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Effect of the Dielectric Constant on the Reaction between the Iodide Ion and Hexacyanoferrate(III) in Acid Media

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In the reaction between the iodide ion and hexacyanoferrate(III), the order is unity with respect to the iodide ion and two with respect to the ferricyanide ion. It has been observed that the rate of the reaction increases with the increase in the dielectric constant of the medium. It has also been observed that the reaction occurred between trivalent and univalent negative ions.

The effect of the dielectric constant on the reaction between the iodide ion and ferricyanide in acid media has not yet been studied. The kinetic data show that the order with respect to ferricyanide is two, while that with respect to iodide is unity. By increasing the dielectric constant of the medium, the rate of the reaction is increased; this effect will be discussed in this paper, using the Brönsted-Christiansen-Scatchard(1) equation. The product of the ionic charges of the two reacting species will be calculated, and lastly we will come to the

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(1) E. S. Amis, "Kinetics of Chemical Change in Solution" (1949), 99.

conclusion that the reaction occurs between trivalent and univalent negative ions.

Experimental

Materials Employed. The solution of potassium ferricyanide was prepared by dissolving an ANALAR (B. D. H.)-grade reagent in distilled water.

The solution of potassium iodide was prepared by dissolving an approximate quantity of a G. R. (E. Merck)-grade reagent in water. The solution was then standardized by titrating it with a standard solution of silver nitrate, employing eosin[2] as an indicator.

ANALAR (B. D. H.)-grade hydrochloric acid was used throughout the experiments.

Absolute ethyl alcohol was redistilled in a quick-fit apparatus; the fraction boiling at 78.2°C was used.

Measurement of the Dielectric Constants. The dielectric constants were measured by a dielectrometer (Dielektrometer Type TRK No. 53015), working on the principle of the heterodyne-beat method. The null point was obtained with the help of a magic eye (Bridge Type). The values for the dielectric constant of absolute alcohol-water mixtures were obtained with a cell 1.68$\mu\mu$F in capacity. This cell had been previously brated with standard liquids of known dielectric constants.

A Study of the Progress of the Reaction. An excess of the potassium ferricyanide solution was placed in a conical flask and kept in a thermostat. The requisite quantities of potassium iodide, an alcohol-water mixture, and a hydrochloric acid solution were placed in a separate conical flask and kept in the same thermostat. When the solutions had attained the temperature of the bath, the requisite quantity of potassium ferricyanide was sucked in a pipette and poured into the solution containing potassium iodide and hydrochloric acid. The progress of the reaction was followed by sucking out an aliquot (10 m*l*) and pouring it into ice cold water in order to quench the reaction. The liberated iodine was then titrated with a standard solution of sodium thiosulphate, using starch as an indicator.

Table 1

Temperature 30°C

$[K_3Fe(CN)_6] = 4.44\times10^{-3}$ N

$[KI] = 5.00\times10^{-2}$ N

$[HCl] = 10.00\times10^{-2}$ N

Time min	Sodium thiosulphate 5.00×10^{-3} N m*l*	$k_2\times10^3$
0	0.00	—
5	0.46	1.23
10	0.94	1.33
20	1.84	1.47
30	2.56	1.54
40	3.08	1.49
50	3.62	1.55
60	4.06	1.58
80	4.74	1.61
100	5.26	1.63
120	5.50	1.53
∞	8.88	—

Average value$=1.50\times10^{-3}$

$k_s=2.89\ l\cdot g\cdot equiv^{-1}\cdot min^{-1}$

The following tables show the results at different concentrations of potassium ferricyanide and at a constant concentration of the other reactant.

A perusal of Tables 1 and 2 will show that the values of the second-order constant are fairly constant throughout the course of reaction. This proves that the order of reaction with respect to ferricyanide is two. The increase in the k_s value with the decrease in the concentration of ferricyanide is not clear at present, but the value of Z_AZ_B has been determined at a fixed concentration of ferricyanide. Therfore, the variation in ferricyanide will not affect the study of the dielectric constant. Similarly, Table 3 contains the results at different concentrations of potassium iodide.

Table 2

Temperature 30°C

$[K_3Fe(CN)_6] = 5.00\times10^{-3}$ N

$[KI] = 5.00\times10^{-2}$ N

$[HCl] = 10.00\times10^{-2}$ N

Time min	Sodium thiosulphate 5.00×10^{-3} N m*l*	$k_2\times10^3$
0	0.00	—
5	0.60	1.27
10	1.10	1.23
15	1.40	1.08
20	1.80	1.07
30	2.56	1.14
40	3.16	1.12
50	3.70	1.17
60	4.14	1.18
70	4.54	1.15
80	4.80	1.15
100	5.36	1.15
120	5.50	1.02
∞	10.00	—

Average value$=1.15\times10^{-3}$

$k_s=2.29\ l\cdot g\cdot equiv^{-1}\cdot min^{-1}$

Table 3

Temperature 30°C

$[K_3Fe(CN)_6] = 5.00\times10^{-3}$ N

$[HCl] = 0.10$ N

Concentration of potassium iodide 10^{-2}	k_s $l\cdot g\cdot equiv^{-1}\cdot min^{-1}$	$k_s/[KI]$
5.00 N	2.29	45.80
4.00 N	1.84	46.00
3.33 N	1.37	45.21
2.00 N	0.95	47.50
1.80 N	0.82	45.10

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2) I. Vogel, "A Text-Book of Quantitative Inorganic Analysis," Longmans, Green & Co., London (1962), p. 262.

The values in the last column are practically constant; this shows that the rate of the reaction is directly proportional to the concentration of potassium iodide.

In the following table the results are summarized for various concentrations of alcohol at 30°C, 35°C, and 40°C.

A perusal of Table 4 shows that the rate of the reaction increases with an increase in the dielectric constant of the medium.

TABLE 4

$[K_3Fe(CN)_6] = 0.005$ N
$[KI] = 0.050$ N $\mu=0.18$
$[HCl] = 0.10$ N

Temperature °C	% Alcohol	Dielectric constant D	Standard second-order constant k_s
30	0	77.25	2.295
30	5	75.15	2.061
30	10	72.83	1.909
30	15	70.95	1.666
30	20	68.44	1.489
35	0	76.03	3.334
35	5	74.15	2.660
35	10	71.67	2.560
35	15	69.36	2.283
35	20	67.32	2.168
40	0	73.38	4.300
40	5	72.06	4.022
40	10	69.53	3.728
40	15	67.16	3.458

Results and Discussion

In order to study the nature of the charge of the reacting ions, the above data were studied in the light of the Brönsted-Christiansen-Scatchard equation:

$$\ln k_s = \ln k_{\substack{\chi=0\\ D=\infty}} - \frac{Z_A Z_B \varepsilon^2 N}{DRTr} + \frac{Z_A Z_B \varepsilon^2 N}{DRT}\chi \tag{1}$$

This equation has been extensively employed by Amis[3-5] in his study of isodielectric and isocomposition activation energies. Here k_s is the observed velocity constant, while $k_{\substack{\chi=0\\ D=\infty}}$ is the velocity at zero ionic strength and at an infinite dielectric constant. N is the Avogadro number, D is the dielectric constant of the medium, and r is the minimum distance of approach. χ is the constant which occurs in the Debye-Hückel theory of strong electrolytes; it can be calculated by the following equation:

$$\chi = \sqrt{\frac{8\pi\varepsilon^2 N^2 \mu}{1000DRT}} \tag{2}$$

By substituting the value of χ into Eq. (1):

$$\log k_s = \log k_{\substack{\chi=0\\ D=\infty}} - \frac{Z_A Z_B \varepsilon^2 N}{2.303RTr}\left[\frac{1}{D} - \frac{2\varepsilon N r}{D^{3/2}}\sqrt{\frac{2\pi\mu}{1000RT}}\right] \tag{3}$$

If in the above equation the quantity in square brackets is plotted against log k_s, a straight line is obtained the slope of which is equal to:

$$-\frac{Z_A Z_B \varepsilon^2 N}{2.303RTr}$$

TABLE 5

Temperature °C	Dielectric constant D	$k_s \times 10^3 l\cdot g\cdot$ equiv^{-1} min$\cdot$sec^{-1}	$3+\log k_s$	$\left[\frac{D^{1/2}-x}{D^{3/2}}\right]\times 10^3$
30	77.25	38.24	1.5826	8.162
30	75.15	34.35	1.5359	8.343
30	72.83	31.82	1.5027	8.509
30	70.95	27.68	1.4422	8.662
30	68.44	24.81	1.3947	8.874
35	76.03	55.56	1.7448	8.296
35	74.15	44.34	1.6468	8.441
35	71.67	42.66	1.6301	8.644
35	69.36	38.05	1.5804	8.843
35	67.32	36.14	1.5568	9.024
40	73.38	71.66	1.8553	8.547
40	72.06	67.01	1.8262	8.648
40	69.53	62.13	1.7862	8.874
40	67.16	57.63	1.7606	9.086

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3) E. S. Amis and F. C. Holmes, *J. Am. Chem. Soc.*, **61**, 2231 (1941).

4) E. S. Amis and S. E. Cook, *ibid.*, **63**, 2621 (1941).

5) E. S. Amis and J. E. Potts, *ibid.*, **63**, 2883 (1941).

The value of the velocity constant, k_s has been calculated in seconds.

The value of r taken here is quite in accordance with the value of r taken in the reaction between potassium persulphate⁵⁾ and the iodide ion. The reaction between persulphate and the iodide ion takes place between bivalent and univalent negative ions; the value of r which Amis and Pottes have taken is 1.76×10^{-8} cm. Therefore, the value of r which we have taken is quite reasonable. By substituting the values;

$\varepsilon=4.8025\times10^{-10}$ e. s. u.; $\boldsymbol{R}=8.31436\times10^{7}$ ergs/deg;

$\boldsymbol{N}=6.023\times10^{23}$ $r=2.65\times10^{-8}$ cm

$\mu=0.18$ $\pi=3.1416$

and $T=(273+30)$, $(273+35)$, and $(273+40)$ into Eq. (3), we obtain for three different temperatures the following equations:

$$\log k_s = \log k_{\substack{\chi=0\\ D=\infty}} - \frac{Z_A Z_B \varepsilon^2 \boldsymbol{N}}{2.303\boldsymbol{R}Tr}\left[\frac{D^{1/2}-x}{D^{3/2}}\right] \qquad (4)$$

where the values of x at three different temperatures (*viz.* 303, 308 and 313) are 3.247, 3.221, and 3.194 respectively.

Table 5 has been reproduced in graphic form (Fig. 1) by employing Eq. (4). The measured slope of the curve and the value of $Z_A Z_B$ obtained therefrom are given in Table 6. From a perusal of Table 6 it is obvious that the product of Z_A and Z_B does not deviate very much from 3. Hence, we may conclude that the rate-determining step occurs between a univalent negative ion and a trivalent negative ion.

TABLE 6

Temperature t°C	Slope	$\dfrac{\varepsilon^2\boldsymbol{N}}{2.303\boldsymbol{R}Tr}$	$Z_A Z_B$
30	274.4	90.35	3.03
35	256.0	88.86	2.88
40	254.5	87.46	2.91

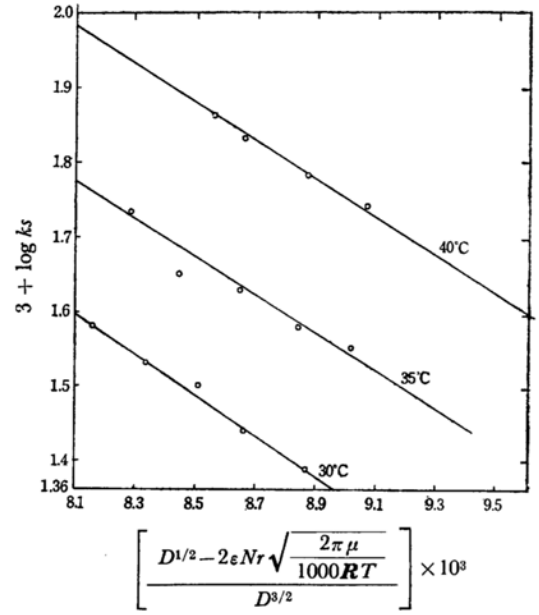

Fig. 1.

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