

CONTRIBUTION TO METHODOLOGY OF DETERMINATION OF DIFFUSION COEFFICIENTS OF DYESTUFFS IN SOLUTION

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Received January 21st, 1972

The method using a porous diaphragm in a modified McBain's cell has been adopted for measuring the diffusion coefficients of disperse dyestuffs in solution. The amount of the substance diffused has been determined polarographically. The method is generally applicable but lengthy. It has been substituted by or combined with a polarographic method which is considerably quicker. The diffusion coefficients have been obtained from the Ilkovič equation. The activation energy of diffusion has been computed from the diffusion coefficients measured at 25 and 45°C.

There are three basic methods described in literature for the measurement of diffusion coefficients of dyestuffs in solution. According to the method by Fürth¹ a more concentrated dyestuff solution is covered with a layer of pure solvent, and the magnitude of diffusion track is determined at definite time intervals. The diffusion coefficient is given by Eq. (1), where x , t and $f(k)$ are the

$$D = (x^2/t) f(k) \quad (1)$$

diffusion track, the diffusion time and a function of the ratio of initial concentrations $k = c/c_1$, resp. Accuracy of the determination depends on the exclusion of convection. The method is practically used only at the room temperature. The refractometric method² of determination of concentration gradient is applicable in those cases when the refractive indices of the solutions measured are sufficiently different (colourless substances). The way of evaluation of the results is usually lengthy. The third method, which can be used for determination of diffusion coefficients even at higher temperatures, is the method of porous plate by Northrup and Anson³. Two solutions are separated by a diaphragm of sintered glass (porosity G 4). Above the diaphragm there is the solution of the substance the diffusion coefficient of which is being measured (concentration c), under the diaphragm there is the pure solvent. The whole apparatus is located in a thermostat. The solution being formed under the diaphragm is analysed, and the final concentration c_1 is determined. The diffusion coefficient is given by Eq. (2), where $\lambda = v_2/v_1$; v_2 is the volume of the solution of concentration c_1 (the solution formed), (g of water at 25°C), v_1 is the volume of the solution introduced having

$$D = (K/t) \log (c/[c - c_1(\lambda + 1)]) \quad (2)$$

the concentration $c(g)$; c and c_1 are given in mol/l; t is the time of diffusion (s), K is the constant of the cell. The advantage of the method is in its relative low sensitivity to temperature changes and vibration, it is, however, very slow, one measurement taking 24 and more hours. It is stated that the method is not reliable in the cases, where the substance dissolved is adsorbed on the porous diaphragm or if a current potential is formed in its capillaries. The original apparatus was modified by McBain and Liu⁴.

The diffusion coefficient obtained by the method of porous diaphragm is an integral one (corresponding to the concentrations $c_x \neq 0$ and $c_x = c$). Under the assumption of the function $D = f(c)$ being roughly linear⁵ this value D can be related to the concentration $c_x \cong \frac{1}{2}c$ (diffusion into a pure solvent and equal volumes v_1 and v_2). D can be considered constant in very diluted solutions. The concentration c_1 was measured mostly colorimetrically. Rulfs⁶ determined the concentration c_1 of the electrolyte diffused through the diaphragm (KCl) from the height of the polarographic wave. Besides this indirect use of polarography for determination of diffusion coefficients, the Ilkovič equation⁷ (or the corrected Ilkovič equation) can be used for their direct measurements⁸ (Eq. (3)); i_d is the diffusion current (A), F is 96500 coulomb, n is the number of the electrons

$$i_d = 0.627FncD^{1/2}m^{2/3}t^{1/6}, \quad (3)$$

consumed during reduction or oxidation of depolarizer, c is the concentration of the depolarizer (mol/cm^3), D is the diffusion coefficient of the depolarizer ($\text{cm}^2 \text{ s}^{-1}$), m is the flow rate of mercury (g/s), and t is the time of one drop (s). If we know the other parameters (which are constant under given conditions) we can calculate, from the diffusion current, the diffusion coefficient of the depolarizer in an indifferent electrolyte of various concentrations. The corrected Ilkovič equation was used by v. Stackelberg and coworkers^{9,10} for determination of diffusion coefficients of some inorganic ions. The temperature dependence¹¹ of a diffusion coefficient is given by Eq. (4), where D_T , D_0 and E are the diffusion coefficient at the temperature T , a constant and the activation energy of diffusion ($\text{J mol}^{-1} \text{ K}^{-1}$ or $\text{kcal mol}^{-1} \text{ K}^{-1}$) respectively

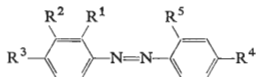
$$D_T = D_0 e^{-E/RT}. \quad (4)$$

The aim of this work was to study the dyestuffs insoluble in water, soluble in organic solvents; many of them are used under the name "disperse dyestuffs" for dyeing synthetic fibers. This work was intended as a starting point to a systematic study of other effects affecting diffusion, connected with particular requirements of dyestuff chemists for improving the quality of Czechoslovak disperse dyestuffs.

EXPERIMENTAL

Dyestuffs. The dyestuffs used were purified by extraction with solvents (if they were commercial samples), crystallization and column chromatography (Al_2O_3). Their homogeneity and purity were checked by silica gel thin layer chromatography (Silufol "UV 254") and usual paper chromatography and by determination of melting points with the use of a Kofler apparatus. The diffusion coefficients were measured for the dyestuffs given with the formulas on p. 3996.

Polarographic measurements of diffusion coefficients. The measurements were carried out with a polarograph LP 60 using compensation of capacity current in a simple polarographic vessel with mercury as anode on the bottom. The vessel was equipped with a temperating jacket, the temperature of solutions being kept at 25 or 45°C. The dyestuffs were dissolved in dimethylformamide. The choice of electrolyte had to meet the requirements of good solubility of the disperse dyestuffs, good polarographic record and pH of medium being about 6.5 (suppressing of other influences). Acetate buffer met these requirements. Composition of the mother electrolyte: 0.2M- $\text{CH}_3\text{CO}_2\text{H}$ + 0.2M- $\text{CH}_3\text{CO}_2\text{Na}$ in 70% ethanol, pH 5.9 (25°C). The solution was made rid of oxygen by bubbling with nitrogen for 15 minutes. The polarograms of the dyestuffs showed no maxima in this medium. The diffusion current was measured for several concentrations of each



- I, $R^1 = R^2 = R^3 = R^4 = R^5 = H$
 II, $R^1 = R^2 = R^3 = R^5 = H$; $R^4 = OH$
 III, $R^1 = R^2 = R^5 = H$; $R^3 = NO_2$; $R^4 = NH_2$
 IV, $R^1 = R^2 = R^3 = R^5 = H$; $R^4 = NH_2$
 V, $R^1 = R^3 = H$; $R^2 = R^5 = CH_3$; $R^4 = NH_2$
 VI, $R^1 = R^2 = R^3 = R^5 = H$; $R^4 = p-N=N-C_6H_4OH$
 VII, $R^1 = R^2 = R^5 = H$; $R^3 = OH$; $R^4 = p-N=N-C_6H_4OH$
 VIII, $R^1 = R^2 = R^5 = H$; $R^3 = NO_2$; $R^4 = N \begin{array}{l} \text{CH}_2\text{CH}_2\text{OH} \\ \text{CH}_2\text{CH}_2\text{CN} \end{array}$
 IX, $R^1 = Cl$; $R^2 = R^5 = H$; $R^3 = NO_2$; $R^4 = N \begin{array}{l} \text{CH}_2\text{CH}_2\text{OCOCH}_3 \\ \text{CH}_2\text{CH}_2\text{CN} \end{array}$
 X, $R^1 = Cl$; $R^2 = R^5 = H$; $R^3 = NO_2$; $R^4 = N \begin{array}{l} \text{CH}_2\text{CH}_2\text{CN} \\ \text{CH}_2\text{CH}_2\text{COOCH}_3 \end{array}$

dyestuff (10^{-5} – 10^{-4} M). The dependence of the diffusion current on the concentration is expressed by a straight line obtained by the least squares method. The time of a drop was measured at 25 or 45°C in the medium of the mother electrolyte after connecting the electrodes. The flow rate m was measured at 25°C and this equation was introduced into the equation for calculation of the diffusion coefficient of the dyestuff at the temperature 45°C, too (the constant error of the measurement was negligible with respect to short drop time).

Measurements of diffusion coefficients in cell with porous diaphragm. 10^{-5} – 10^{-4} M dyestuff solutions were introduced into the cell A. The mother electrolyte was the same as during the polarographic measurement, temperature 45°C. Time of the diffusion of a dyestuff was 25–44 hours. The concentration of the dyestuff solution in the vessel B was determined polarographically. Calibration of the cell was carried out by measuring the diffusion of an aqueous 0.1M-KCl solution. The concentration of the KCl solution diffused was determined by potentiometric titrimetry with 0.1M-AgNO₃ solution. The value of the diffusion coefficient in 0.1M-KCl equals $1.873 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (ref.^{12,13}, Fig. 1).

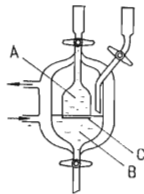


FIG. 1

Cell for Measurements of Diffusion of Disperse Dyestuffs

A The proper cell; B the outer vessel; C the porous diaphragm (sintered glass 2 mm thickness, porosity G 3).

RESULTS AND DISCUSSION

Although the Ilkovič equation corrected for spherical diffusion¹⁴ should correspond better to real conditions, the use of the simple Ilkovič equation practically results in a good agreement between the found and the calculated mean currents, which is caused by that the increase of the

current due to spherical diffusion is compensated by the decrease due to the transfer of concentration polarization⁸. *Monoazo dyestuffs* were reduced in one polarographic wave, whereas in the case of disazo dyestuffs two reduction steps could be distinguished, however, only the current corresponding to the sum of the both steps was read. The monoazo dyestuffs with one nitro group gave two perfectly developed and well separated polarographic waves. *Azo dyestuffs* can be reduced in a two- or four-electron process¹⁶⁻²¹ depending mainly on the medium. Nitro dyestuffs are reduced polarographically on a Hg-cathode to give the corresponding primary aromatic amines²². If both the azo and nitro groups are present side by side in a dyestuff molecule, their reduction usually proceeds separately²³.

Most commercial dyestuffs contain besides a reducible azo (in the case of anthraquinone dyestuffs C=O) group a further group which can be reduced under given conditions, *e.g.* $-\text{NO}_2$. Whereas the $-\text{N}=\text{N}-$ group can be reduced in a two- or four-electron way, nitro group can be maximum reduced in a six-electron way. If a substance is measured which contain *e.g.* two groups reducible under the experimental conditions ($-\text{NO}_2$, $-\text{N}_2-$), the diffusion coefficient must be practically the same irrespective of its being calculated from the diffusion current of either reduction process. Thus, if the ratio of two diffusion currents in a polarogram of a dyestuff equals 1 : 3, the only possible process taking place is of two- and six-electron types in the case of pure nitroazo dyestuff.

Simple model monoazo dyestuffs (*I*, *II* - 4-hydroxyazo dyestuffs) were reduced in two-electron way, yellow monoazo dyestuffs (*IV*, *V* - 4-aminoazo compounds) were reduced in four-electron way, whereas a complete (eight-electron) reduction took place in the case of disazo dyestuffs (*VI*, *VII*). In most cases of mononitroazo dyestuffs having higher molecular weights the first polarographic wave corresponded to a two-electron reduction of the azo group, the nitro group being reduced in six-electron way in all the cases investigated. In a number of cases, however, the reduction wave of nitro group was increased, because azo group of these dyestuffs was reduced in the four-electron way at the higher potential of the nitro group reduction. Therefore, we calculated independently the diffusion coefficients from either of the both waves and that corresponding to the sum of the both reduction processes, too.

The temperature dependence of diffusion coefficient is given by Eq. (4), the logarithmic form of which expresses¹¹ a linear dependence between $\log D_T$ and $1/T$. From the angular coefficient of this straight line the value of activation energy of diffusion was calculated, an average value of measurements of the diffusion coefficient at a temperature T being used for D_T .

The diffusion current was always read on a vertical at a point of the half-wave potential of the respective polarographic wave after elimination of the capacity current. Every value of the diffusion current was measured minimum twice. The general equation (Eq. (5)) of the straight line was obtained from the experimental values by the least squares method¹⁵.

$$i_d = b_1 c + b_0 \quad (5)$$

At the same time the standard deviation s was calculated. The tests carried out showed that the value b_0 can be considered to be zero. The values of diffusion coefficients and activation energies (though only rough estimates in the latter case) given in Table I indicate the influence of structure. The substitution of hydrogen by $\text{C}_6\text{H}_5\text{N}=\text{N}$ group or NH_2 group results in lowering of diffusion coefficients and increase in activation energy of a dyestuff (the substances *II* and *VI*, *I* and *IV*).

TABLE I

Polarographic Determination of Diffusion Coefficients of Azo Dyestuffs

 b_1 Coefficient of Eq. (5); n number of electrons; D_e diffusion coefficient from individual measurement; D average value of diffusion coefficient.

Dyestuff	°C	b_1	n	$D_e \cdot 10^6$ $\text{cm}^2 \text{s}^{-1}$	$D \cdot 10^6$ $\text{cm}^2 \text{s}^{-1}$	E $\text{kcal mol}^{-1} \text{K}^{-1}$	Note
I	25	5.510	2	4.63	4.63	6.62	A ^a
	45	7.825	2	9.34	9.34		A ^b
II	25	5.124	2	4.00	3.96	4.32	A ^a
		4.578	2	3.93			A ^c
	45	6.410	2	6.27	6.27		A ^b
III	25	4.365	2	2.90	2.80	5.00	A ^a
		15.566	8	2.31			B ^a
		4.234	2	3.35			A ^c
		14.934	8	2.62			B ^c
	45	5.713	2	4.98	4.75		A ^b
		21.783	8	4.53			B ^b
IV	25	8.696	4	2.88	2.88	8.33	A ^a
	45	13.521	4	6.97	6.97		A ^b
V	25	9.445	4	3.40	3.07	5.98	A ^a
		7.649	4	2.74			A ^c
	45	12.315	4	5.79	5.79		A ^b
VI	25	16.698	8	2.66	2.56	6.65	A + B ^a
		14.541	8	2.46			A + B ^c
	45	23.325	8	5.19	5.19		A + B ^b
VII	25	15.798	8	2.38	2.42	5.83	A + B ^a
		14.534	8	2.46			A + B ^c
	45	21.704	8	4.49	4.49		A + B ^b
VIII	25	4.300	2	3.47	3.35	2.03	A ^c
		12.462	6	3.24			B ^c
		16.941	8	3.35			A + B ^c
	45	4.720	2	4.19	4.16		A ^d
		18.480	8	4.00			B ^d
		23.875	10	4.28			A + B ^d
IX	25	3.873	2	2.81	2.49	4.53	A ^c
		13.622	8	2.18			B ^c
		18.876	10	2.66			A + B ^c
		3.775	2	2.66			A ^c
	45	13.558	8	2.16	4.03		B ^c
		4.746	2	4.24			A ^d
		17.063	8	3.65			B ^d
		23.694	10	4.20			A + B ^d

TABLE I
(Continued)

Dyestuff	°C	b_1	n	$D_e \cdot 10^6$ $\text{cm}^2 \text{s}^{-1}$	$D \cdot 10^6$ $\text{cm}^2 \text{s}^{-1}$	E $\text{kcal mol}^{-1} \text{K}^{-1}$	Note
X	25	3.538	2	1.91	1.90	7.44	A ^a
		10.594	6	1.90			B ^a
	45	4.891	2	3.65	4.19	A ^b	
		16.171	6	4.43		B ^b	
		21.752	8	4.49		A + B ^b	

A The wave of reduction of azo group; B that of nitro group (six electrons) or that of reduction of nitro group plus further reduction of azo group (8 electrons).

^a m 0.00235 gs^{-1} , t 2.96 s; ^b m 0.00235 gs^{-1} , t 2.94 s; ^c m 0.00208 gs^{-1} , t 2.60 s; ^d m 0.00208 gs^{-1} , t 2.59 s.

A p -NO₂ group (with respect to azo group) and OH or CH₃ groups lower both the diffusion coefficient and activation energy (*I* and *II*, *VI* and *VII*, *IV* and *III*, *IV* and *V*).

The diffusion coefficients were determined also by the measurement in the cell with porous diaphragm (Table II). The cells used were very small to meet the requirement of analyses of small samples. As the solutions used were rather diluted,

TABLE II

Comparison of the Diffusion Coefficients Obtained by Measurement in a Cell with Porous Diaphragm at 45°C (D') with those Obtained Polarographically (D)

c Concentration of the solution introduced into the cell, c_1 concentration of the dyestuff in outer vessel.

Dyestuff	Number of cell	$c \cdot 10^5$ M	$c_1 \cdot 10^5$ M	Time min	$D' \cdot 10^6$ $\text{cm}^2 \text{s}^{-1}$	$D \cdot 10^6$ $\text{cm}^2 \text{s}^{-1}$
<i>I</i>	1	18.98	1.463	1 800	8.80	9.34
	1	18.98	2.017	2 550	8.97	—
<i>II</i>	2	17.96	1.252	2 520	6.54	6.27
<i>III</i>	3	7.68	0.525	2 520	4.60	4.75
<i>IV</i>	1	19.98	1.276	1 800	7.16	6.97
<i>V</i>	4	14.64	1.931	2 580	6.32	5.79
<i>VI</i>	4	21.30	1.346	1 470	4.85	5.19
<i>VII</i>	2	21.36	0.891	2 580	3.67	4.49
X	2	17.84	0.725	2 520	3.65	4.19
		17.84	0.793	2 520	4.02	—

the diffusion time was long. It is disadvantageous that the constant of a cell changes during the measurements at higher temperatures¹¹. Therefore it is necessary to check it frequently. (In our particular case the mean of the following cell constants measured was taken for one of the cells used: 10·486, 9·307, 8·268, 11·085, 9·514, 11·013).

As the concentration gradient changes with time at the diaphragm (diffusion coefficient is a function of concentration), the above calculation gives an integral diffusion coefficient. In a "micro-cell" in the diffusion layer on the surface of a mercury drop, the diffusion of the dyestuff of a given concentration into pure solvent is always measured (the diffusion layer is rid of the dyestuff by reduction). Of course, in solutions so diluted as those used in our work, the diffusion coefficient is constant, independent of concentration. The diffusion coefficient measured under given conditions and calculated from Eq. (2) for a definite dyestuff concentration can thus be compared with that calculated from the Ilkovič equation. The values of diffusion coefficients obtained by the measurement in the cell and those obtained polarographically stood in a good accord (Table II). Eventual differences do not exceed those within each of the methods. Polarographic determination of diffusion coefficients is quicker than the determination in the cell.

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Translated by J. Panchartek.