THE DIFFUSION OF FERROCYANIDE AND FERRI-CYANIDE IONS IN AQUEOUS SOLUTIONS OF POTASSIUM HYDROXIDE*

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Abstract—The diffusion of ferro- and ferricyanide ions in potassium hydroxide solutions has been studied with the rotating disk electrode between 24 and 50°C.

The quotient $D\eta/T$ was satisfactorily constant and temperature-independent. A comparison with previous results obtained for solutions containing sodium hydroxide and potassium chloride as supporting electrolytes is made.

Résumé—La diffusion des ions de ferro- et ferricyanure dans des solutions d'hydroxyde de potassium a été étudié par la technique de l'électrode à disque tournant à des températures de 24 à 50°C.

Le rapport $D\eta/T$ apparait raisonablement constant et indépendent de la température. Une comparaison est établie avec des résultats antérieurs obtenus pour des solutions à contenus d'hydroxyde de sodium et chlorure de potassium comme électrolytes de support.

Zusammenfassung—Die Diffusion der Ferro- und Ferricyanidionen in Kaliumhydroxidlösungen wurde mittels einer rotierenden Scheibelektrode bei verschiedenen Konzentrationen und Temperatur en untersucht.

Das Verhältnis $D\eta/T$ ist befriedigend konstant und temperaturunabhängig zwischen 24 und 50°C. Ein Vergleich mit früheren Ergebnissen für Lösungen mit Natriumhydroxid-und Kaliumchlorid als Trägerelektrolyten wird angestellt.

INTRODUCTION

As part of a research on the diffusion coefficients of aqueous ions in complex ionic media, the present report refers to the study of the aqueous systems containing potassium ferro- and ferricyanide in potassium hydroxide solutions, under different experimental conditions.

No systematic data related either to the physical properties or particularly to the diffusion coefficients of the ferro- and ferricyanide ions in those solutions were available, although they are of special interest for studying mass-transfer problems in electrochemistry. Results for solutions containing sodium hydroxide as the supporting electrolyte were published recently[1] and compared with previous information.[2] The present results show the effect of the nature of the supporting electrolyte on the transport properties of the solutions.

EXPERIMENTAL TECHNIQUE

The diffusion coefficients of ions were determined by employing the rotating disk electrode. The electrolysis cell has been described elsewhere[1,3]. Working electrodes of pure nickel and platinum were used after polishing as usual to a mirror surface before assembling the electrolysis cell. The area of the electrodes was $7.07 \times 10^{-2} \text{ cm}^2$.

The working electrode was driven by a low voltage dc 1/8 hp electric motor coupled to a voltage generator, whose rate of rotation was regulated electronically. The motor runs at a constant potential and maintains a constant torque on the rotation shaft. The rotation rate could be read on a previously calibrated voltmeter

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connected to the voltage generator. This calibration was performed by attaching an insulator disk with two small magnets to the rotating shaft. During rotation those magnets generate an ac voltage on a fixed coil, and the frequency of the signal depending on the rotation rate was read using a Tektronix Oscilloscope.

The rest of the experimental arrangement was the same as already described.[1,3]

Analytical reagents and doubly-distilled water were employed in the preparation of the solutions. They were deaerated with purified nitrogen. Two types of solutions
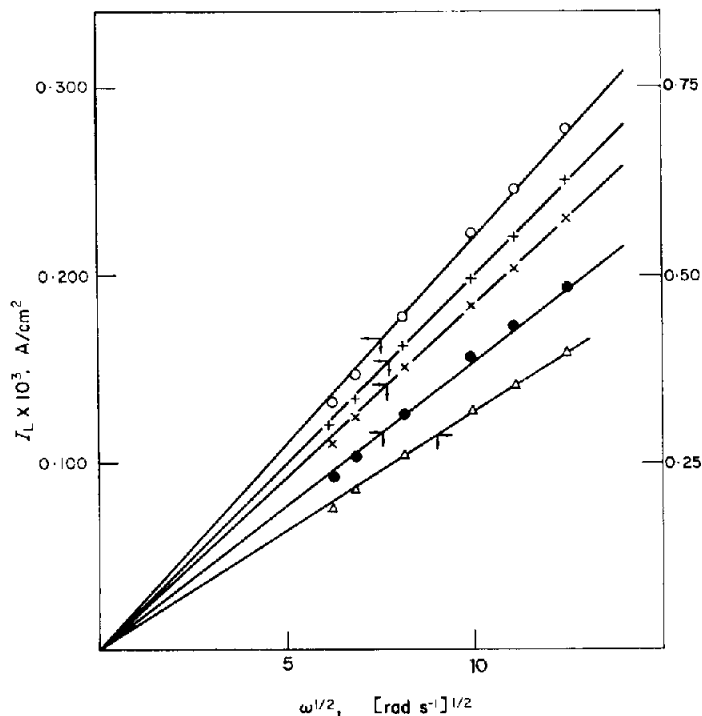

FIG. 1. Limiting current vs square root of rotation rate: reduction of ferricyanide ion.
● 25·3°C. C_3 0·005, C_4 0·01, C_h 1
× 34·7°C. C_3 0·005, C_4 0·01, C_h 1
○ 46·5°C. C_3 0·005, C_4 0·01, C_h 1
+ 35·3°C. C_3 0·005, C_4 0·005, C_h 0·5
△ 30·1°C. C_3 0·01, C_4 0·05, C_h 2·02 M

were tested (i) equimolar solutions of potassium ferro- and ferricyanide, where the concentration of each salt changed from 0·05 to 0·005 M; (ii) solutions where the concentration ratio between the two salts covered the range 0·2–5. In either case the potassium hydroxide concentration was varied from 0·5 to 2 M, the ratio between the concentration of the supporting electrolyte to the concentration of the diffusing solutes being kept at 20 or higher. Both concentrations were varied within the range where it could be assumed that the migration term was negligible compared to the convective diffusion term in the ionic mass-transfer equation. The viscosity and density of solutions were determined by standard procedures.

With symmetrical solutions both the cathodic and the anodic reactions were studied. When asymmetrical solutions were employed, only the reaction involving the solute of lower concentration was considered.

Current/voltage curves were recorded by means of a Varian F-80 X/Y recorder, at rotation speeds from 300 to 1300 rpm. Experiments were performed at temperatures from 24 to 50°C.

RESULTS

The current/voltage curves exhibited the usual behaviour of reversible reactions comprising two soluble species in an electrochemical process under convective-diffusion control. The limiting current density for a particular solution was proportional to the square root of the rotation speed, as shown in Figs. 1 and 2 for a set of typical
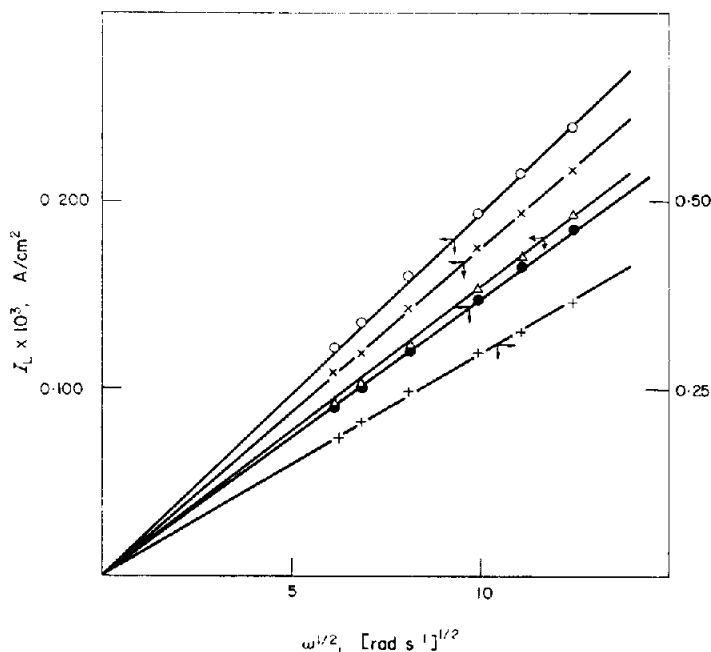

FIG. 2. Limiting current vs square root of rotation rate: oxidation of ferrocyanide ion.
● 26·9°C. C_3 0·005, C_4 0·005, C_h 1
× 35·6°C. C_3 0·005, C_4 0·005, C_h 1
○ 41·3°C. C_3 0·005, C_4 0·005, C_h 1
+ 30·1°C. C_3 0·05, C_4 0·01, C_h 2·02
△ 26·6°C. C_3 0·005, C_4 0·005, C_h 0·5 M

records. Taking into account the dependence of the limiting current density on rotation speed, the experimental diffusion coefficients were evaluated with Levich's equation for the rotating disk electrode[4]. No further refinement was required as regards the experimental errors.

Numerical compilations are in Tables 1–3. There the following nomenclature and units are used: C_h, C_4 and C_3 are the molar concentrations of potassium hydroxide, potassium ferrocyanide and potassium ferricyanide, respectively, t the temperature in °C, ν the kinematic viscosity in stokes, ρ the specific gravity in g/cm^3, D_4 and D_3 are respectively the experimental diffusion coefficients of ferro- and ferricyanide ions in potassium hydroxide solutions in cm^2/s, and finally, the quotient $D\eta/T$, in cm^2 poise s^{-1} °K^{-1}, where η is the dynamic viscosity in poise.

TABLE 1

$C_3 \times 10^2$	$C_4 \times 10^2$	t	ρ	$\nu \times 10^2$	$D_3 \times 10^6$	$D_4 \times 10^6$	$\dfrac{D_3\eta}{T} \times 10^{10}$	$\dfrac{D_4\eta}{T} \times 10^{10}$
M	M	°C	g/cm³	Stokes	cm²/s	cm²/s	cm² poise s⁻¹ °K⁻¹	cm² poise s⁻¹ °K⁻¹
				$C_h = 2.069$				
1·00	1·00	28·4	1·120	1·210	6·09	5·54	2·74	2·49
		32·0	1·100	1·128	6·77	6·15	2·76	2·50
		40·8	1·096	0·9663	7·94	7·46	2·68	2·52
5·00	5·00	28·9	1·099	1·199	6·43	5·75	2·81	2·51
		34·4	1·096	1·100	7·26	6·38	2·85	2·50
		38·9	1·095	1·015	7·81	7·23	2·78	2·58
1·00	5·00	30·1	1·098	1·183	6·68	—	2·86	—
		38·4	1·096	1·028	7·55	—	2·73	—
		48·4	1·091	0·8792	9·88	—	2·95	—
				$C_h = 2.016$				
1·00	1·00	29·8	1·092	1·174	6·99	—	2·96	—
		37·5	1·089	1·177	8·03	7·28	2·85	2·60
		45·6	1·085	0·9059	8·71	8·18	2·69	2·52
0·50	0·50	28·4	1·092	1·213	—	5·82	—	2·56
		35·8	1·089	1·076	7·60	—	2·88	—
		44·0	1·085	0·9368	8·61	—	2·76	—
0·50	1·00	26·7	1·094	1·236	6·04	—	2·72	—
		38·6	1·089	1·000	7·57	—	2·65	—
1·00	0·50	24·8	1·095	1·290	—	5·06	—	2·40
		33·7	1·091	1·088	—	6·25	—	2·42

$$\left(\frac{D_3\eta}{T}\right)_{av} = (2.80 \pm 0.16) \times 10^{-10} \text{ cm}^2 \text{ poise s}^{-1} \text{ °K}^{-1}; \quad \left(\frac{D_4\eta}{T}\right)_{av} = (2.53 \pm 0.13) \times 10^{-10} \text{ cm}^2 \text{ poise s}^{-1} \text{ °K}^{-1}.$$

TABLE 2

$C_3 \times 10^2$ M	$C_4 \times 10^2$ M	t °C	ρ g/cm³	$\nu \times 10^2$ Stokes	$D_3 \times 10^6$ cm²/s	$D_4 \times 10^6$ cm²/s	$\frac{D_3\eta}{T} \times 10^{10}$ cm² poise s⁻¹ °K⁻¹	$\frac{D_4\eta}{T} \times 10^{10}$ cm² poise s⁻¹ °K⁻¹
				$C_A = 1.035$				
1.00	1.00	27.9	1.048	1.165	7.23	6.43	2.93	2.60
		34.8	1.046	0.9876	8.46	7.59	2.84	2.54
		43.8	1.042	0.8515	9.99	9.31	2.80	2.61
2.50	2.50	27.8	1.053	1.132	6.77	—	2.68	—
		33.9	1.050	1.014	7.95	—	2.76	—
		39.9	1.048	0.9105	8.95	—	2.73	—
5.00	5.00	27.9	1.053	1.134	6.76	6.27	2.68	2.49
		32.5	1.051	1.040	7.59	6.94	2.71	2.48
		40.6	1.046	0.9105	8.96	8.30	2.72	2.52
				$C_A = 1.008$				
0.50	0.50	26.9	1.047	1.123	7.07	6.12	2.77	2.40
		35.6	1.044	0.9730	8.37	7.34	2.75	2.41
		41.3	1.041	0.8860	9.17	8.50	2.69	2.49
0.50	1.00	25.9	1.048	1.180	6.59	—	2.73	—
		34.7	1.045	0.9953	7.96	—	2.69	—
		46.5	1.040	0.8358	10.11	—	2.75	—
1.00	0.50	28.0	1.048	1.129	—	6.15	—	2.42
		38.4	1.044	0.9298	—	8.20	—	2.56
		44.8	1.041	0.8390	—	9.44	—	2.59
1.00	2.50	26.0	1.053	1.166	6.79	—	2.79	—
		36.3	1.049	0.9635	8.11	—	2.65	—
2.50	1.00	26.3	1.052	1.178	—	6.02	—	2.49
		44.2	1.045	0.8505	—	9.30	—	2.61

$\left(\dfrac{D_3\eta}{T}\right)_{av} = (2.75 \pm 0.18) \times 10^{-10}$ cm² poise s⁻¹ °K⁻¹; $\left(\dfrac{D_4\eta}{T}\right)_{av} = (2.52 \pm 0.10) \times 10^{-10}$ cm² poise s⁻¹ °K⁻¹.

TABLE 3

$C_3 \times 10^2$ M	$C_4 \times 10^2$ M	t °C	ρ g/cm³	$\nu \times 10^2$ Stokes	$D_3 \times 10^6$ cm²/s	$D_4 \times 10^6$ cm²/s	$\dfrac{D_3\eta}{T} \times 10^{10}$ cm² poise s⁻¹ °K⁻¹	$\dfrac{D_4\eta}{T} \times 10^{10}$ cm² poise s⁻¹ °K⁻¹
					$C_h = 0.517$			
1·00	2·50	27·5	1·028	1·111	7·22	—	2·75	—
		36·1	1·026	0·9497	9·33	—	2·94	—
		42·8	1·023	0·8690	10·40	—	2·94	—
2·50	1·00	31·1	1·026	1·014	—	7·36	—	2·52
		39·5	1·023	0·8791	—	9·23	—	2·65
		48·5	1·019	0·7653	—	10·67	—	2·59
1·00	5·00	28·8	1·034	1·074	7·67	—	2·82	—
		35·7	1·031	0·9450	8·71	—	2·75	—
		44·4	1·027	0·8250	10·42	—	2·78	—
5·00	1·00	27·7	1·032	1·095	—	6·87	—	2·58
		37·6	1·028	0·9080	—	8·95	—	2·68
		44·9	1·024	0·7945	—	9·89	—	2·53
					$C_h = 0.504$			
0·50	0·50	26·6	1·023	1·134	7·28	6·32	2·82	2·45
		35·3	1·020	0·9441	8·98	7·78	2·80	2·43
		44·0	1·016	0·8293	10·64	9·42	2·83	2·50
1·00	1·00	26·7	1·025	1·112	7·23	6·12	2·75	2·38
		37·7	1·021	0·9068	9·63	8·13	2·87	2·42
		45·4	1·018	0·8054	10·71	9·34	2·76	2·41
0·50	1·00	28·3	1·024	1·073	7·83	—	2·85	—
		34·7	1·022	0·9520	8·73	—	2·76	—
		42·7	1·019	0·8344	10·11	—	2·72	—
1·00	0·50	28·2	1·024	1·070	—	6·98	—	2·54
		37·7	1·020	0·9156	—	8·65	—	2·60
		45·6	1·018	0·7971	—	10·33	—	2·63

$$\left(\frac{D_3\eta}{T}\right)_{av} = (2.81 \pm 0.13) \times 10^{-10} \text{ cm}^2 \text{ poise s}^{-1}\,°\text{K}^{-1}; \quad \left(\frac{D_4\eta}{T}\right)_{av} = (2.52 \pm 0.13) \times 10^{-10} \text{ cm}^2 \text{ poise s}^{-1}\,°\text{K}^{-1}.$$

The diffusion coefficients fit the following equation, as far as temperature dependence is concerned,

$$D_i = (D_i)_0 \exp\left[\frac{-\Delta E_i}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right],\tag{1}$$

where $\Delta E_4 = 4150 \pm 700$ cal/mole and $\Delta E_3 = 3800 \pm 600$ cal/mole.

Similarly for the temperature dependence of the dynamic viscosity,

$$\eta = \eta_0 \exp\left[\frac{\Delta E_\eta}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right],\tag{2}$$

where $(D_i)_0$ and η_0 relate to a reference temperature such as T_0, $\Delta E_\eta = 3350 \pm 250$ cal/mole. Within the errors involved in the present work, the experimental activation energies related to (1) and (2) are close. As earlier stated,[1] the maximum experimental error affecting the diffusion coefficients is 7·5 per cent.

DISCUSSION

The main purpose of this report is to give experimental results, but we can also point out certain facts related to the influence of the supporting electrolyte on the parameters evaluated.

The results show a relatively small effect of the concentration of diffusing species on the diffusion coefficients of ferro- and ferricyanide ions. These depend principally on the concentration of the supporting electrolyte, which affects to a larger extent the total ionic strength of the solution.

It is of interest to analyse the results taking into account the ratio $D\eta/T$ for each ion in solutions containing potassium hydroxide, sodium hydroxide and potassium chloride as supporting electrolytes[1,5]. The ratios are indicated in Table 4. Their magnitudes and constancy are consistent with the molecular theories of mass transport[6,7]. The values for solutions containing potassium hydroxide are slightly higher than those for solutions of sodium hydroxide, but the differences are more evident when the quotients obtained with solutions containing potassium chloride are considered.

From the experimental results we conclude that, within the errors, the ratio $D\eta/T$ is in this case independent of the total ionic strength. This is certainly the case when the electrochemical system contains a mixture of strong electrolytes. The mean sizes of the solvodynamic units can, therefore, be estimated from those ratios, in terms of the Einstein–Stokes equation. The mean values of the solvodynamic units, r_i, are also assembled in Table 4.

TABLE 4

Supporting electrolyte	$\dfrac{D_3\eta}{T} \times 10^{10}$ cm^2 poise s^{-1} °K^{-1}	$\dfrac{D_4\eta}{T} \times 10^{10}$ cm^2 poise s^{-1} °K^{-1}	$r_3 \times 10^8$ cm	$r_4 \times 10^8$ cm
KOH	2·78 ± 0·18	2·52 ± 0·13	2·65 ± 0·17	2·91 ± 0·15
NaOH	2·52 ± 0·17	2·09 ± 0·17	2·92 ± 0·20	3·53 ± 0·28
KCl	2·00 ± 0·12	1·75 ± 0·12	3·68 ± 0·22	4·21 ± 0·29

These figures can be compared to the ionic radii calculated from Walden's rule which includes the molar ionic conductivity at infinite dilution and the viscosity of the solvent. Taking values from the literature[6] the following results are obtained: $r_3 = 2·74 \times 10^{-8}$ cm and $r_4 = 3·34 \times 10^{-8}$ cm. These radii are comparable to the mean

sizes of diffusing units obtained from the Einstein–Stokes ratios for solutions involving potassium hydroxide and sodium hydroxide. We must point out here that the actual difference observed in the $D\eta/T$ ratio for both solutions may be considered unimportant as far as their fluctuations are concerned. These differences however, are appreciable when referred to the results for potassium chloride solutions.

This problem is a complex one because of the nature of the systems involved and the concurrence of the influence of the supporting electrolyte on the viscosity. A systematic investigation would therefore take account of the way in which those magnitudes change for the same redox couple when different types of ions are the predominant species in the solutions, in order to attempt an explanation of the actual effect of the supporting electrolyte on both the diffusion coefficient and the Einstein–Stokes ratio.

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