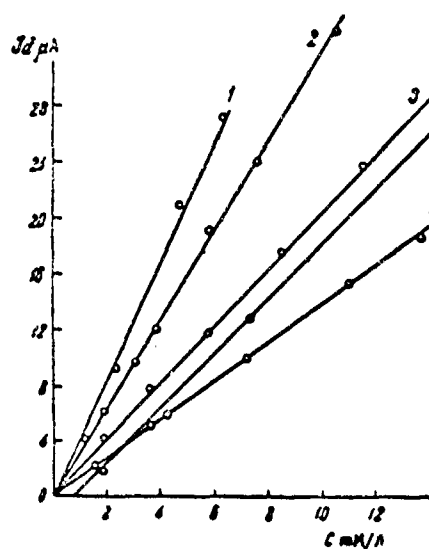


Рис. 4. Градуировочный график для N-ацетилсульфаниламида на фоне $0,05\text{ N } (\text{CH}_3)_4\text{NJ}$

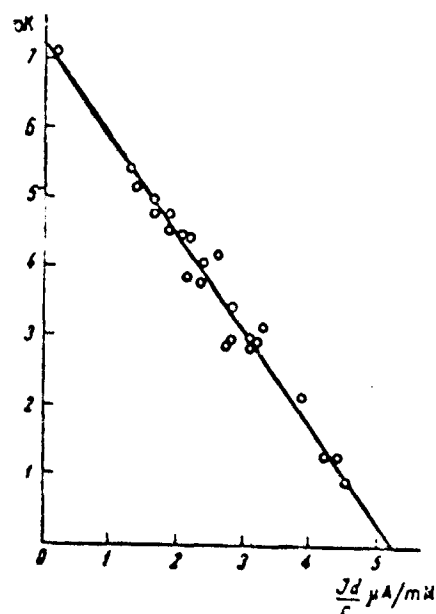


Рис. 5. Зависимость между коэффициентом диффузионного тока K_d и J_d для слабых кислот