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Application of New Methods to the Kinetic Study of Diazotization and Azo Coupling Reactions

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SUMMARY

New applications are described of the direct injection enthalpimetry (DIE method) and analysis of electrochemical currentless potential–time dependences to the kinetic study of the diazotization and azo coupling reactions. Basic principles of the methods used are given together with methods of treatment of the results obtained from the measurements of selected reaction systems. Applicability of the methods described is documented by a number of experimental results obtained in the field of both homogeneous and heterogeneous reactions.

1. INTRODUCTION

The diazotization and azo coupling reactions have been treated systematically by many authors who have discussed in detail the kinetics and mechanism of these reactions. Most authors, however, have

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restricted their studies to reactions proceeding in homogeneous media at analytical concentrations not usually encountered in industrial production; such results may not provide relevant information about larger scale processes. The choice of the reaction medium and thermodynamic conditions used in earlier studies also did not often correspond to the application possibilities and was governed by the aspect of a facile spectrophotometrical measurement of time dependences of concentrations of the starting substances and/or products. The azo coupling reactions at concentrations used industrially proceed by complex mechanisms involving heterogeneous phases and are accompanied by various physical phenomena such as nucleation, agglomeration, crystallization, phase transitions, etc. Moreover, coupling components can exhibit limited solubility or even insolubility in the reaction medium and thus form heterogeneous reaction systems with solid or immiscible liquid phases (depending on the temperature). Nevertheless, if such reactions proceed at large phase interfaces (emulsion, dispersion, colloidal systems) and the physical factors affecting the rate of chemical transformation do not exceed the chemical ones, then the rates of such reaction types can be approximated by the mathematical models used for homogeneous reactions, and the results obtained do not lose their basic physical meaning. This fact, however, necessitates finding such physicochemical methods which could enable one to follow not only the formal kinetic course of the chemical transformation of the reaction starting components, but also the processes connected with the intimate behaviour of the reaction system, and which would also make possible characterization of the reaction mechanism. Out of the new methods suggested and checked, two methods proved applicable, namely direct injection enthalpimetry (DIE) and analysis of the potential–time curves: they both fulfil the requirements of study of complex reaction systems.

The DIE method belongs to the group of enthalpimetric methods which have found extensive applications recently (not only in analytical but also in physical chemistry and biochemistry). Heats of chemical or phase transformations are high enough to be determined relatively easily. Time dependences of reaction temperature can also be advantageously applied to kinetic studies of chemical reactions. A critical survey of papers published before 1968 and dealing with applications of enthalpimetric methods to kinetic studies of chemical reactions is given in the introductory part of ref. 1. This paper by Meites *et al.* also describes the construction of an isoperibolic double microcalorimeter and its application to kinetic studies of the saponification of ethyl acetate in excess hydroxide. The same reaction was also investigated by West and co-workers[2,3] who utilized adiabatic calorimetry. Takashima *et al.*[4] used thermometry to follow the hydrolysis of acetic anhydride and determined the heat, rate constant, and order of this reaction. The experimental technique of following the temperature–time dependences has been described by Frankvoort and Dammers[5] (who also give methods of mathematical treatment of these dependences) and also by Alexeeva & Solomonov.[6] Panov *et al.*[7] used thermometry to study the hydrolysis of ethyl acetate and the inversion of saccharose. Sargent and Moeschler[8] similarly followed the kinetics of pseudomonomolecular reactions. Velich and Stehlík[9] studied the kinetics of the oxidation of 1,2-dioles with periodic acid (which proceeds by a complex mechanism) using the DIE method. Shin and Cris,[10] Pinnick and Smith ,[11] Jandík *et al.*[12] and Velich *et al.*[13] have developed systems of automatic data treatment applicable to titration calorimeters and to all apparatus with the output in the form of voltage changes with time.

The DIE method was used for kinetic studies of the diazotization and azo coupling reactions. Moreover, this method allows quantitative determination of the reaction components from the measured heats of the said reactions. Velich and co-workers[14] have confirmed the experimental applicability of the DIE method to kinetic studies of azo coupling: the model reaction of diazotized aniline-4-sulphonic acid with 1,8-dihydroxynaphthalene-3,6-disulphonic acid giving the azo dyestuff soluble in the reaction medium was followed by the DIE method, and the rate constants found corresponded fully to those obtained spectrophotometrically and potentiometrically. The DIE method has also been used for studies of azo coupling in heterogeneous systems[14–16] and for kinetic studies of diazotization reactions.[17]

The method of currentless potential–time curves has previously been used in successful studies of redox reactions[18–31] and in the investigation of reaction mechanisms. In all these cases the reaction components were electroactive, i.e. they all imparted a certain potential to the indication electrode. It was later shown that it is quite sufficient if only one of the reacting components forms an electroactive system: kinetics of such reactions can be followed by this method. In this way, Dlask studied the diazotization reactions of aromatic amines in hydrochloric acid media[32] and azo coupling reactions in both homogeneous and heterogeneous media.[33,34]

2. RESULTS AND DISCUSSION

2.1. The DIE method

The temperature–time dependence of a diazotization or coupling reaction proceeding in the isoperibolic calorimeter can be recorded either graphically with a compensation recorder connected with the thermistor differential bridge or numerically with a suitable digital voltmeter (again connected with the thermistor differential bridge) and suitable microcomputer. Using the integrated form of the kinetic equation of a reaction of the second order with equal initial concentrations of the reacting components, it is possible to derive eqn (1) for the time dependence of temperature changes of the reaction mixture.[9]

$$T_\infty - T_0)/(T - T_0) = \Delta T_\infty/\Delta T = 1 + (k[\mathrm{A}]_0 t)^{-1} \qquad (1)$$

where T_0, T and T_∞ are the temperatures of the reaction mixture at times $t = 0$, t and $t \rightarrow \infty$ respectively, k is the reaction rate constant ($\mathrm{dm^3\ mol^{-1}\ s^{-1}}$), $[\mathrm{A}]_0$ stands for the initial concentrations of the two reaction components ($\mathrm{mol\ dm^{-3}}$), and t is time (s). Equation (1) expresses the linear dependence of $\Delta T_\infty/\Delta T$ versus $1/t$. It can be used for verification of the reaction mechanism suggested and for the calculation of the reaction rate constant (the values ΔT_∞ and ΔT are experimentally accessible), provided the temperature changes of the reaction mixture are so small that the rate constant values remain practically unchanged. Correct calculation of the rate constant value necessitates a high accuracy of determination of the temperature of the reaction mixture at the time $t \rightarrow \infty$, which is difficult, because this temperature value can be affected in an undesirable way by heat exchange between the reaction vessel and its environment. Therefore, it is more advantageous to treat the experimental data of the temperature–time dependence numerically using the method of multiparameter non-linear regression and a suitable optimization program. The aim of the program is the estimation of parameters of the S function:

$$S = \sum_{i=1}^{n} [y_i - f_i(t_i, P(1), P(2))]^2 \qquad (2)$$

where the f_i function has the form of eqn (3) for the case of second order reaction with equal initial concentrations of the reacting components.

$$f_i(t_i, P(1), P(2)) = P(1)/(1 + 1/(P(2) * t_i * [\mathrm{A}]_0)) \qquad (3)$$

The individual parameters of the S function have the following meaning: $P(1)$ is the temperature (or output voltage of the bridge) of the reaction mixture at the time $t \rightarrow \infty$ [ΔT_∞ (K) or ΔU_∞ (mV), respectively], and $P(2)$ is the reaction rate constant ($dm^3\ mol^{-1}\ s^{-1}$).

If the diazotization or azo coupling reaction is carried out with a sufficient excess of one of the reacting components, the reaction takes pseudo first-order course, and the corresponding temperature–time dependence can be represented as:[9]

$$\ln(1 - \Delta T/\Delta T_\infty) = -k't \tag{4}$$

where k' is the rate constant of the pseudo first-order reaction (s^{-1}).

In this case the f_i function has the following form:

$$f_i(t_i, P(1), P(2)) = P(1) * (1 - \exp(-P(2) * t_i)) \tag{5}$$

These calculations provide not only the rate constant but also the ΔT_∞ value which can be compared with the value read from the recorded temperature–time dependence.

Table 1 presents the rate constants of diazotized aniline-4-sulphonic acid with 1,8-dihydroxynaphthalene-3,6-disulphonic acid in acetate buffer of pH = 4 and ionic strength $I = 1$ at various temperatures determined by the DIE method,[13] spectrophotometrically,[13] and potentiometrically.[33] The reaction was followed as a second-order one with equal concentrations of the reaction components being initially present. All the three methods give comparable results. Also compared

TABLE 1

Rate Constants of Reaction of Diazotized Aniline-4-sulphonic Acid with 1,8-Dihydroxynaphthalene-3,6-disulphonic Acid at Various Temperatures

(In acetate buffer of pH = 4, $I = 1$, with equal initial concentrations of the two reacting components)

T (°C)	*k* ($dm^3\ mol^{-1}\ s^{-1}$)		
	Spectrophotometry $[A]_0 = 1{\cdot}6666 \times 10^{-5}$ M	*DIE* $[A]_0 = 1{\cdot}4563 \times 10^{-3}$ M	*Potentiometry*[33] $[A]_0 = 3{\cdot}440 \times 10^{-3}$ M
15	26·56 ± 0·89	27·47 ± 0·99	24·60 ± 1·49
20	30·49 ± 1·34	31·47 ± 1·24	—
25	37·09 ± 0·40	37·48 ± 0·38	39·29 ± 1·68
30	40·82 ± 0·97	43·44 ± 2·28	—
35	—	—	50·2 ± 4·4

TABLE 2

Rate Constants of Reaction of Diazotized *p*-Nitroaniline with 2-Hydroxynaphthalene-6-sulphonic Acid (A) and with *N*-Ethyl-*N*-cyanoethylaniline (B) and of Diazotized *p*-Aminoacetanilide with *p*-Cresol (C) (Equal initial concentrations of the reacting components, at 25 °C, at various pH values, Ionic Strength $I = 1$)

Reaction	*pH*	*k* ($dm^3\,mol^{-1}\,s^{-1}$)	
		DIE	*Potentiometry*[34]
A	5·6	$77{\cdot}85 \pm 5{\cdot}23$	$80{\cdot}49 \pm 4{\cdot}03$
A	4·0	$21{\cdot}7 \pm 0{\cdot}7$	—
B	4·0	$22{\cdot}98 \pm 0{\cdot}67$	$21{\cdot}7 \pm 0{\cdot}8$
C	10·0	$0{\cdot}86 \pm 0{\cdot}19$	$0{\cdot}89 \pm 0{\cdot}11$

was the Arrhenius dependence of the rate constants on temperature. In this case, both the starting components and the resulting azo dyestuff are soluble in the reaction medium.

Table 2 gives the rate constants of azo coupling reactions of diazotized *p*-nitroaniline with 2-hydroxynaphthalene-6-sulphonic acid (A) and with *N*-ethyl-*N*-cyanoethylaniline (B), the latter component being present in the reaction medium in the form of an emulsion, and that of diazotized *p*-aminoacetanilide with *p*-cresol (C) at various pH values, ionic strength $I = 1$, at 25 °C. Again the rate constants presented agree with those found potentiometrically by Dlask[34] and Poláčková.[35] In these cases the azo coupling reactions involve the existence of heterogeneous phases. The results presented in Tables 1 and 2 were obtained with the use of an

TABLE 3

Rate Constants of Azo Coupling Reaction of Diazotized *p*-Nitroaniline with *N*-Ethyl-*N*-cyanoethylaniline (Equal initial concentrations of the two components ($9{\cdot}6154 \times 10^{-4}$ M), pH = 4, Ionic Strength $I = 1$, Temperature $T = 25$ °C)

Experiment no.	*k* ($dm^3\,mol^{-1}\,s^{-1}$)	ΔU_∞ (*mV*)	*Residual square sum function* U_1/n	*Exner's test*
1	20·68	39·8	$2{\cdot}07 \times 10^{-3}$	$6{\cdot}9 \times 10^{-5}$
2	22·19	36·0	$1{\cdot}19 \times 10^{-3}$	$4{\cdot}8 \times 10^{-5}$
3	22·16	35·8	$1{\cdot}01 \times 10^{-2}$	$4{\cdot}1 \times 10^{-4}$

isoperibolic calorimetric adapator with graphical recording of the temperature–time dependence.

Application of the isoperibolic calorimeter with an on-line computer[13] is illustrated by the rate constants (Table 3) of the coupling reaction of diazotized *p*-nitroaniline with *N*-ethyl-*N*-cyanoethylaniline at 25 °C in acetate buffer pH = 4. The reaction was followed as a second-order one with equal initial concentrations of the two reacting components. Figure 1 gives the temperature–time dependence recorded simultaneously with the digital record in experiment no. 1 (Table 3). From the graphical record the temperature of the reaction mixture at the time $t \to \infty$ ($\Delta U_\infty = 39{\cdot}5$ mV) can be measured and the value agrees very well with the value calculated by the optimizing method from the temperature–time experimental data read from the curve ($\Delta U_\infty = 40{\cdot}13$ mV) as well as with that calculated by the optimization method from the data read by the computer ($\Delta U_\infty = 39{\cdot}78$ mV). At the same time, these results confirm the validity of the integrated form of the kinetic equation used. Statistical evaluation of the parameters calculated from the data read by the computer and those calculated from the data obtained from the graphical record is given in Table 4. Obviously, the digital record gives better reproducibility and more accurate results. The said azo coupling reaction was also studied as a pseudo first-order process using a tenfold excess of the diazonium salt.

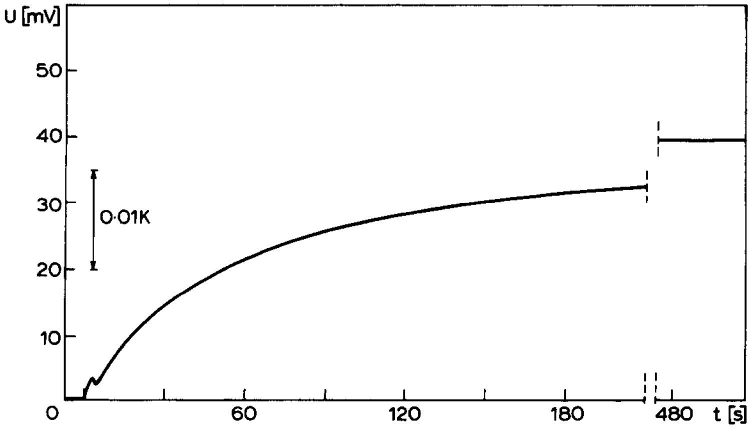

Fig. 1. The temperature–time dependence recorded for the azo coupling reaction of diazotized *p*-nitroaniline with *N*-ethyl-*N*-cyanoethylaniline at equal initial concentrations of the two components ($9{\cdot}6154 \times 10^{-4}$ M), temperature 25 °C, pH = 4, $I = 1$. The calculation gave: $k = 20{\cdot}68\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, $\Delta T_\infty = 39{\cdot}79$ mV (from the graphical record in Fig. 1: $\Delta T_\infty = 39{\cdot}5$ mV).

TABLE 4
Statistical Evaluation of the Parameters Calculated from the Data Read by the Computer and of Those Read from the Graphical Record in Fig. 1

Parameter	*Data read by computer (no. of data: 87)*	*Data read from the curve (no. of data: 28)*
k ($dm^3 mol^{-1} s^{-1}$)	$20{\cdot}6838 \pm 0{\cdot}1462$	$19{\cdot}4215 \pm 0{\cdot}8539$
ΔU_∞ (mV)	$39{\cdot}7869 \pm 0{\cdot}0697$	$40{\cdot}1263 \pm 0{\cdot}269$
Residual square sum function U_1/n	$2{\cdot}07 \times 10^{-3}$	$5{\cdot}65 \times 10^{-3}$
Exner's test	$6{\cdot}94 \times 10^{-5}$	$1{\cdot}17 \times 10^{-4}$

In this case the calculated ΔT_∞ values were multiplied by the heat capacity Q of the reaction vessel, which allowed simultaneous determination of the heat of the reaction. The results are presented in Table 5. The average value of the rate constant k of second-order reaction calculated from the rate constant k' of pseudo first-order reaction $k = 23{\cdot}30 \pm 1{\cdot}8\ dm^3\ mol^{-1}\ s^{-1}$) stands in good accordance with the rate constant determined in the reaction with equal initial concentrations of the two components (Table 3). Average value of the reaction enthalpy is $\Delta H_r = -14650 \pm 360\ J\ mol^{-1}$.

Table 6 presents, as examples, the rate constants of the diazotization reactions of some aromatic amines studied by Velich *et al.*[17] Again the reactions were studied at equal initial concentrations of the two reacting components, and the rate constants found agree with the results obtained potentiometrically by Dlask.[32] From the examples mentioned it follows

TABLE 5
Rate Constants and Reaction Heats of Azo Coupling of Diazotized *p*-Nitroaniline with *N*-Ethyl-*N*-cyanoethylaniline (with Excess of the Diazonium Salt)
(Initial concentrations: coupling component $a = 9{\cdot}6154 \times 10^{-5}$ M, diazonium salt $b = 9{\cdot}6154 \times 10^{-4}$ M)

Experiment no.	$k' = kb$ (s^{-1})	ΔT_∞ (K)	*Residual square sum function* U_1/n	*Exner's test*	$-\Delta H$ (J)	$-\Delta H_r$ ($J mol^{-1}$)
1	0·0236	0·0246	1·78E—9	$9{\cdot}0 \times 10^{-3}$	13·72	14269
2	0·0221	0·0261	8·43E—10	$3{\cdot}6 \times 10^{-3}$	14·57	15150
3	0·0238	0·0247	7·43E—10	$3{\cdot}9 \times 10^{-3}$	13·79	14343
4	0·0201	0·0256	7·86E—10	$8{\cdot}9 \times 10^{-4}$	14·27	14836

TABLE 6
Diazotization Rate Constants of Various Aromatic Amines $ArNH_2$ in 0·2 M Hydrochloric Acid
(Equal initial concentrations of $ArNH_2$ and $NaNO_2$)

$ArNH_2$	*T (°C)*	*k ($dm^3\,mol^{-1}\,s^{-1}$)*		
		DIE[17]	*Potentiometry*[32]	*Ref. 32*
Aniline	25	7·84 ± 1·38	8·93 ± 1·35	8·66
3-Chloroaniline	25	60·74 ± 4·2	74·48 ± 2·66	76·73 ± 1·03
4-Methoxyaniline	20	1·18 ± 0·31	—	—
4-Methoxyaniline	25	2·93 ± 0·44	—	—

that the DIE method can be applied successfully in the field of dyestuff chemistry.

2.2. Method of currentless potential–time curves

The method described in the Experimental section was used to record sets of *E–t* curves for various diazotization and azo coupling reactions. The set of *E–t* curves corresponding to the reaction of diazotized *p*-aminoacetanilide with *p*-cresol is presented in Fig. 2. The rate constants were determined from the sets of *E–t* curves recorded by plotting the dependences of $t(1-n)$ against $\ln n$ as described in our previous paper.[33] Equation (6) gives the relation between the time t at a certain constant potential E and the value n,

$$a_1kt(1-n) = \frac{\ln\left(n^\theta(1-n) + D_{(E)}n^\theta\right)}{B_{(E)}(1-n) + D_{(E)}n^\theta} \tag{6}$$

where a_1 is the initial concentration of the aromatic amine or the 'passive' component, k is the reaction rate constant, t is time at the potential level $E=$ constant, $B_{(E)}$ and $D_{(E)}$ are constants depending on the E potential, θ is the parameter characterizing ideal ($\theta = 1$) or non-ideal behaviour ($\theta \neq 1$) of the electrode and must be determined from experimental data, and n is the number of equivalents of the reagent added.

The eqn (6) represented in the coordinates $t(1-n)$ versus $\ln n$ gives various types of curves depending on values of the θ parameter and especially on B and D. Figure 3 gives this relation determined from the set of *E–t* curves given in Fig. 2. The reaction rate constant is obtained by

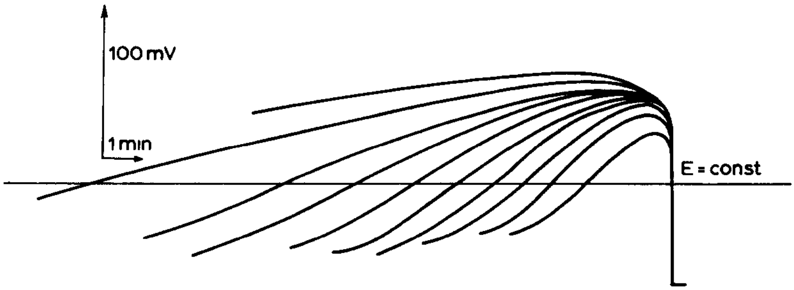

Fig. 2. A set of *E–t* curves recorded for the azo coupling reaction of diazotized *p*-aminoacetanilide with *p*-cresol: $n = 0{\cdot}1,\ 0{\cdot}2, \ldots, 1{\cdot}0$; $T = 25\,°C$; pH = 10; initial concentration of *p*-cresol $6{\cdot}9 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$.

linearization of eqn (6). The procedure for this linearization and its theoretical basis are given in refs 31, 33. The present paper gives only its description and practical conclusions. First of all, time values are read from the *E–t* curves set for various n at E = constant, and $t(1-n)$ is plotted against $\ln n$. An auxiliary graphical dependence is obtained by transferring the intercepts $a, b, \ldots, s$ to the second section of the curve, i.e. $a', b', \ldots, s'$, maintaining $a = a'$, $b = b'$, etc. This curve is transformed into a straight line for $\theta = 1$. The maximum ($n_{\max}$) of the curve is obtained by constructing the tangent thereof from the point $n_{t=0}$. The point of intersection of the tangent and the parallel to the $\ln n$ axis crossing the maximum of the curve gives the position of the n_z point. Its coordinates

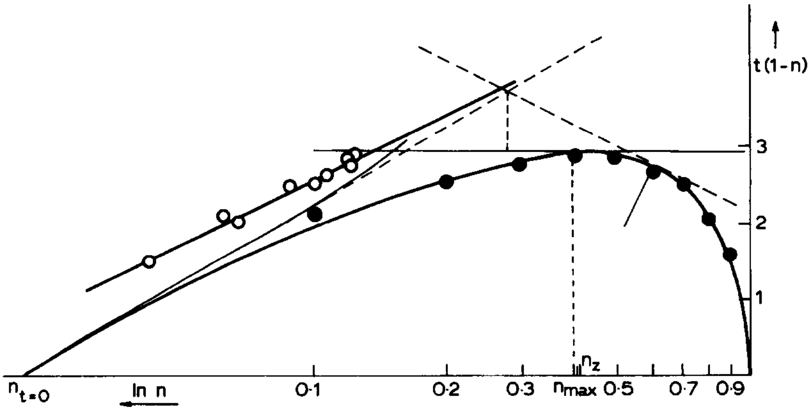

Fig. 3. The dependence of $t(1-n)$ vs. $\ln n$ obtained from the set of *E–t* curves given in Fig. 2, and its linearization: $n_{t=0} = 0{\cdot}022$; $n_{\max} = 0{\cdot}390$; $n_{-1} = 0{\cdot}599$; $n_z = 0{\cdot}405$; $\theta_{\mathrm{calc}} = 1{\cdot}12$; $\theta_{\mathrm{graph}} = 1{\cdot}20$.

are determined by transferring the distance ($n_{\max}$, q). Further calculation is carried out numerically using, e.g., a TI-58 calculator (Texas Instruments) with a linearization program. The calculation starts from the following input data: times $t_1, \ldots, t_n$ and the $n_1, \ldots, n_n$ values corresponding thereto, and the read values $n_{t=0}$, $n_{\max}$, n_z. The calculation provides the values of θ, n_{-1} and D/B. The θ value is then verified graphically. A tangent (dashed line in Fig. 3) is constructed to the curve from the point having the coordinate n_{-1}. The distance ratio $\overline{pr}/\overline{rq}$ found graphically must correspond to the θ value calculated numerically. Final calculation concerns linearization of the dependence $t(1-n)$ versus $\ln((1-n+D)n^{\theta}/((1-n)+D/Bn^{\theta}))$. Figure 4 represents the straight line with slope S, the points ○ and ● being used for the increasing and decreasing sections, respectively. The rate constant k is determined from the slope S by the application of eqn (7).

$$k = 2{\cdot}303/a_1 S \tag{7}$$

Table 7 gives the found values of rate constants of diazotization reactions together with literature data. The glossy platinum electrode always showed non-ideal behaviour ($\theta \neq 1$). The rate constant values given in the literature were obtained by biamperometry[36,37] and polarography.[38] The rate constants of the azo coupling reactions are given in Tables 1, 2 and 6 and are compared with the values obtained by the DIE method. Although the gold electrode used has a constantly regenerated surface, it cannot be considered ideal. The values of the θ parameter differed from

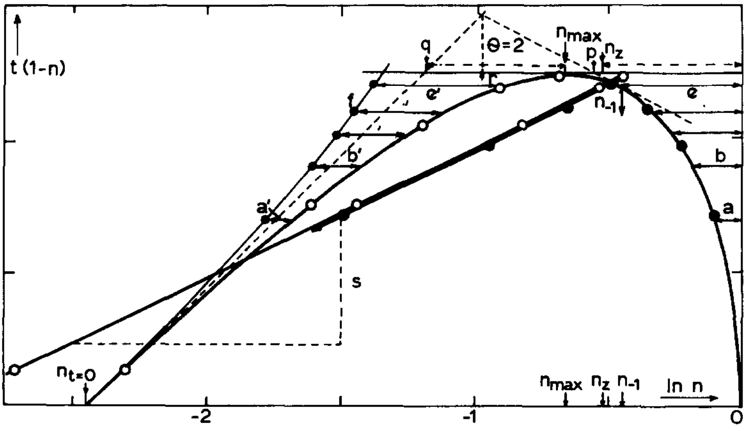

Fig. 4. The linearization procedure of the dependence of $t(1-n)$ vs. $\ln n$.

TABLE 7

Diazotization Rate Constants k ($dm^3 mol^{-1} s^{-1}$) of Various Aromatic Amines $ArNH_2$ in Hydrochloric Acid of Various Concentrations c_{HCl} ($mol\,dm^{-3}$)
(Equal initial concentrations of $ArNH_2$ and $NaNO_2$)

$ArNH_2$	T (°C)	c_{HCl}	k	k (ref. 32)
Aniline	15	0·2	2·51 ± 0·22	2·93
4-Chloroaniline	10	0·5	12·06 ± 1·67	12·7
Aniline-3-sulphonic acid	0·1	0·1	3·32 ± 0·42	3·4
Aniline-4-sulphonic acid	1·5	0·1	13·21 ± 0·87	16·46
4-Nitroaniline	0·2	0·1	261 ± 16	300
2-Nitroaniline	0·2	0·1	125·9 ± 6·1	105
3-Nitroaniline	0·2	0·1	33·00 ± 6·1	32

the value $\theta = 1$ depending on the reaction conditions of the individual measurements. Quality and reproducibility of the sets of *E–t* curves depended on concentration of the insoluble azo dyestuff formed.

On the basis of the results given in Tables 1, 2, 6 and 7, it can be stated that the method of analysis of the *E–t* curves is applicable to following kinetics of the diazotization and azo coupling reactions. The method is particularly useful in the cases of formation of an insoluble reaction product, when the other methods fail.

3. CONCLUSIONS

In this work the methods of direct injection enthalpimetry and of analysis of the potential–time curves have been used for investigation of the kinetics of diazotization and azo coupling reactions. The results obtained confirmed the applicability of the two methods in the field mentioned; these methods are particularly useful for investigations of the kinetics of azo coupling reactions proceeding in heterogeneous phases, when other methods are inapplicable. It was confirmed that, in the cases when these reactions proceed at large phase interfaces (in the presence of surfactants) and the physical factors affecting the chemical reactions do not exceed the chemical factors, the rates of this type of reaction can be approximated by mathematical models valid for reactions in homogeneous phases, and the results obtained do not lose their basic physical meaning. The graphical temperature–time dependences found experimentally when following the azo coupling reactions can also contribute in the elucidation of the kinetics of the growth of crystalline phase of the azo dyestuffs formed.

4. EXPERIMENTAL

4.1. The apparatus for the DIE method

Isoperibolic calorimeters proved most useful for investigation of the diazotization and azo coupling reactions. Figure 5 shows a calorimetric adaptor for commercial thermostats used by Velich *et al.*[8,14] Figure 6 gives a schematic representation of the isoperibolic calorimeter with 'on-line' computer suggested by Velich *et al.*[13] Both calorimeters described can be used for thermometrical titrations (TET) (the reagent is added

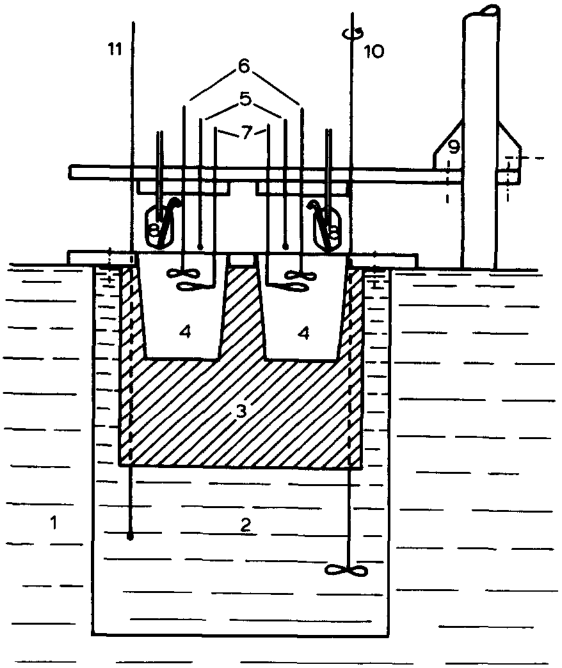

Fig. 5. Calorimetric adaptor of an NBE thermostat. 1,2, water; 3, a copper vessel with thermoinsulating foam layer; 4, reactors; 5, thermistors; 6,10, stirrers; 7, calibration resistance bodies; 8, immersed polyethylene pipettes; 9, the shaft of the calorimeter lid; 11, thermometer.

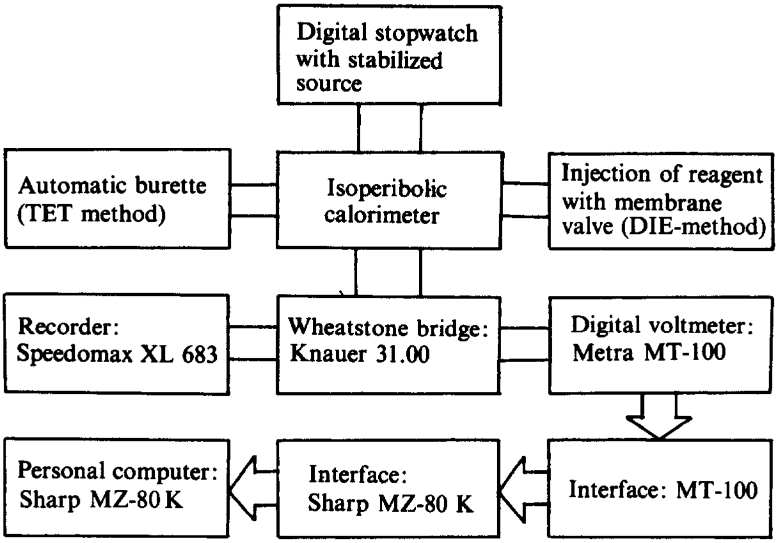

Fig. 6. Schematic diagram of the isoperibolic calorimeter with on-line computer.

continuously into the measuring and reference vessels by means of a suitable doser or automatic burette) as well as for direct injection enthalpimetry (DIE) (the reagent is added at once into the measuring and reference vessels by means of immersed polyethylene pipettes and a twin blower with diaphragm-operated valves). The isoperibolic calorimeter with an on-line computer brings a number of advantages: high objectivity of the measurement, high accuracy of the data recording, optimizing procedures involving sufficient numbers of data, possibility of routine analyses with lower demands on qualification of the calorimeter operators, possibility of storage of the experimental data in a compact cassette or disc and their treatment by suitable optimizing procedures with the use of a large computer. If the diazotization or azo coupling reaction is investigated as pseudo first-order reaction with sufficient excess of one reagent, then it is possible to determine the heat of the reaction together with the rate constant. Determination of the heat of reaction can be further used, e.g. for analytical determination of the reaction components.

Measurement method

At the beginning it is necessary to adjust suitably the sensitivity of the compensation recorder and differential resistance bridge according to the reaction type and concentration of the reacting components. After careful thermostatting of the reaction and reference solutions at the temperature required for the measurement, the pre-reaction process is followed for 2–4 min (the recorded temperature–time dependence should exhibit practically zero slope). After injection of the reagent into each vessel, the temperature–time dependence of the reaction process is recorded using either a compensation recorder (the method with 'off-line' computer) or a computer (the 'on-line' method). The experimental data are treated by a suitable optimizing method using a microcomputer.

4.2. The apparatus for the method of analysis of *E–t* curves

The potentiometric measurements were carried out with glossy platinum or ground gold indication electrodes[39] and a saturated calomel reference electrode. The two electrodes were connected with a suitable millivoltmeter with an *X–t* recorder. The apparatus is represented schematically in Fig. 7.

The sets of currentless potential–time curves were obtained in the following way: the jacketed reaction vessel with mechanical stirrer was charged with 25 or 50 cm^3 of the respective reaction medium, and a certain amount or aromatic amine (in the case of diazotization) or coupling component (for azo coupling) was added thereto from a pipette. The solution was thermostatted, and after reaching the required temperature the pen of the recorder was adjusted to the beginning of the scale and the registration chart was started at a suitable rate. At constant time intervals, the given volume of reagent (solution of nitrite or diazonium salt) was added all at once from a 5 cm^3 paraffin-coated vessel. The addition of the reagent is apparent by an abrupt increase of potential

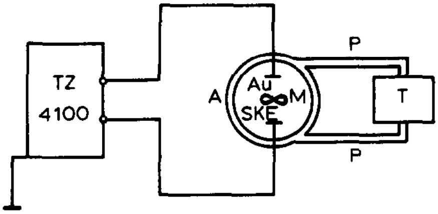

Fig. 7. Scheme of the apparatus for recording of the potential–time curves. *A*, glass-jacketed reaction vessel; *P*, inlet of heating/cooling medium; *T*, thermostat; *TZ 4100*, line recorder; *Au*, gold electrode with regenerated surface; *SCE*, saturated calomel electrode; *M*, teflon-coated magnetic stirrer.

which is changed with time. The potential–time curves were recorded until the potential remained constant. The procedure was repeated with increasing additions of the reagent. The procedure gave a set of potential–time curves with the parameter $n = [NaNO_2]_{t=0}/[amine]_{t=0}$ or $[RN_2^+]_{t=0}$/[coupling component]$_{t=0}$. The n values were varied usually within the limits|from 0·1 to 1·0 by steps of 0·1.

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