

# POLAROGRAPHIC BEHAVIOUR OF ORGANIC IODOCOMPOUNDS

## Part II. Iodonaphthalene

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### INTRODUCTION

IN a previous communication,<sup>1</sup> it has been stated that in the case of iodobenzene the diffusion current constant increases with an increase in the concentration of the organic solvent. This is in contrast to the diminution in the diffusion current constant with an increase in the concentration of the organic solvent observed by many workers<sup>2-4</sup> for different substances both organic and inorganic. It was therefore thought desirable to extend these studies to the case of 2-iodonaphthalene which has a two-ring system in the molecule and compare the results with those obtained in the case of iodobenzene. In the present communication, the influence of different proportions of ethanol, dioxane and acetone in the aqueous base solutions on the polarographic behaviour of 2-iodonaphthalene is presented.

### EXPERIMENTAL

The experimental polarographic technique has been essentially the same as that described previously.<sup>1</sup> The values of '*m*' of the dropping mercury electrodes employed have been 1.183 and 1.059 mg./sec. and the drop-time '*t*' has been adjusted to be 5 seconds a drop in 1 normal potassium chloride. The temperature of recording the polarograms has been  $30^{\circ} \pm 0.1^{\circ}$  C. Diffusion coefficients have been measured by the diaphragm cell technique as already described.<sup>1</sup> The cell constant has been determined by employing potassium chloride as the reference substance and is found to be 0.5782 log units per sec. The King and Cathcart<sup>1</sup> equation is employed for calculating the diffusion coefficient.

2-Iodonaphthalene was prepared by diazotisation of 2-aminonaphthalene and subsequent decomposition of the diazonium salt with potassium iodide as suggested by Schmidl.<sup>5</sup> The crude product is recrystallised from

ethanol and dried *in vacuo* (m.p. 54.5° C.). Alcohol, dioxane and acetone have been purified by standard methods.<sup>6,7</sup> One molar lithium chloride (prepared from reprecipitated lithium carbonate) was used as the indifferent electrolyte. As no maximum appeared on the C-V curve no gelatin was added to the base solution.

*Measurement of polarographic characteristics of 2-iodonaphthalene*

1. Effect of concentration of ethanol, dioxane and acetone on the diffusion current constant, half-wave potential and  $E_2-E_1$  of 2-iodonaphthalene.

Some of the polarograms showing the influence of the concentration of ethanol and dioxane are given in Figs. 1 and 2. For purposes of comparison the curves obtained employing 30%, 40% and 60% are also included in Fig. 1. It is clear that the wave heights are practically the same in all cases. The waves in acetone media are similar to those in ethanol. The results of analysis of various polarograms are presented in Table I.

TABLE I

*Effect of concentration of organic solvent on the polarographic behaviour of 2-iodonaphthalene*

Organic solvent		% by volume of organic solvent	Diffusion current constant	$E_1$ vs. S.C.E. (Volt)	$E_2-E_1$ (Volt)
Ethanol	..	10	2.56	-1.543	0.096
		25	2.52	-1.557	0.104
		50	2.49	-1.568	0.102
		75	2.49	-1.581	0.103
		98	2.46	-1.602	0.109
Dioxane	..	10	2.42	-1.502	0.093
		25	2.40	-1.547	0.098
		40	2.40	-1.581	0.105
		50	2.38	-1.603	0.100
		60	2.34	-1.655	0.102
Acetone	..	10	3.24	-1.521	0.090
		20	3.22	-1.542	0.092
		25	3.21	-1.563	0.100
		50	3.17	-1.580	0.105
		60	3.14	-1.620	0.108

It has to be pointed out that solutions containing more than 60% dioxane or acetone have not been used as it is not possible to employ one molar lithium chloride, when higher concentrations of dioxane or acetone are employed in the base solution. Increase in the concentration of dioxane or acetone increases the resistance of the cell circuit.

The above results indicate that there is very little change in the diffusion current constant of 2-iodonaphthalene with an increase in the concentration of the organic solvent. This is surprising since in the case of iodobenzene<sup>1</sup> an increase in the diffusion current constant has been observed with an enhancement in the organic solvent concentration. The diffusion current constant in acetone solutions is greater than in alcohol or dioxane systems. The half-wave potential shifts slightly to more negative values with an increase in the concentration of the organic solvent as in the case of iodobenzene. The values of  $E_2-E_1$  are of the order 0.1 V indicating that the reduction process is irreversible in character.

*Measurement of the diffusion coefficient of iodonaphthalene*

1. *Diaphragm cell method.*—Since the diffusion current constants of 2-iodonaphthalene (Table I) were practically the same at different concentrations of the organic solvent, the diffusion coefficients have been determined only at one concentration of the organic solvent, namely, 50% by volume. The diffusion coefficients under the above conditions are  $5.098 \times 10^{-6}$ ,  $4.71 \times 10^{-6}$  and  $7.40 \times 10^{-6}$  sq. cm. per sec. in ethanol, dioxane and acetone respectively, showing that the diffusion coefficient depends upon the solvent used.

2. *Equivalent conductivity data.*—The diffusion coefficient of iodonaphthalene has been computed from the equivalent conductivity of *o*-iodobenzoic acid by the method described previously.<sup>1</sup> The value is found to be  $9.28 \times 10^{-6}$  sq. cm. per sec. at 30° C.

3. *Viscosity method.*—Employing the viscosities of the base solutions determined by the Ostwald viscometer, the diffusion coefficients of iodonaphthalene in different concentrations of the organic solvent have been calculated employing the Stokes-Einstein diffusion equation modified to suit the polarographic conditions.<sup>1</sup> The molar volume of iodonaphthalene is taken to be 181.9. The viscosities of the base solutions and the diffusion coefficients calculated on their basis are presented in Table II.

It is seen that the values of the diffusion coefficient decrease with an increase in the concentration of the organic solvent, while the values of the diffusion current constants (Table I) remain practically the same at all concentrations of the organic solvent used.

TABLE II

*Diffusion coefficient of iodonaphthalene at different concentrations of organic solvent computed from viscosity data*

Concentration of lithium chloride = 1 M.

Ethanol			Dioxane			Acetone		
% by volume	$\eta$ of the base solution (centipoises)	$D \times 10^6$ (sq. cm. per sec.)	% by volume	$\eta$ of the base solution (centipoises)	$D \times 10^6$ (sq. cm. per sec.)	% by volume	$\eta$ of the base solution (centipoises)	$D \times 10^6$ (sq. cm. per sec.)
10	1.184	4.48	10	1.150	4.63	10	1.093	4.86
25	1.650	3.22	25	1.559	3.41	20	1.263	4.21
50	2.318	2.29	40	2.079	2.55	25	1.371	3.87
75	2.653	2.00	50	2.444	2.17	50	1.445	3.68
98	2.820	1.88	60	2.638	2.01	60	1.445	3.68

Comparison of the diffusion coefficients obtained by the three methods reveals significant differences in the values. The diffusion coefficients obtained by the diaphragm cell method are different from those calculated by viscosity data under similar conditions. The value derived from equivalent conductivity data does not agree with the values obtained either by the diaphragm cell method or the viscosity method.

*Calculation of the number of electrons involved in the reduction process from the Ilkovic Equation*

The number of electrons involved in the reduction process has been calculated on the basis of the Ilkovic Equation<sup>1</sup> by employing the diffusion coefficients obtained by the diaphragm cell, viscosity and equivalent conductivity methods. It is noteworthy that when the diffusion coefficients determined by the diaphragm cell are used, the number of electrons involved in the reduction of 2-iodonaphthalene is found to be 1.8, 1.8 and 1.9 in 50% ethanol, dioxane and acetone respectively. The number of electrons as calculated by employing the diffusion coefficients from the other two methods are given in Table III. It is clear that the values of 'n' vary very widely from two though there is fortuitous coincidence in some cases.

TABLE III

*Number of electrons involved in the reduction of 2-iodonaphthalene in aqueous mixtures of ethanol, dioxane and acetone calculated employing the diffusion coefficients from the conductivity and viscosity methods*

Concentration of lithium chloride = 1 M.

Organic solvent	% by volume of organic solvent	'n' calculated from the diffusion coefficient by		
		conductivity method	viscosity method	
Ethanol	..	10	1.4	2.0
		25	1.4	2.3
		50	1.3	2.7
		75	1.3	2.8
		98	1.3	2.9
Dioxane	..	10	1.3	1.9
		25	1.3	2.1
		40	1.3	2.5
		50	1.3	2.7
		60	1.3	2.7
Acetone	..	10	1.8	2.4
		20	1.7	2.6
		25	1.7	2.7
		50	1.7	2.7
		60	1.7	2.7

#### DISCUSSION

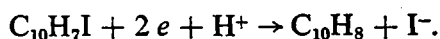
1. Influence of solvent on the diffusion current constant and diffusion coefficient and the mechanism of the reduction process of 2-iodonaphthalene.

It has been found that, in the case of iodonaphthalene (Table I), the diffusion current constant is practically constant with an increase in the concentration of the organic solvent in contrast to the behaviour of iodobenzene<sup>1</sup> where an increase has been noticed. This is surprising since iodonaphthalene is closely related to iodobenzene in structure. In the case of iodobenzene it has been shown that the variations in the diffusion current constants in all the three solvents are solely due to the variations in the diffusion coefficients determined by the diaphragm cell method under polarographic conditions.

Even in the case of iodonaphthalene, it has to be pointed out that the diffusion current constants in 50% ethanol, dioxane and acetone are proportional to the square-root of the diffusion coefficients determined by the diaphragm cell method. It is therefore reasonable to conclude that even in the case of iodonaphthalene the diffusion coefficient as determined by the diaphragm cell method accounts for the constant value of the diffusion current constant at different concentrations of each of the organic solvents employed in the investigation. On the other hand, the diffusion coefficients derived from viscosity data decrease with an increase in the concentration of the organic solvent, indicating that it is not possible to explain the constancy of the diffusion current constant on this basis.

As already pointed out the number of electrons involved in the reduction process calculated on the basis of the diffusion coefficient by the diaphragm cell technique is two. The values of 'n' calculated using the diffusion coefficients from viscosity data vary from 1.9–2.7. The diffusion coefficient from the equivalent conductivity data does not explain the differences in the diffusion current constant values in the various solvents and also lead to values of 'n' varying between 1.3–1.8. It can therefore be concluded that it is not possible to depend upon the diffusion coefficients computed either from the viscosity or equivalent conductivity methods to arrive at the reduction mechanism by using these values in the Ilkovic Equation.

The following mechanism can be suggested for the reduction of iodonaphthalene in all the three solvents:—



The above mechanism is similar to the one suggested in the case of iodobenzene.<sup>1</sup>

2. Effect of concentration of the organic solvent on the half-wave potential and  $E_3-E_4$ .

As in the case of iodobenzene,<sup>1</sup> an enhancement of the proportion of the organic solvent in the base solution shifts the half-wave potential to more negative values (Table I), indicating greater difficulty of reduction. The values of  $E_3-E_4$  are of the order of 0.1 V indicating the irreversible nature of the reduction process.

#### SUMMARY

1. The polarographic behaviour of 2-iodonaphthalene has been studied in aqueous mixtures of ethanol, dioxane and acetone containing 1 M lithium chloride. The diffusion current constant is practically unaltered with the solvent concentration. Employing the diffusion coefficients determined by

the diaphragm cell method in the Ilkovic Equation the number of electrons involved in the reduction process has been calculated as two. The limitations in employing the diffusion coefficients obtained by equivalent conductivity and viscosity methods for arriving at the reduction mechanism have been pointed out.

2. The half-wave potential shifts to more negative values with an increase in the concentration of the organic solvent. The values of  $E_{\frac{1}{2}}-E_{\frac{1}{2}}$  have been found to be of the order of 0.1 V. indicating the irreversibility of the electrode process.

#### ACKNOWLEDGEMENT

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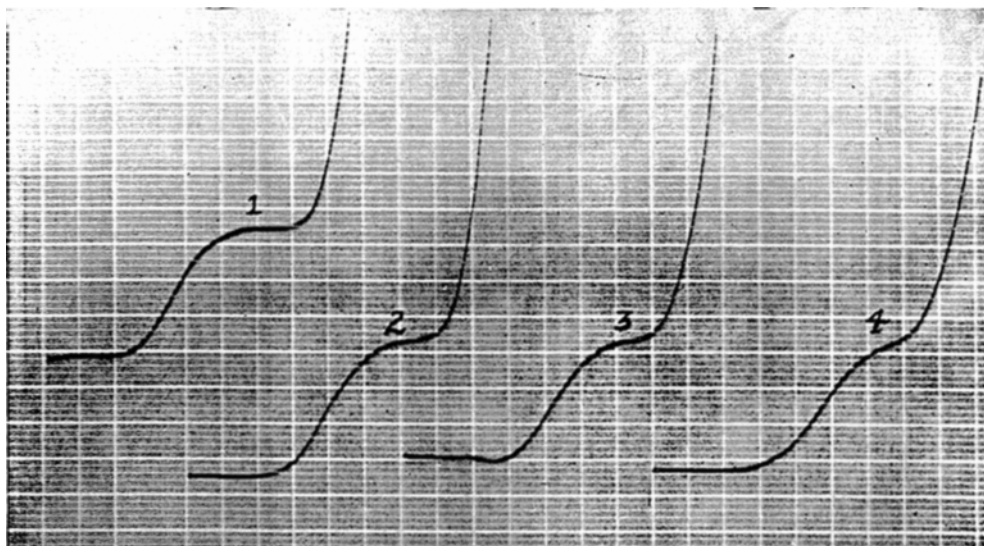


FIG. 1. Effect of concentration of ethanol on the polarographic behaviour of 2-iodonaphthalene (1.268 millimolar) employing 1 M lithium chloride as indifferent electrolyte. Curves 1-4 are obtained using 30%, 40%, 50% and 60% ethanol respectively. Sensitivity : S/70. The voltage line just before the beginning of each polarogram corresponds to  $-1.173$  V. vs. S.C.E.

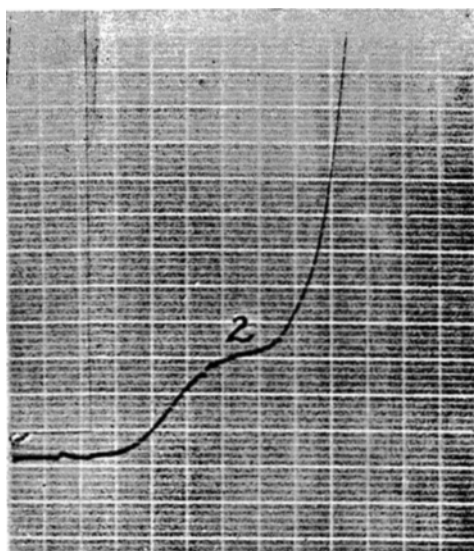
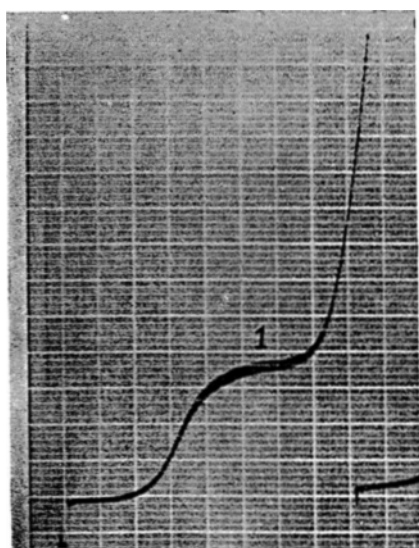


FIG. 2. Effect of concentration of dioxane on the polarographic behaviour of 2-iodonaphthalene (1.032 millimolar) employing 1 M lithium chloride as indifferent electrolyte. Curves 1-2 are obtained using 10% and 60% dioxane respectively. Sensitivity: Curve 1, S/50; Curve 2, S/70. The voltage line just before the beginning of each polarogram corresponds to  $-1.173$  V. vs. S.C.E.