USE OF CURRENTLESS POTENTIAL–TIME CURVES
FOR DETERMINING THE RATE CONSTANTS
OF DIAZOTATION REACTIONS

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The kinetics and the rate constants for the diazotation of nine aromatic amines at various conditions (temperature, medium) were determined by the method of currentless potential–time curves. A comparison with an independent method and with literature data is presented.

It has been shown in our previous work[1] that even reactions in other than redox systems, *e.g.* diazotation, can be studied by the method of currentless potential–time curves. The usual methods for following the diazotation kinetics are based on biamperometry[2−6], amperometry[7−10], polarography[11], spectrophotometry[12−17] of the diazo compound in the UV region, and most frequently on determining the diazo compound by coupling it with a passive component and photocolorimetry of the dye thus formed[18−27].

Our aim was to show on several examples that the diazotation of aromatic amines can be at least equally reliably but more rapidly and simply followed by using the currentless potential–time curves.

EXPERIMENTAL

Chemicals

Aqueous solutions of hydrochloric acid of reagent grade (Lachema, Brno) in concentrations of 0·1, 0·2, and 0·5 mol/l were used as base solutions. Sodium nitrite (Spolana, Neratovice) in 0·01 and 0·1 mol/l aqueous solutions was used as diazotation agent. Its solutions were stored in the dark at 2°C and their factor was determined potentiometrically with respect to sulphanilic acid. The following aromatic monoamines were used in 0·1 mol/l solutions: aniline hydrochloride pure (Spolana, Neratovice) purified twice by dissolving in ethanol, filtering through active carbon and precipitating with ether; *m*-chloroaniline of technical grade, purified twice by dissolving in ethanol saturated with HCl and precipitating with ether as hydrochloride; *p*-chloroaniline of technical grade, purified by four-fold recrystallization from boiling water. Further amines were used in concentrations of 0·01 and 0·05 mol/l in 0·1M-HCl: *o*-, *m*-, and *p*-nitroaniline (pure, Lachema, Brno), and 3-methyl-*p*-nitroaniline (Research Institute of Organic Syntheses, Rybitví) were purified by dissolving in hot water, hot filtering through active carbon, and cooling. Their purity was checked chromatographically in a system with an anchored phase formed by 30% formamide solution in methanol and a mobile phase cyclohexane–benzene[34] (3 : 1). Aniline-

-3-sulphonic acid and aniline-4-sulphonic acid of reagent grade (Lachema, Prague) were puri-
fied in the same way and their purity was checked chromatographically in the system butanol–
–pyridine–water (3 : 1 : 1). Their 0·05 mol/l aqueous solutions were used. Sulphanilic acid dried
for 4 h at 105°C served as standard. Factors of the amine solutions were determined potentio-
metrically by diazotation with sodium nitrite[35].

Apparatus

Potential–time curves were recorded on an apparatus described previously[36]. A platinum indicator
electrode of the type DPT-3 (Labora, Prague) was used. To improve the reproducibility of $E–t$
curves, the platinum electrode was freed from reaction products and nitrogen oxides by immersing
for 2 min in a solution of 10% urea and 2M-HCl prior to every measurement. The reaction solu-
tion contained a suspension of glass particles causing abrasion of the platinum electrode during
stirring, whereby its surface was more or less renewed. A saturated calomel electrode with a salt
bridge served as reference.

RESULTS AND DISCUSSION

The reaction cell with a thermostated jacketed vessel was filled with 10 or 25 ml of HCl
solution and an equal volume of the aromatic amine solution, its initial concentration
being chosen in the interval $10^{-3} - 5 \cdot 10^{-3}$ mol/l. The nitrate additions were chosen
such that the ratio $n = [NaNO_2]_{t=0}/[amine]_{t=0}$ increased from 0·1 to 1·0 at 0·1
steps. The set of $E–t$ curves thus obtained will be further referred to as "normal set".

When the rate of diazotation was too high and the $E–t$ curves recorded in the way
indicated were ill-developed (the reaction proceeded markedly during establishing
of the mixed potential), we proceeded by adding first the nitrite solution to the
solution and, after equilibration of the potential, the amine solution according
to the desired concentration and parameter n. ("Inversed set.")

The concentration–time curves were derived from the current–time curves; the
apparatus was based on biamperometric indication of nitrous acid[37] with a polariza-
tion voltage 400 mV and the $I–t$ curves were recorded on an EZ-3 type pen recorder.
The reaction cell was filled with 25 ml of an HCl solution and after thermostating
the nitrite solution was added; after attainment of a stationary current, the recorder
was switched on and after 1 min the aromatic amine was added. The initial con-
centration of nitroanilines was about $2 \cdot 10^{-4}$ mol/l, that of other amines about
by an order of magnitude higher.

The sets of $E–t$ curves corresponding to diazotation of aromatic monoamines
were used to determine the rate constant k according to ref.[28–40] from the dependence
of $t(1 - n)$ on ln n. The platinum electrode showed a nonideal behaviour as assumed
earlier[1]. A "normal set" of $E–t$ curves is shown in Fig. 1 for illustration. In addition,
the dependence of $t(1 - n)$ on ln n and the parameters $n_{t=0}$, n_{ex}, and n_2 are given
These were used to calculate numerically the values of θ D/β, and n_{-1}; the value
of θ was also determined graphically and the rate constant was calculated after

linearization[1]. Fig. 2 shows an "inversed set" of E–t curves; the method of evaluation is the same.

As an independent method, the concentration–time curves were linearized by using a kinetic equation for a reaction of the second order. The rate constant was determined from the slope of the straight lines. The results are given in Table I together with published values of the rate constants.

It can be concluded that the method of current-less potential–time curves is suitable for studies of the kinetics of diazotation. A comparison of the results of two independent methods with the published data implies that the diazotiation of aromatic monoamines can be followed by the new method with the same accuracy as with bi-amperometry or polarography, but the equipment is much simpler.
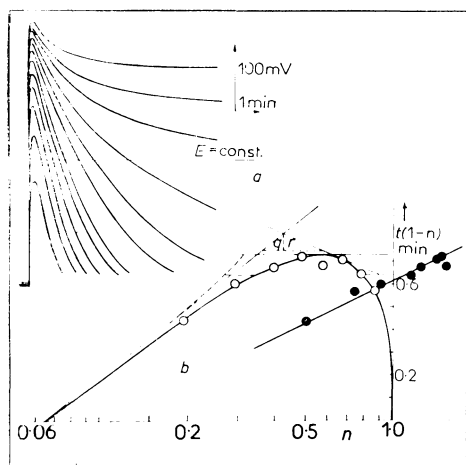

FIG. 1

Diazotation of aniline-3-sulphonic acid. a Set of E–t curves with parameter n equal to 0.194, 0.291, 0.387, 0.484, 0.58, 0.67, 0.77, and 0.87. Pt electrode — s.c.e.; 10 cm³ of 0.1M--HCl; 273.5 K, initial concentration of aniline-3-sulphonic acid $1.666 \cdot 10^{-2}$ mol/l. b Dependence of $t(1-n)$ on $\log n$ (open circles) found from t and n data for constant E. Parameters: $n(t=0) = 0.065$; $n_e = 0.56$; $n_2 = 0.61$; calculated $\theta = 1.74$, $n_{-1} = 0.67$; graphically found $\theta = 1.78$ (r/q). Linearization based on these data (solid circles); — · — · — construction of auxiliary curves, — — — — auxiliary curve
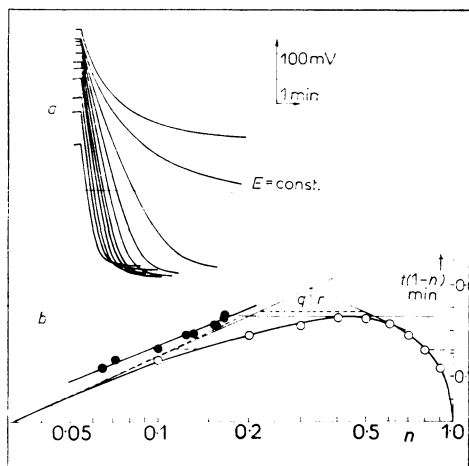

FIG. 2

Diazotation of m-chloroaniline. a Set of E–t curves with parameter n equal to 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9. Pt electrode — s.c.e; 53 cm³ of 0.2M-HCl; 298 K; initial concentration of m-chloroaniline $9.43 \cdot 10^{-4}$ mol/l. b Dependence of $t(1-n)$ on $\log n$ (open circles) found from t and n data for constant E. Parameters: $n(t=0) = 0.032$; $n_e = 0.44$; $n_2 = 0.45$; calculated $\theta = 1.09$, $n_{-1} = 0.63$; graphically found $\theta = 1.00$ (r/q). Linearization based on these data (solid circles); — — · — · — auxiliary curve construction, — — — — — auxiliary curve

TABLE I

Rate constants of diazotation reactions

Amine	[HCl] mol/l	t, °C	n.s.[a]	i.s.[b]	k dm³ mol⁻¹ s⁻¹ lit. data	biamp.[d]
Aniline	0·1	10	1·61 ± 0·1		1·1[38,x,l]	
Aniline	0·1	20	2·48 ± 0·029	2·88 ± 0·51	3·16[38,x,l]	4·6—5·5
Aniline	0·2	25	8·93 ± 1·35	8·33 ± 0·28	8·66[38,x,l]	
Aniline	0·2	15	2·51 ± 0·22		2·93[38,x,l]	
3-Chloraniline	0·2	25	67·55 ± 3·6	74·48 ± 2·66	76·73 ± 1·03[39,c]	86—100
4-Chloraniline	0·5	10	12·06 ± 1·67	12·53 ± 0·32	12·7[38,x,l]	
Aniline-3-sulphonic acid	0·1	0·1	3·32 ± 0·42	3·01 ± 0·33	3·4[11,x,p]	2·8—3·1
Aniline-4-sulphonic acid	0·1	1·5	13·21 ± 0·87	13·73 ± 0·75	16·46[11,x,p]	
4-nitroaniline	0·1	0·2		261 ± 16	300[37,y,c] 216—283[l]	
4-Nitroaniline	0·1	25		786·8 ± 84·4		668—829
2-Nitroaniline	0·1	0·2		125·9 ± 6·08	105[37,y,l] 70—105[c]	
2-Nitroaniline	0·1	25		360·53 ± 20·66		345—403
3-Nitroaniline	0·1	0·2		33·0 ± 0·61	32[37,y,l] 31[c]	
3-Nitroaniline	0·1	25		131·2 ± 7·33		147—179
3-Methyl-4-nitroaniline	0·1	25		538·7 ± 23·9		644—783

[a] Normal set; [b] inversed set; [c] from colorimetry; [d] values from biamperometry giving the limits of 16 measurements; [l] from biamperometry; [p] from polarography; [x] standard deviation not given; [y] mean error 3% for colorimetry, 5% for biamperometry.

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