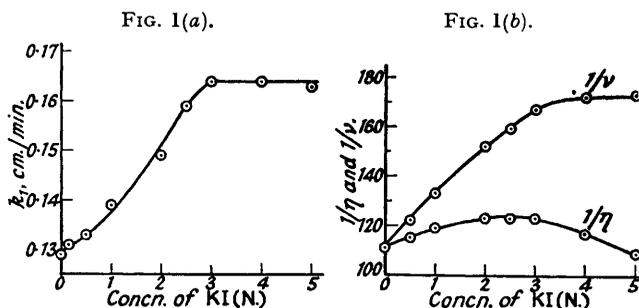


342. *The Kinetics of the Dissolution of Zinc in Aqueous Iodine Solutions. Part II.*

By L. L. BIRCUMSHAW and A. C. RIDDIFORD.

An increase in the concentration of potassium iodide produces a marked increase in the rate of dissolution of zinc in aqueous iodine solutions. This increase is comparable with the increase in the coefficient of diffusion of iodine under the same conditions, and both have been correlated with the decrease in the kinematic viscosity, ν , of the solution. By varying the viscosity of the solutions it is shown that the relation between the observed rate constant per unit area per unit volume, k_1 , and ν at 25° may be expressed: k_1 (cm. min.⁻¹) = 0.00342(1/ ν)^{0.75}. The observed rate is at least partly determined by the rate of transport of iodine to the zinc surface; it is independent of the rate of recession of products from the surface.

THE results reported in Part I (*J.*, 1951, 598) are consistent with the view that the observed rate of dissolution of zinc in aqueous iodine solutions is at least partly determined by the rate of a transport process. The observed rate should therefore be a function of the viscosity of the solution. Van Name and Hill (*Amer. J. Sci.*, 1913, **36**, 543) have shown this to be the case for the dissolution of cadmium in such solutions, but were unable to establish the relation between the observed velocity constant and the viscosity.



In view of the importance of the point, and the fact that Edgar and Diggs (*J. Amer. Chem. Soc.*, 1916, **38**, 253) and Miller (*Proc. Roy. Soc.*, 1924, *A*, **106**, 724) experienced difficulty in correlating the change in the diffusion coefficient of iodine in aqueous iodide solutions with the viscosity, it seemed desirable to study the viscous effect in some detail. Accordingly, this part of the present work reports the investigation of the following points: (1) the effect of varying the concentration of potassium iodide; (2) the effect of varying the viscosity of the solution by the addition of sucrose; (3) the effect of replacing potassium iodide by other iodides.

EXPERIMENTAL.

The apparatus and experimental method have been described (Part I, *loc. cit.*). The solutions were initially $N/25$ with respect to iodine and $N/100$ with respect to sulphuric acid. Zinc specimens (3.0×4.0 cm.), polished in the standard manner, were rotated in the solutions at 100 r.p.m. The temperature was $25^\circ \pm 0.01^\circ$.

Concentration of Potassium Iodide.—The concentration of potassium iodide was varied over the range 0.5–5.0N., the experimental conditions being otherwise standard. An Ostwald viscometer was used to determine the viscosity of the solutions. A correction for the deviation from Poiseuille's law was applied, using the method proposed by Barr ("A Monograph of Viscometry," 1931), whereby the viscometer is calibrated by using a series of liquids of known viscosity.

The observed values of the rate constant per unit area per unit volume, k_1 , together with the values of the coefficient of dynamic viscosity, η , kinematic viscosity, and density of the solutions are recorded in Table I. Values of k_1 for runs in which the concentration of potassium iodide was zero and $N/6.25$, respectively (Table III, Part I), have been included for comparison. In Fig. 1(a) the mean values of k_1 are plotted against concentration of potassium iodide. In Fig. 1(b) values of the fluidity ($1/\eta$), and of the function $1/\nu$, are similarly plotted.

TABLE I.

KI, g.-equiv./l.	k_1 (obs.), cm. min. ⁻¹ .	Mean k_1 , cm. min. ⁻¹ .	d , g./ml.	η , cp.	ν , cs.
0	0.129, 0.129	0.129	0.9972	0.901	0.903
0.16	0.131	0.131	1.0205	0.889	0.870
0.5	0.134, 0.132	0.133	1.0611	0.869	0.819
1.0	0.138, 0.139, 0.139	0.139	1.1176	0.839	0.751
2.0	0.147, 0.149, 0.151	0.149	1.2378	0.816	0.659
2.5	0.158, 0.159	0.159	1.2957	0.814	0.628
3.0	0.163, 0.164	0.164	1.3549	0.813	0.600
4.0	0.164	0.164	1.4699	0.854	0.581
5.0	0.160, 0.166	0.163	1.5852	0.915	0.577

Viscosity of the Solution.—The viscosity of the solutions was increased by the addition of sucrose. Preliminary tests on $N/25$ -iodine which was 1.0M. with respect to sucrose showed that the concentration of iodine remained unchanged at 25° for 3 days. This solution was then made 0.01N. in sulphuric acid, whereafter the iodine titre remained constant for 5 hours.

The results are recorded in Table II. Values of the function $(\Sigma \nu \Delta \log c)/A$ (see Part I) for one run at each different concentration of sucrose are plotted against time in Fig. 2.

TABLE II.

Sucrose, g.-mol./l.	k_1 (obs.), cm. min. ⁻¹ .	Mean k_1 , cm. min. ⁻¹ .	d , g./ml.	η , cp.	ν , cs.
0	0.131	0.131	1.0205	0.889	0.870
0.25	0.108, 0.105	0.107	1.0551	1.124	1.065
0.5	0.0857, 0.0854	0.0856	1.0832	1.462	1.350
0.75	0.0684, 0.0690	0.0687	1.1182	1.992	1.782
1.0	0.0524, 0.0530	0.0527	1.1441	2.836	2.479
1.5	0.0291, 0.0289	0.0290	1.2039	6.610	5.490
2.0	0.0140, 0.0144	0.0142	1.2447	20.64	16.58

Other Iodides.—The effect of replacing potassium iodide by other iodides was investigated. May and Baker "Laboratory" grade sodium and ammonium iodides were used without further purification. Zinc iodide solutions were prepared from "AnalaR" zinc and hydriodic acid. The effect of each iodide was studied at three concentrations. In addition, k_1 was determined for a solution which was $4N/25$ with respect to potassium iodide and $4M/25$ with respect to zinc iodide. The results are recorded in Table III.

TABLE III.

Iodide, g.-equiv./l.	k_1 (obs.), cm. min. ⁻¹ .	Mean k_1 , cm. min. ⁻¹ .	d , g./ml.	η , cp.	ν , cs.
<i>Sodium iodide.</i>					
0.16	0.129, 0.131	0.130	1.0210	0.908	0.889
1.0	0.130, 0.131	0.131	1.1141	0.928	0.833
2.0	0.138, 0.139	0.139	1.2296	0.967	0.786
<i>Ammonium iodide.</i>					
0.16	0.132, 0.129	0.131	1.0167	0.891	0.876
1.0	0.139	0.139	1.0919	0.840	0.769
2.0	0.152, 0.153	0.153	1.1823	0.800	0.677
<i>Zinc iodide.</i>					
0.32	0.127, 0.127	0.127	1.0396	0.940	0.904
0.5	0.123, 0.125	0.124	1.0698	0.968	0.905
1.0	0.121, 0.121	0.121	1.1362	1.042	0.917
<i>Zinc iodide (+ 4N/25-KI).</i>					
0.32	0.126, 0.127	0.127	1.0648	0.934	0.877

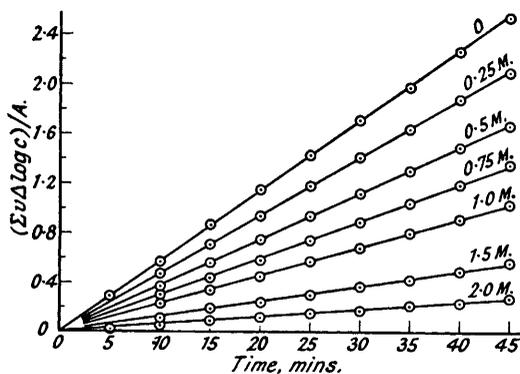
DISCUSSION.

An increase in the concentration of potassium iodide results in an increase in the observed rate. Similar results have been reported by Van Name and Edgar (*Amer. J. Sci.*, 1910, **29**, 237) and by Bircumshaw and Everdell (*J.*, 1942, 598). These authors have noted the similarity between the increase in the velocity constant and in the coefficient of diffusion of iodine, D , under the same conditions. Edgar and Diggs's values for D at 25° (*loc. cit.*) are plotted in Fig. 3, which may be compared with Fig. 1(a). Miller (*loc. cit.*) found a similar increase in D at 19.91° Edgar and Diggs, and Miller, found difficulty in correlating this increase in D with variation in the viscosity of the solution. Miller, in particular, stated that the Stokes-Einstein relation is not applicable to this system.

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Now potassium iodide belongs to the class of electrolytes exhibiting the characteristic of so-called negative viscosity (see Rabinovich, *J. Amer. Chem. Soc.*, 1922, **44**, 954; Hatschek, "The Viscosity of Liquids," 1928, p. 125). Examination of the results reported in Table I shows that as the concentration of potassium iodide is increased the viscosity of the solution passes through a minimum at *ca.* 2.5N. At high concentrations the solutions are more viscous than water. Thus the plot of the fluidity of the solution against iodide concentration [Fig. 1(b)] bears no resemblance to the corresponding plots of D and k_1 . On the other hand, the plot of the function $1/\nu$, which may be termed the kinematic fluidity, against concentration is distinctly similar in shape to the plots of D and k_1 , a limiting value being reached in each case at *ca.* 3N. For sodium iodide solutions (Table III), the rate increases with increasing salt concentration over the range studied. Over the same range ν decreases whereas η increases.

FIG. 2.



(Molarities on curves refer to added sucrose.)

FIG. 3.

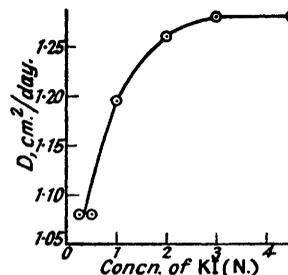


FIG. 4.

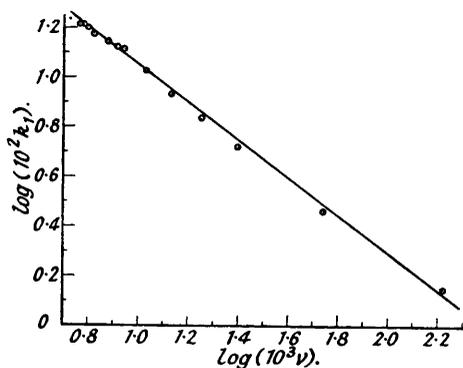
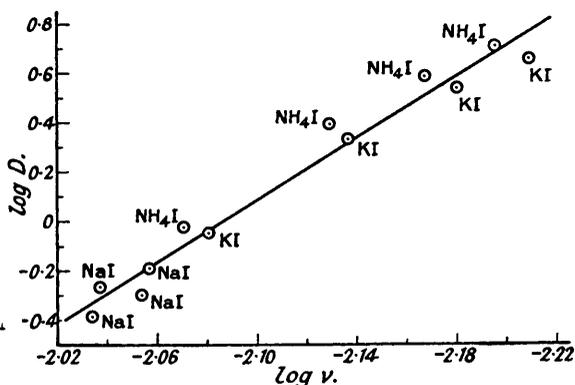


FIG. 5.



Thus it is difficult to escape the conclusion that, for this system at least, the effects are governed by the value of ν rather than of η .

Although the variation in ν is comparatively small, the results are sufficiently accurate to show that neither k_1 nor D is directly proportional to the kinematic fluidity. The results are rather to be expressed by relations of the form $k_1 = \text{constant}(1/\nu)^{\text{const}}$, where the power is smaller than unity and, on general grounds, is assumed to be temperature invariant. Since the temperature coefficients of k_1 and D differ from that of $(1/\nu)$ (Part I, *loc. cit.*), the constant of proportionality will be temperature dependent.

The 15 values of k_1 recorded in Tables I and II correspond to a range in ν from 0.58 to 16.58 centistokes. Application of the method of least squares gives the expression $k_1 = 0.00342(1/\nu)^{0.75}$. The plot of $\log k_1$ against $\log \nu$ is shown in Fig. 4; the solid line corresponds to the above expression, and is seen to correlate the results satisfactorily. Moreover the relation expresses the results recorded in Table III with a maximum deviation of 5.4%, the average

deviation being 2.7%. Hence it seems permissible to conclude that the equation expresses the relation between k_1 and ν within the limits of experimental error.

It is of interest to see whether the data for the diffusion of iodine in aqueous solutions may similarly be correlated with ν . Miller's data for the diffusion of iodine in solution of potassium, sodium, and ammonium iodides at 19.91° are the more extensive, and may be expressed as $D_{19.91}$ (cm.²/day) = $0.0486(1/\nu)^{0.63}$. The data plotted logarithmically in Fig. 5 are seen to be expressed reasonably well by the above relation. On the assumption that the power on the viscous term is temperature invariant, Edgar and Diggs's results are reasonably expressed as $D_{25} = 0.0529(1/\nu)^{0.63}$.

It is concluded that the results reported in this paper support the view that the overall rate of reaction between zinc and aqueous solutions of iodine is at least partly determined by the rate of a transport process. Of the two taking place, it is certain that it is the rate of transport of iodine to the surface of the specimen which affects the observed rate, and not the transport of products from the surface. This is shown by the fact that the observed velocity is strictly of the first order with respect to the concentration of iodine in the bulk of the solution over the time interval studied. Moreover the observed lowering of the rate in the presence of added zinc iodide is quantitatively accounted for by the increase in the kinematic viscosity of the solution. Apart from the viscous effect, then, the concentration of product is without effect on the observed rate under the conditions studied.

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