JOURNAL OF APPLIED ELECTROCHEMISTRY 23 (1993) 51–55

Physical properties of the ternary electrolyte potassium ferri-ferrocyanide in aqueous sodium hydroxide solution in the range 10–90°C

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Received 30 October 1991; revised 17 March 1992

Density, viscosity, and diffusivity data have been obtained for equimolar ferri and ferro-cyanide (0.01–0.2 M) in 0.5 M aqueous sodium hydroxide solutions in the temperature range 10 to 90°C. For the determination of the diffusivity of the ferricyanide ion, limiting currents were measured by means of a rotating disc electrode, and the apparent diffusivities calculated from these measurements were corrected taking into account the migration term which became significant at high concentration. All data have been presented both graphically and as second order polynominals.

Notation

C	species concentration (mol dm^{-3})
D	diffusivity (m^2 s^{-1})
F	Faraday's constant (96 487 C mol^{-1})
i_L	current density (A m^{-2})
n	number of electrons transferred in reaction
t	transference number
T	temperature (K)
z	ionic charge

Greek symbols

Γ	ionic strength (mol m^{-3})
λ	conductance (Ω^{-1} m^2 mol^{-1})
ν	kinematic viscosity (m^2 s^{-1})
ρ	density (kg m^{-3})
ω	angular frequency (rad s^{-1})

Subscripts

i	ionic species
∞	bulk

1. Introduction

Electrolytes involving potassium ferri-ferrocyanide in excess sodium hydroxide electrolyte solution have been extensively used for mass transfer studies on activated nickel, platinum or stainless steel electrodes, [1–4].

A current programme of work in this laboratory is concerned with combined thermal and concentration driven natural convection using the ferri-ferrocyanide redox scheme. This involves use of the electrolyte at high temperature, even approaching the boiling point. The work described in this communication was, therefore, stimulated by the need for accurate viscosity, density and diffusivity measurements to be used for mass transfer data treatment over a range of temperature.

A considerable array of data concerning these physical properties already exists over more restricted temperature ranges. Eisenberg *et al.* [5] determined selected physical data for ferri-ferrocyanide in sodium hydroxide solution in the temperature range 25–30°C. Bazan *et al.* [6] measured the diffusion of potassium ferri-ferrocyanide ions in aqueous solutions of sodium hydroxide in the range 25–40°C.

Gordon *et al.* [7] dealt with diffusivity in solutions with non-negligible migration effects. They analysed the concentration profile and mass flux at the rotating disc electrode, considering the migration effect, and obtained a correlation equation linking the limiting current with the real diffusivity. Hiraoka *et al.* [8] analysed the effect of migration on the limiting current by use of a numerical method. They also derived a ratio of the real diffusivity to the experimental diffusivity, D_{real}/D_{exp}, in steady-state experiments using the rotating disc electrode.

More recently Bourne *et al.* [9] presented data for the physical properties of potassium ferri-ferrocyanide (0.01 and 0.02 M, respectively) in various sodium hydroxide solutions (0.5–3.0 M). The measured diffusivities were correlated in terms of solution concentration by means of a second order polynominal.

2. Experimental details

The concentrations of aqueous solutions of equimolar potassium ferri-ferrocyanide ranged from 0.01 to 0.20 M in 0.5 M NaOH supporting electrolyte. Ferricyanide ion and ferrocyanide ion were determined by spectrophotometric analysis and the hydroxyl ion was titrated with standard HCl to a bromomethyl blue endpoint.

Densities were measured using a hydrometer [10]

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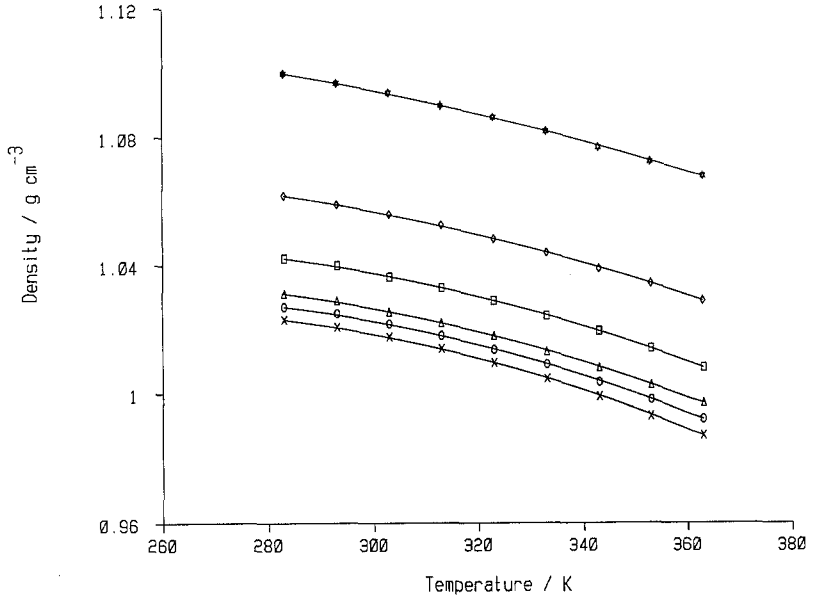

Fig. 1. Density of equimolar potassium ferri-ferrocyanide in 0.5 M NaOH. C/M: (○) 0.00985, (△) 0.02030, (□) 0.0511, (◇) 0.10200, (*) 0.20700 and (x) 0.00 (0.5 M NaOH).

(type BS718, series S50) suspended in a constant temperature bath. The electrolyte and bath temperature were adjusted within the range 10–90°C and were controlled within ±0.1°C during each individual measurement. Measurements of viscosity were made using a U-tube viscometer [11] (type BS/U) suspended in the constant temperature bath.

For the diffusivity measurements a cylindrical 1 dm^3 glass container was used as the electrolysis cell and immersed in a constant temperature bath. A nickel sheet positioned around the periphery of the cell acted as anode. The rotating disc electrode (r.d.e.) was positioned axially in the middle of the cell. The cathode was a nickel rod, 10 mm in diameter, embedded in a PTFE cylinder. The r.d.e. system (Thompson Electrochem Ltd) was driven by a 1/4 h.p. electronically regulated a.c. motor. The rotation rate was controlled between 100 and 5000 r.p.m. with relative error of 0.5%. The current–potential curves were determined as a function of rotation rate and limiting currents were evaluated.

3. Results

3.1. *Density*

Density data are shown in Fig. 1; a second degree polynomial in T was fitted to the data for each concentration. Results are represented by the following equations:

$$\rho_{0.00985\,\mathrm{M}} = 0.8700 + 1.3305 \times 10^{-3}\,T - 2.7413 \times 10^{-6}\,T^2$$

$$\rho_{0.02030\,\mathrm{M}} = 0.8940 + 1.1984 \times 10^{-3}\,T - 2.5220 \times 10^{-6}\,T^2$$

$$\rho_{0.05110\,\mathrm{M}} = 0.9093 + 1.1685 \times 10^{-3}\,T - 2.4709 \times 10^{-6}\,T^2$$

$$\rho_{0.10200\,\mathrm{M}} = 0.9878 + 0.7842 \times 10^{-3}\,T - 1.8473 \times 10^{-6}\,T^2$$

$$\rho_{0.20700\,\mathrm{M}} = 1.0630 + 0.5460 \times 10^{-3}\,T - 1.4685 \times 10^{-6}\,T^2$$

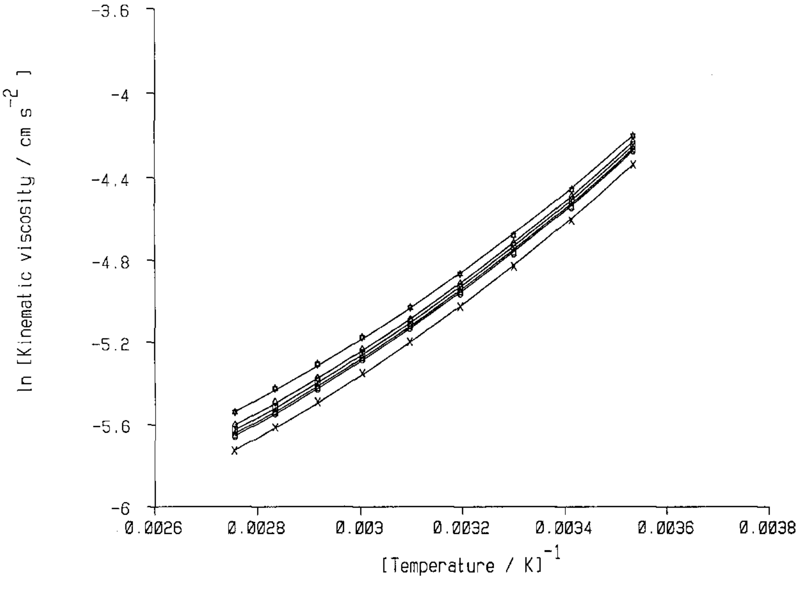

Fig. 2. Kinematic viscosity of equimolar potassium ferri-ferrocyanide in 0.5 M NaOH. Key as for Fig. 1, but with (x) 0.0 M (for water only).

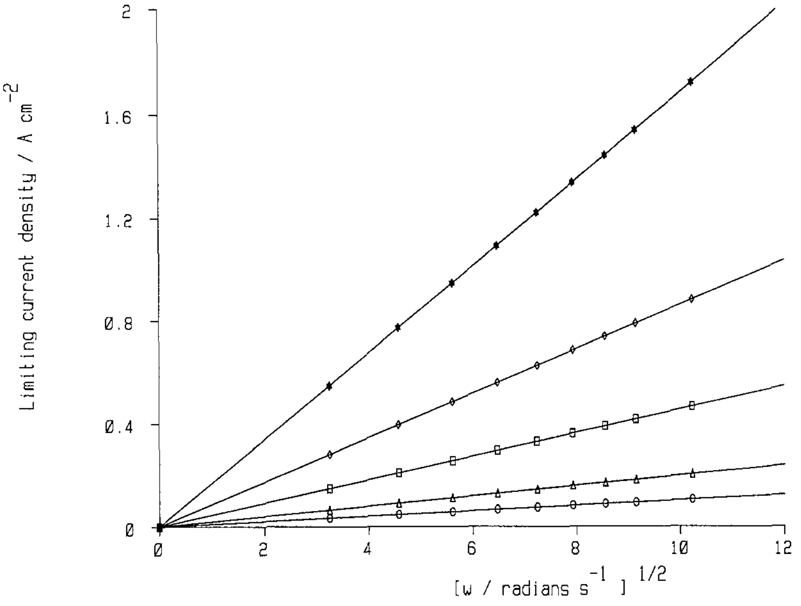

Fig. 3. Limiting current against $\omega^{1/2}$ for reduction of ferricyanide ion at 20°C. Key as for Fig. 1, but without (x).

Here ρ is the density in g cm^{-3} and T is temperature in kelvin in the range 283–363 K.

3.2. *Kinematic viscosity*

Kinematic viscosity data are shown graphically in Fig. 2, and represented as functions of temperature for each concentration by

$$\nu_{0.00985\,\mathrm{M}} = \exp\left[-5.2580 - 1.6428 \times 10^3/T + 5.4386 \times 10^5/T^2\right]$$

$$\nu_{0.02030\,\mathrm{M}} = \exp\left[-5.2215 - 1.6586 \times 10^3/T + 5.4625 \times 10^5/T^2\right]$$

$$\nu_{0.05110\,\mathrm{M}} = \exp\left[-5.1186 - 1.7116 \times 10^3/T + 5.5436 \times 10^5/T^2\right]$$

$$\nu_{0.10200\,\mathrm{M}} = \exp\left[-4.8458 - 1.8653 \times 10^3/T + 5.7752 \times 10^5/T^2\right]$$

$$\nu_{0.20700\,\mathrm{M}} = \exp\left[-4.8176 - 1.8079 \times 10^3/T + 5.6160 \times 10^5/T^2\right]$$

Here ν is kinematic viscosity in cm^2 s^{-1} and T is temperature in kelvin in the range 283–363 K.

3.3 *Diffusivity*

The limiting current density for a rotating disc electrode, as originally derived by Levich [12], is given by

$$i_L = 0.621 nFC_\infty (\nu\omega)^{1/2} Sc^{2/3} \qquad (1)$$

This equation is valid when the Schmidt number is large, $Sc > 1000$. Gregory and Riddiford [13] proposed an improved expression for $Sc > 250$,

$$i_L = \frac{0.6201 nFC_\infty (\nu\omega)^{1/2} Sc^{2/3}}{(1 + 0.31442 Sc^{-0.36})} \qquad (2)$$

An extended version of the Levich equation was developed by Newman [14] for $Sc > 100$ in the form

$$i_L = \frac{0.6205 nFC_\infty (\nu\omega)^{1/2} Sc^{2/3}}{(1 + 0.298 Sc^{-1/3} + 0.14514 Sc^{-2/3}} \qquad (3)$$

Later Liu and Stewart [15] and then Levart and Schuhmann [16] developed further expressions for application to low Schmidt number systems ($Sc \geqslant 1$). The expressions include further terms in Sc and take the form [16]

$$i_L = \frac{0.62045 nFC_\infty (\nu\omega)^{1/2} Sc^{2/3}}{\left[\begin{array}{l}1 + 0.29801 Sc^{-1/3} + 0.14514 Sc^{-2/3} + 0.07020 Sc^{-1} \\ + 0.03515 Sc^{-4/3} + 0.01585 Sc^{-5/3} + \ldots\end{array}\right]} \qquad (4)$$

In their work on diffusivity in the ferri-ferrocyanide system Etman *et al.* [17] found it necessary to use only the first two terms in the denominator of Equation 4 i.e. they based their calculations on Equation 3. At the high temperatures used in the present work the Schmidt numbers of ferri-ferrocyanide electrolyte solutions are approximately 150 (at $T = 363$ K for 0.00985 M solution) so that the use of Equation 3 rather than Equation 4 is justified. Calculation via the simple Levich expression (Equation 1) in these circumstances leads to errors in diffusivity values of around 6% below those calculated using Equation 3.

A typical plot of the square root of the rotating disc electrode rotation rate against the limiting current density is shown in Fig. 3. The slopes of the straight lines obtained from this plot were used in the calculation of experimental ionic diffusion coefficients using Equation 3.

Further to the problem of Schmidt number range, the changing concentrations in the mass transfer boundary layer are important in determining the contribution of ionic migration to the limiting current. For the special case of a constant potential gradient, the limiting current, including migration effects, can be calculated rigorously. The diffusion potential contributes to the electric field which promotes migration. Hiraoka *et al.* [8] derived a relationship between experimental and real diffusivities for the rotating disc

Table 1. Conductance and transfer number of ions in equimolar ferri-ferrocyanide solution in 0.5 M NaOH

Ion	λ /Ω^{-1} m^2 mol^{-1}	t_i $C = 0.01$ M	$C = 0.02$ M	$C = 0.05$ M	$C = 0.1$ M	$C = 0.2$ M
$Fe(CN)_6^{3-}$	3.020	0.0220	0.0404	0.0806	0.1208	0.1608
$Fe(CN)_6^{4-}$	4.420	0.0322	0.0590	0.1178	0.1764	0.2348
OH^-	1.992	0.7257	0.6647	0.5309	0.3975	0.2646
Na^+	0.501	0.1825	0.1672	0.1335	0.1000	0.0665
K^+	0.735	0.0376	0.0687	0.1372	0.2053	0.2733

electrode in the form

$$\frac{D_{\text{real}}}{D_{\text{exp}}} = \left(1 - \frac{nt_i}{z_i}\right), \tag{5}$$

where the transfer numbers for each ion, t_i, were calculated from the Equation 6,

$$t_i = \frac{|z_i|\lambda_i C_i}{\sum_i |z_i| C_i \lambda_i} \tag{6}$$

The conductances, λ_i, were taken from the data of Selman and Newman [18].

Transport numbers of the ions constituting the present system are displayed in Table 1. Using these values along with Equation 5, the corrected diffusivities of the ferricyanide ion were calculated, D_{real}, and are shown plotted in Fig. 4. These data may also be expressed in the form of the following second order polynominals as a function of T.

$$D_{0.00985\,\text{M}} = (75.131 - 0.6324T + 1.3603 \times 10^{-3}T^2) \times 10^{-6}$$

$$D_{0.02030\,\text{M}} = (72.194 - 0.6086T + 1.3068 \times 10^{-3}T^2) \times 10^{-6}$$

$$D_{0.05110\,\text{M}} = (71.936 - 0.6032T + 1.2868 \times 10^{-3}T^2) \times 10^{-6}$$

$$D_{0.10200\,\text{M}} = (70.828 - 0.5918T + 1.2552 \times 10^{-3}T^2) \times 10^{-6}$$

$$D_{0.20700\,\text{M}} = (62.655 - 0.5336T + 1.1482 \times 10^{-3}T^2) \times 10^{-6}$$

D is diffusivity in $cm^2\,s^{-1}$ and T is temperature in kelvin in the range 283–363 K.

The calculated real diffusivities of the ferricyanide ion were correlated in the form of the Stokes–Einstein parameter, $D_{\text{real}}\mu/T$, as a function of the ionic strength, Γ, of the solution.

$$\frac{D_{\text{real}}\mu}{T} = (2.529 - 0.308\Gamma + 0.0639\Gamma^2) \times 10^{-15}\,\text{N}\,\text{K}^{-1} \tag{7}$$

where

$$\Gamma = \tfrac{1}{2}\sum_i z_i^2 C_{i,\infty} \tag{8}$$

Results show that the ratio, $D_{\text{real}}\mu/T$, is independent of temperature but shows a slight dependence on concentration. Table 2 summarizes data of various authors in terms of $D\mu/T$ values.

Table 2. Values of the constants in the equation $D\mu/T$ = a + bΓ + cΓ^2 from different authors [$(D\mu/T)/10^{-15}$ NK^{-1}]

	a	b	c
Bazan *et al.* [5]	2.500	–	–
Gordon *et al.* [7]	2.340	0.014	–
Hiraoka *et al.* [8]	2.250	0.044	–
Bourne *et al.* [9]	2.511	–	–
Present study	2.529	–0.308	0.0639

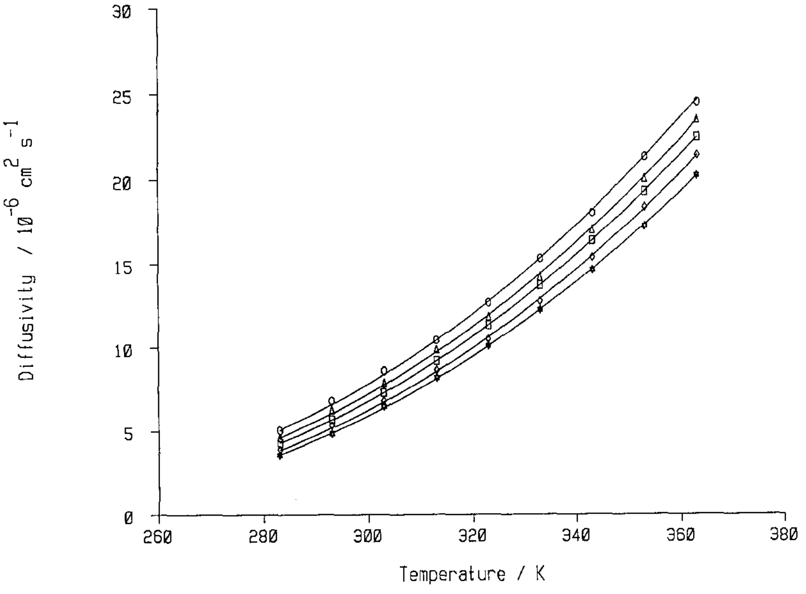

Fig. 4. Diffusivity of ferricyanide ion in 0.5 M NaOH. Key as for Fig. 1, but without (x).

Table 3. Diffusivities from various authors over the common temperature and concentration range

Source	*Concentration* (*Fe(CN)$_6^{3-}$*) /mol dm^{-3}	*Concentration* (*NaOH or KOH* [8]) /mol dm^{-3}	*Temperature* /°C	*D*/10^{-6} /cm^2 s^{-1}
Bazan *et al.* [5]*	0.0118	0.5001	30.5	8.13
	0.0118	0.5001	36.0	8.99
	0.0240	0.5980	25.0	6.56
Gordon *et al.* [7]*	0.01	0.50	25.0	7.78
	0.02	0.50	25.0	7.62
	0.05	0.50	25.0	7.56
	0.20	0.50	25.0	6.85
Hiraoka *et al.* [8]†	0.02	1.00	30.0	7.83
	0.10	1.00	30.0	7.50
	0.20	1.00	30.0	7.19
Bourne *et al.* [9]*	0.01	0.50	20.0	6.46
	0.01	0.50	30.0	8.38
Present study	0.01	0.50	20.0	6.81
	0.01	0.50	30.0	8.60
	0.02	0.50	25.0	7.10
	0.02	0.50	30.0	7.90
	0.05	0.50	25.0	6.51
	0.10	0.50	25.0	6.08
	0.10	0.50	30.0	6.81
	0.20	0.50	25.0	5.67
	0.20	0.50	30.0	6.49

* Selected experimental data
† Selected and corrected experimental data

Some sample data from the various available sources for comparable concentrations and temperatures are assembled in Table 3. As can be seen the present results coincide well with the data of Bazan *et al.* [5] and Bourne *et al.* [9] over the common temperature range. The diffusivity data of Hiraoka *et al.* [8] also agree with this work over the common concentration and temperature range. Although Gordon *et al.* [7] treated their data with due consideration of migration effects, these appear to lie some 10% higher than those found in the present work.

References

[1] S. M. Chouikhi, M. A. Patrick and A. A. Wragg, *J. Appl. Electrochem.* **17** (1987) 1118.

[2] F. P. Berger and K. F. F. L. Hau, *Int. J. Heat and Mass Transfer* **20** (1977) 1185.

[3] D. J. Tagg, M. A. Patrick and A. A. Wragg, *Trans. Inst. Chem. Eng.* **57** (1979) 179.

[4] M. Simek and I. Roušar, *J. Appl. Electrochem.***21** (1991) 583.

[5] M. Eisenberg, C. W. Tobias and C. R. Wilke, *J. Electrochem. Soc.* **103** (1956) 413.

[6] J. C. Bazan and A. J. Arvia, *Electrochim. Acta* **10** (1965) 1025.

[7] L. Gordon, J. N. Newman and C. W. Tobias, *Ber. Bunsenges. Phys. Chem.* **70** (1966) 414.

[8] S. Hiraoka, I. Yamada, H. Ikeno, H. Asano, S. Nomura, T. Okada and N. Nakamura, *J. Chem. Eng. Japan* **14** (1981) 345.

[9] J. R. Bourne, P. Dell'Ava, O. Dossenbach and T. Post, *J. Chem. Eng. Data* **30** (1985) 160.

[10] *BS718* (1979), Density Hydrometers.

[11] *BS188* (1977), Determination of the Viscosity of Liquids.

[12] V. G. Levich, 'Physico-Chemical Hydrodynamics' (English edition) (1962) Prentice-Hall, NJ.

[13] D. P. Gregory and A. C. Riddiford, *J. Chem. Soc.* (1956) 3756.

[14] J. S. Newman, *Adv. Electrochem. and Electrochem. Eng.* **5** (1967) 88.

[15] K. T. Liu and W. E. Stewart, *Int. J. Heat and Mass Transfer* **17** (1972) 187.

[16] E. Levart and D. Schuhmann, *ibid.* **17** (1974) 555.

[17] M. Etman, R. Molina, D. Schuhmann, E. Levart, O. Contamin and G. Scarbeck, *Analysis* **5** (1977) 11.

[18] J. R. Selman and J. Newman, *J. Electrochem. Soc.* **118** (1971) 1070.