The Diffusion Coefficient of Ferricyanide Ions in Aqueous Potassium Chloride Solutions with and without Polyethylene Oxide Addition

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The diffusion coefficient of ferricyanide ions in aqueous potassium chloride solutions containing up to 1000 ppm of polyox has been determined using the rotating disk electrode. Correlations for viscosity and density as a function of temperature are given and results are discussed in terms of the Einstein–Stokes ratio.

Diffusion controlled mass transfer rates in flow systems may conveniently be studied by determining current densities at concentration polarized electrodes imbedded in the transfer surfaces (*4*). Such electrolytic systems find increasing application in determining local transfer rates in complicated geometries and are used as mass transfer analogues in the study of heat transfer problems.

A commonly used electrolyte is a dilute equimolar solution of potassium ferri- and ferrocyanide in a 1 or 2 M solution of sodium hydroxide (*4*). The sodium hydroxide acts as a carrier electrolyte; at the potentials used, the currents are determined solely by the diffusion rate of ferricyanide to the cathode and ferrocyanide to the anode.

To convert the measured currents to significant transfer numbers it is essential to have reliable data for the physical properties—diffusion coefficient, viscosity and density—of the electrolyte solution. A considerable amount of data has been published for the ferro–ferricyanide–sodium hydroxide system (*4*).

It is sometimes desirable to use a carrier electrolyte other than sodium hydroxide. Thus, although it is corrosive, potassium chloride may be used, if a neutral pH is required; it requires fewer safety precautions than sodium hydroxide. For instance, if mass transfer rates are to be determined in the presence of drag reducing polymers, potassium chloride is preferred because many polymers are degraded by sodium hydroxide (*2*).

Experimental Technique

For the rotating disk electrode an electrode to disk diameter ratio of 1 to 3 was selected. The electrode diameter was 3 mm. The electrical contact to the spinning electrode was made by using a mercury/platinum contact; a graphite brush was unsatisfactory as a change in resistance with time was recorded. The rotation speed of the disk was constant at 750 rpm ±0.2%.

All solutions were stored in black painted glass vessels to exclude light, which slowly degrades the ferricyanide ion. Solutions were prepared using Merck analytical grade reagents, dissolved in deionized water (*1*). The solutions were purged with nitrogen for 1 h and during measurement they were kept under a nitrogen pressure blanket with a bleeding valve. The nitrogen was first bubbled through distilled water for saturation, because otherwise a change in concentration of ferricyanide was found during a day's measurements.

Temperature was controlled to within 0.1 °C by using a thermostat bath, covering a temperature range from 20 to 35 °C.

Platinum foil, with a surface area far in excess of that of the disk electrode, and a saturated calomel electrode were used as anode and reference electrode, respectively.

Before each run the disk electrode was cleaned with soft paper.

The potential was increased continuously at a rate of -1 mV s^{-1} until -500 mV to the calomel reference electrode was reached.

The concentration of ferricyanide was determined by potentiometric titration (*2*) using isonicotinic acid hydrazide (isoniazid).

The average ferro–ferricyanide concentration was in the order of 5 mol m^{-3}.

The apparent viscosity of the solutions was determined with an Ostwald type viscometer, the density by using a pycnometer.

The average molecular weight of the polyethylene oxide, as given by the supplier, was 4×10^6.

Results

The diffusion coefficients were obtained from Levich's equation (*3*):

$$D = \left(\frac{1}{0.62nFA\omega^{1/2}}\right)^{3/2}\left(\frac{i_{\text{lim}}}{C_f}\right)^{3/2}\nu^{1/4} \qquad (1)$$

For the meaning of the symbols the reader is referred to the glossary.

The viscosity and density of the solutions may be calculated from

$$\mu = (\alpha_1 - \ln t)/\alpha_2 \quad \text{kg m}^{-1}\,\text{s}^{-1} \qquad (2)$$

and

$$\rho = (\beta_1 - \ln t)/\beta_2 \quad \text{kg m}^{-3} \qquad (3)$$

where α and β are given in Tables I and II for the various solutions. The concentration of potassium chloride is indicated by C_c; the concentration of polyethylene oxide with C_P and the temperature t is expressed in degrees Celsius.

In Tables III and IV and Figures 1 to 3, the results are given in terms of Einstein–Stokes ratios.

In order to compare this work with the results of Arvia et al. (*1*), three different ratios are calculated: R_1, R_2, and R_3, defined by eq 4–6

Table I. Constants for Correlation of Viscosity Data

C_c, kmol m^{-3}	C_P, ppm	α_1	α_2	ϵ, %
0.5	0	5.1243	2123.07	0.15
1.0	0	5.1355	2134.50	0.04
2.0	0	5.2388	2215.37	0.10
1.0	10	5.0821	2049.86	0.11
1.0	25	5.0297	1965.15	0.06
1.0	50	4.9440	1829.10	0.06
1.0	75	4.9537	1810.53	0.04
1.0	100	4.9951	1829.10	0.11
1.0	140	5.0391	1774.50	0.25
1.0	200	5.1766	1770.10	0.29
1.0	350	4.8842	1340.88	0.10
1.0	500	5.0104	1280.85	0.30
1.0	750	4.7261	885.05	0.19
1.0	1000	4.5347	646.37	0.33

Table II. Constants for Correlation of Density Data

C_c, kmol m^{-3}	β_1	β_2	ϵ, %
0.5	117.483	0.1049	0.01
1.0	122.648	0.1143	0.02
2.0	138.279	0.1321	0.01

Table III. The $D\mu/T$ Ratio for Various Solutions and Temperatures in the Range from 20 to 35 °C

C_c, kmol m^{-3}	C_P, ppm	10^{15} R_1, kg m s^{-2} K^{-1}	10^{15} R_2 kg m s^{-2} K^{-1}	10^{15} R_3 kg m s^{-2} K^{-1}
0.5	0	2.296		
1.0	0	2.259		
2.0	0	2.256		
1.0	10	2.187	2.156	2.163
1.0	25	2.290	2.228	2.241
1.0	50	2.220	2.092	2.117
1.0	75	2.345	2.174	2.207
1.0	100	2.262	2.072	2.106
1.0	140	2.456	2.086	2.116
1.0	200	2.700	2.087	2.193
1.0	350	2.955	1.994	2.158

$$R_1 = D_s\mu_s/T \tag{4}$$

$$R_2 = D_c\mu_c/T \tag{5}$$

$$R_3 = D_s\mu_c/T \tag{6}$$

although we would prefer the use of R_1 only.

Arvia et al. (*1*) relate the different ratios to the average radius of a solvodynamic unit.

The viscosity μ_s stands for the real viscosity of the solution with polymer; the viscosity μ_c stands for the viscosity of the same solution without polymer.

The diffusion coefficient D_s is calculated from eq 1 by using the kinematic viscosity and current for the solution with polymer; the diffusion coefficient D_c, however, is calculated by using the kinematic viscosity for the solution without polymer and the current for the same solution with polymer.

For polymer solutions up to 350 ppm the Einstein-Stokes ratios R_1, R_2, and R_3 are constant over the whole temperature range from 20 to 35 °C, as can be seen from Table III.

From Table IV it can be seen that at higher polymer concentrations these ratios are temperature dependent.

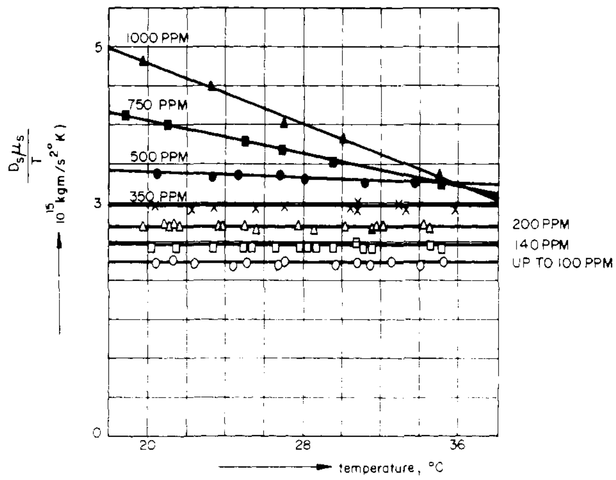

Figure 1. Einstein–Stokes ratio as a function of temperature.

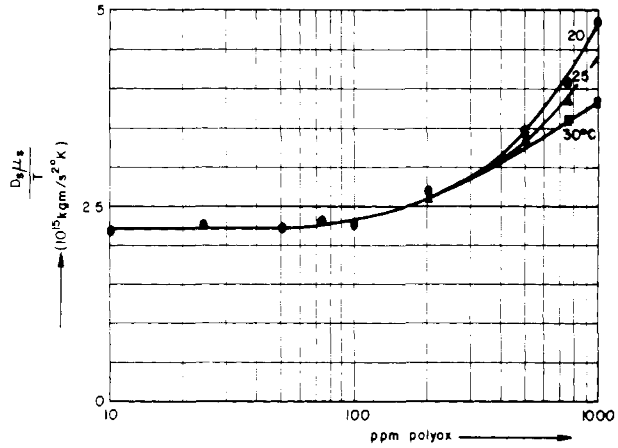

Figure 2. Einstein–Stokes ratio as a function of the polyethylene oxide concentration.

In Figure 1, R_1 is given as a function of temperature for different polymer concentrations.

The dependence of R on the polymer concentration can be seen from Table III and Figures 2 and 3.

Up to 100 ppm the ratio R_1 is independent of the polyox

Table IV. The $D\mu/T$ Ratio for High Concentrated Polyox Solutions, at a Potassium Chloride Concentration of 1.0 kmol m^{-3}

C_f, mol m^{-3}	C_P, ppm	T, °C	i, μA	10^{10} D_s, m^2 s^{-1}	10^{10} D_c m^2 s^{-1}	10^{15} R_1, kg m s^{-2} K^{-1}	10^{15} R_2, kg m s^{-2} K^{-1}	10^{15} R_3, kg m s^{-2} K^{-1}
4.69	500	20.8	124	6.518	5.830	3.420	1.954	2.185
4.69	500	23.7	132	7.047	6.304	3.424	1.962	2.195
4.69	500	24.4	133	7.090	6.354	3.392	1.946	2.171
4.69	500	26.6	140	7.581	6.784	3.431	1.969	1.968
4.69	500	28.0	143	7.764	6.953	3.387	1.951	1.951
4.69	500	31.2	152	8.347	7.504	3.335	1.959	1.959
4.69	500	33.8	160	8.875	8.009	3.300	1.979	2.190
4.69	750	18.6	111	5.927	5.005	4.140	1.779	2.106
4.69	750	21.0	116	6.223	5.274	4.022	1.757	2.073
4.69	750	24.8	123	6.623	5.642	3.807	1.708	2.005
4.69	750	26.8	126	6.778	5.791	3.673	1.671	1.956
4.69	750	29.5	131	7.064	5.538	3.533	1.643	1.916
4.69	750	35.0	141	7.627	6.596	3.275	1.585	1.833
4.56	1000	17.0	100	5.634	4.507	5.115	1.677	2.096
4.56	1000	19.9	104	5.833	4.698	4.757	1.611	2.000
4.56	1000	23.4	110	6.176	5.013	4.454	1.571	1.935
4.56	1000	27.0	114	6.341	5.193	4.051	1.492	1.821
4.56	1000	30.4	120	6.680	5.516	3.816	1.466	1.612
4.56	1000	35.0	124	6.786	5.674	3.338	1.364	1.632

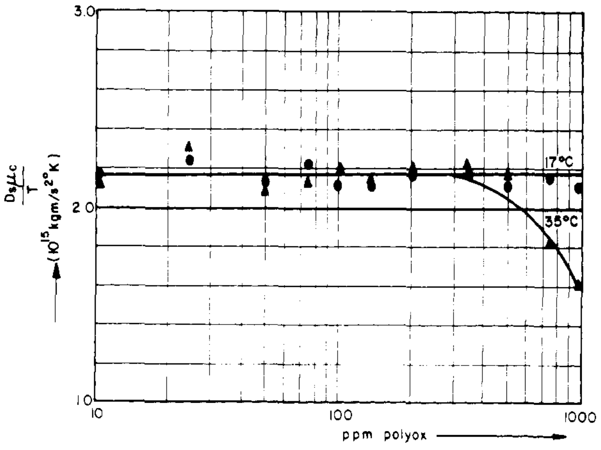

Figure 3. Einstein–Stokes ratio for different polyox solutions.

concentration; the ratios R_2 and R_3 are independent up to 350 ppm. The results can be summarized by: for $20 < t < 35$ °C, $C_P \leq 100$ ppm:

$$D_s\mu_s/T = (2.27 \pm 0.09)10^{-15}\ \mathrm{kg\ m\ s^{-2}\ K^{-1}} \quad (7)$$

for $20 < t < 35$ °C, $C_P < 350$ ppm:

$$D_c\mu_c/T = (2.11 \pm 0.12)10^{-15}\ \mathrm{kg\ m\ s^{-2}\ K^{-1}} \quad (8)$$

and

$$D_s\mu_c/T = (2.16 \pm 0.08)10^{-15}\ \mathrm{kg\ s^{-2}\ K^{-1}} \quad (9)$$

For higher polymer concentrations the Einstein-Stokes ratio becomes temperature and concentration dependent, and must be obtained from the results presented in the tables and figures.

Discussion

The value of the Einstein-Stokes ratio for aqueous potassium chloride solutions without polymer addition is, according to Table III, found to be $(2.28 \pm 0.08)10^{-15}$ kg m s^{-2} K^{-1}. Arvia et al. (*1*) found in this case a value of $(2.00 \pm 0.12)10^{-15}$ kg m s^{-2} K^{-1}, hence a difference of about 14%. One explanation for this difference may be the fact that Arvia et al. used an electrode to disk diameter ratio of about 1 to 1.15, although a ratio of at least 1 to 2.4 is recommended (*4*). In our study we used a 1 to 3 ratio. For the diffusion coefficient in carboxymethyl cellulose solutions Arvia et al. found that the value of R_3 was constant for the whole range of polymer solutions between 0.2 and 1.6% CMC, at $(2.13 \pm 0.31)10^{-15}$ kg m s^{-2} K^{-1}. In our investigation we found a constant value of R_3 equal to $(2.16 \pm 0.08)10^{-15}$ kg m s^{-2} K^{-1}, only when the polyethylene oxide concentration was below 350 ppm. For more concentrated polymer solutions the ratio R_3 became temperature and concentration dependent.

Although the accuracy of the determination of the diffusion coefficient by Arvia is within 15%, our data are accurate within 6%.

The measured diffusion coefficients are not the true binary diffusion coefficients (n^2 diffusion coefficients are required to describe isothermal diffusion in a system with n solute components) but they are the correct ones to be used in the evaluation of the results of electrochemical studies of transfer problems. Besides, as the concentration gradients of the shared counterions (K^+) and the coions (Cl^-), both present in large excess are negligible or zero, respectively (only the ferricyanide ions produced at the electrode would cause a gradient for this coion), we consider it reasonable to treat the system as if binary diffusion were occurring.

Glossary

A	area, m^2
B	constant
C	concentration, kmol m^{-3}
D	diffusion coefficient, m^2 s^{-1}
F	Faraday constant, C kmol^{-1}
i	current, A
R	ratio $D\mu/T$, kg m s^{-2} K^{-1}
t	temperature, °C
T	temperature, °K
α	constant in eq 2
β	constant in eq 3
ϵ	error
μ	viscosity, kg m^{-1} s^{-1}
ν	kinematic viscosity, m^2 s^{-1}
ρ	density, kg m^{-3}
ω	angular velocity, rad s^{-1}

Subscripts

c	solution without polymer
f	ferricyanide
lim	limiting
P	polymer
s	solution with polymer

Literature Cited

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Received for review October 11, 1976. Accepted March 21, 1977.