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SHORT COMMUNICATION

Physical properties of aqueous solutions containing $NaClO_3$ and/or $NaClO_4$

L. J. J. JANSSEN
Faculty of Chemical Engineering, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

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Nomenclature

D_i	diffusion coefficient for species i ($m^2 s^{-1}$)
ΔH_{act}	energy of activation ($J mol^{-1}$)
n_i	concentration of species i in mol kg^{-1} water (m or molality) (mol kg^{-1})
M	$n_{ch} + n_{pe}$ (dimensionless)
N_{ch}	n_{ch}/M (dimensionless)
N_{pe}	n_{pe}/M (dimensionless)
T	absolute temperature (K)
x_i	mass fraction of species i (dimensionless)

Greek symbols

η	dynamic viscosity of the solution ($kg s^{-1} m^{-1}$)
ν	kinematic viscosity of the solution ($m^{-2} s^{-1}$)
ρ	density of the aqueous solution ($kg m^{-3}$)
ρ_M	density of a mixture of a $NaClO_3$ and a $NaClO_4$ solution ($kg m^{-3}$)
ρ_w	density of water ($kg m^{-3}$)
ρ_{ch}^M	density of a $NaClO_3$ solution with a $NaClO_3$ concentration of M ($kg m^{-3}$)
ρ_{pe}^M	density of a $NaClO_4$ solution with a $NaClO_4$ concentration of M ($kg m^{-3}$)

Subscripts

ch	chlorate ions or $NaClO_3$
fo	$Fe(CN)_6^{4-}$ ions
pe	perchlorate ions or $NaClO_4$
T	absolute temperature
w	water

1. Introduction

Perchlorate is formed industrially by electrolysis of aqueous solutions containing high contents of sodium chlorate and sodium perchlorate [1]. Mass transfer of chlorate to the anode strongly affects the current efficiency for perchlorate formation [2]. To correlate experimental data on the mass transfer coefficient for chlorate in solutions of different compositions, the density and the dynamic viscosity for aqueous $NaClO_3$ and $NaClO_4$ solutions are required. In the literature only few data are known. No experimental data on the diffusion coefficient for chlorate in concentrated perchlorate solutions are available. To describe the mass transfer of ClO_3^- to a platinum anode under forced convection as a function of a large number of experimental variables, relations for solution density, kinematic viscosity, dynamic viscosity and diffusion coefficient for ClO_3^- are given. The data are important for continued research on chlorate oxidation and the optimization of perchlorate electrolysis.

2. Experimental details

Densities of solutions containing $NaClO_3$ and/or $NaClO_4$ were determined at various temperatures using a density meter (PAAR Precision Density meter, DMA 10). The density meter was calibrated with two different solutions, water and a 25 wt % aqueous solution of NaCl. Density data for these solutions are available [3, 4]. The measurement of the kinematic viscosity was carried out with a viscosimeter (Schott viscosimeter, type AVS 350). The measuring cell was a capillary cell (Ubbelohde, type 530, 10/I). The obtained results were related to the kinematic viscosity of pure water [3].

Experiments to determine the effect of the sodium perchlorate concentration on the diffusion coefficient of $Fe(CN)_6^{4-}$ ions were carried out in a thermostated three-compartment cell. The working electrode was a rotating platinum disc electrode of geometric surface area $0.50 \times 10^{-4} m^2$, the counter electrode a platinum plate electrode of a geometric surface area $5 \times 10^{-4} m^2$ and the reference electrode a saturated calomel electrode. The rotation speed of the working electrode was varied from 4 to 64 r.p.s. The potential/current curve was measured automatically using a potentioscan (working POS73) and recorded by an X–Y recorder (Philips PM8043). The potential scan rate was $10 mV s^{-1}$.

3. Results and discussion

3.1. *Density*

The densities of the binary systems $H_2O{-}NaClO_3$ and $H_2O{-}NaClO_4$ were obtained from literature data. For the $H_2O{-}NaClO_4$ system the most recent data over a wide range are given by Miller and Doran [5]. Relations between density and concentration in mol dm^{-3} at the temperature designated are presented for 0, 29.87 and 49.3° C. From these data it was found that a linear relationship between $\ln[(\rho - \rho_w/x_{pe}]$ and T^{-1} exists and that the slope of the line is constant for the investigated range of $NaClO_4$ mass fraction, x_{pe}, i.e. from 0.05 to 0.4. Moreover, it was found that $(\rho - \rho_w)/x_{pe}$ increases

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linearly with increasing x_{pe}. From the literature data it was obtained that

$$(\rho - \rho_{\mathrm{w}})_T = (0.632x_{\mathrm{pe}} + 0.44x_{\mathrm{pe}}^2) \times \exp\left[-220\left(\frac{1}{T} - \frac{1}{298}\right)\right] \quad (1)$$

The reliable data over a wide concentration range for the H_2O–$NaClO_3$ system were published by Campbell *et al.* [6].

Similarly, from experimental data at 25 and 35° C for H_2O–$NaClO_3$ solutions it was found that

$$(\rho - \rho_{\mathrm{w}})_T = (0.657x_{\mathrm{ch}} + 0.40x_{\mathrm{ch}}^2) \times \exp\left[-130\left(\frac{1}{T} - \frac{1}{298}\right)\right] \quad (2)$$

The density of a ternary system can be correlated to those of two suitable binary systems. The usefulness of the mixture rule has been investigated analogously to the mixture rule for viscosity [7]. The mixture rule for the density of the H_2O–$NaClO_3$–$NaClO_4$ system gives

$$\rho_{\mathrm{M}} = N_{\mathrm{ch}}\rho_{\mathrm{ch}}^M + N_{\mathrm{pe}}\rho_{\mathrm{pe}}^M \quad (3)$$

where $N_{\mathrm{ch}} = n_{\mathrm{ch}}/M$, $N_{\mathrm{pe}} = n_{\mathrm{pe}}/M$ and $M = n_{\mathrm{ch}} + n_{\mathrm{pe}}$.

To verify the mixture rule, the densities of 5.39 M $NaClO_3$, 5.39 M $NaClO_4$ and a mixed 3.76 M $NaClO_3$ + 1.63 M $NaClO_4$ solution were determined at 25, 35, 50 and 65° C. It was found that for both binary systems the experimental densities and the densities calculated from the derived equations agree reasonably. The difference between the results was about 0.2% of the experimental density. Moreover, for the ternary system the mixture rule gave good results. The difference between the experimental and calculated densities was smaller than 0.1% of the experimental density.

3.2. *Kinematic viscosity*

Experimental results are given in Table 1 for the binary systems H_2O–$NaClO_3$ and H_2O–$NaClO_4$ and the ternary system H_2O–$NaClO_3$–$NaClO_4$.

Table 1. Kinematic viscosity, ν, for H_2O, the binary systems H_2O–$NaClO_3$ and H_2O–$NaClO_4$ and the ternary system H_2O–$NaClO_3$–$NaClO_4$ at various temperatures

Weight fraction for water, $x_{\mathrm{w}} = 1 - x_{\mathrm{ch}} - x_{\mathrm{pe}}$

x_{ch}	x_{pe}	$10^6\nu/\mathrm{m^2\,s^{-1}}$			
		25° C	*35° C*	*50° C*	*65° C*
–*	–	0.8904	0.7194	0.5468	0.4335
0.0476	–	0.882	0.722	0.559	0.452
0.1304	–	0.908	0.747	0.584	0.476
0.3333	–	1.161	0.954	0.743	0.608
–	0.05771	0.862	0.705	0.547	0.422
–	0.1667	0.857	0.707	0.552	0.451
–	0.286	0.911	0.751	0.590	0.483
–	0.375	1.032	0.849	0.664	0.544
0.125	0.250	1.115	0.908	0.708	0.580
0.250	0.123	1.180	0.974	0.758	0.620

* pure water.

If the kinematic viscosity is plotted against the concentration or weight fraction of the solute, the curves obtained for the H_2O–$NaClO_3$ and the H_2O–$NaClO_4$ solution show a clear minimum at 25° C. This minimum does not exist at 65° C.

It was found that for these systems plots of $\ln\nu$ against T^{-1} gave straight lines; the slope of the $\ln\nu/T^{-1}$ curve does not depend on the salt concentration and the slope of the $\ln\nu/T^{-1}$ curves is practically equal to the slope of the $\ln\nu_{\mathrm{w}}/T^{-1}$ curve.

Similarly, the kinematic viscosity of the H_2O–$NaClO_3$–$NaClO_4$ system was correlated to those of both the binary systems, i.e. H_2O–$NaClO_3$ and H_2O–$NaClO_4$ system. According to the mixture rule the kinematic viscosity of the ternary system is given by

$$\nu_{\mathrm{M}} = N_{\mathrm{ch}}\nu_{\mathrm{ch}}^M + N_{\mathrm{pe}}\nu_{\mathrm{pe}}^M \quad (4)$$

It was found that, for two concentrated solutions of the H_2O–$NaClO_3$–$NaClO_4$ system at various temperatures, the experimental kinematic viscosity (Table 1) agrees well with the kinematic viscosity calculated by the mixture rule. The differences are smaller than about 0.5%.

3.3. *Diffusion coefficient*

The diffusion coefficient of chlorate ion in a perchlorate solution cannot be determined directly by measurement of potential–current curves owing to simultaneous side reactions. The ferrocyanide ion is often used to study mass transfer problems in electrochemistry. It was found that the potential–current curves for the oxidation of $Fe(CN)_6^{3-}$ at a rotating platinum disc electrode in a $NaClO_4$ solution as supporting electrolyte were well shaped and showed a well defined limiting current for the oxidation of $Fe(CN)_6^{4-}$. From this limiting current the diffusion coefficient for $Fe(CN)_6^{4-}$, D_{fo}, was obtained as described in [8].

For the $NaClO_4$ solutions investigated the plots of $\ln D_{\mathrm{fo}}$ against T^{-1} gave straight lines. From the slopes the energy of activation for diffusion of $Fe(CN)_6^{4-}$ ions ($\Delta H_{\mathrm{act,fo}}$) was calculated. It was found that $\Delta H_{\mathrm{act,fo}}$ does not depend on the $NaClO_4$ concentration and is equal to $12 \pm 1\,\mathrm{kJ\,mol^{-1}}$. From D_{fo} at various temperatures and using $\Delta H_{\mathrm{act,fo}}$, the average value for D_{fo} at $T = 25°$ C was calculated. This value for D_{fo} is much more reliable than D_{fo} from a single experiment. The estimated inaccuracy

Table 2. The diffusion coefficient for $Fe(CN)_6^{4-}$, D_{fo}, the dynamic viscosity of solution, η, and the factor of $D_{fo}\eta$ for various mass fractions of sodium perchlorate and at 25° C

x_{pe}	$10^{10}D_{\mathrm{fo}}/\mathrm{m^2\,s^{-1}}$	$10^3\eta/\mathrm{kg\,m^2\,s^{-1}}$	$10^{13}D_{\mathrm{fo}}\eta/\mathrm{kg\,m\,s^{-2}}$
0.05771	5.88	0.892	5.25
0.1667	5.83	0.954	5.56
0.2986	5.38	1.105	5.95
0.375	4.64	1.337	6.20

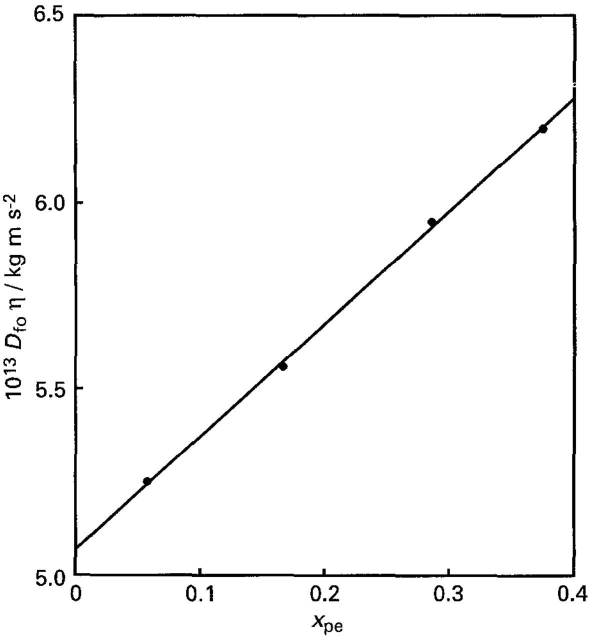

Fig. 1. Factor $D_{fo}\eta$ as a function of mass fraction for $NaClO_4$, x_{pe}, at 25° C.

in the average D_{fo} is about $0.1 \times 10^{-10}\,m^2\,s^{-1}$. Table 2 shows the average D_{fo}, the dynamic viscosity η of the relevant $NaClO_4$ solutions and the factor $D_{fo}\eta$ at 25° C.

The factor $D_{fo}\eta$ at 25° C is plotted against the mass fraction of $NaClO_4$ in Fig. 1. This shows that $D_{fo}\eta$ increases linearly with increasing $NaClO_4$ mass fraction. This increase is caused by a decrease in the hydration number for $Fe(CN)_6^{4-}$ in a $NaClO_4$ solution with increasing $NaClO_4$ concentration. Linear extrapolation of the $D_{fo}\eta/x_{pe}$ curve gives $D_{fo}\eta$ at $x_{pe} = 0$, $(D_{fo}\eta)_0$, i.e. $5.2 \times 10^{-13}\,kg\,m\,s^{-2}$, being the factor for the solution without supporting electrolyte, i.e. 5×10^{-3} M $K_4Fe(CN)_6$ solution. From the straight line it follows that at 25° C $D_{fo}\eta/(D_{fo}\eta)_0 = 1 + 0.48x_{pe}$. Moreover, it was found that the temperature has practically no effect on the relation between $D_{fo}\eta/(D_{fo}\eta)_0$ and x_{pe} in the temperature range 25 to 65° C.

The ratio between the differential diffusion coefficient for $K_4Fe(CN)_6$ in a 5×10^{-3} M $K_4Fe(CN)_6$ solution and that in infinite dilution at 25° C is 0.80 [9]. Using D_{fo} in infinite dilution, i.e. $7.4 \times 10^{-10}\,m^2\,s^{-1}$ at 25° C [10], and the assumption that D_{fo} decreases to the same extent, it was calculated that D_{fo} in 5×10^{-3} M $K_4Fe(CN)_6$ at 25° C is $5.9 \times 10^{-10}\,m^2\,s^{-1}$. Since the dynamic viscosity of 5×10^{-3} M $K_4Fe(CN)_6$ is almost equal to that of water, i.e. $\eta = 0.89 \times 10^{-3}\,kg\,m^{-1}\,s^{-1}$ at 25° C, it was calculated that for this solution $D_{fo}\eta = 5.25 \times 10^{-13}\,kg\,m\,s^{-2}$. This value is practically equal to that obtained by linear extrapolation of the $D_{fo}\eta/x_{pe}$ curve to $x_{pe} = 0$. This agreement indicates that the assumptions used are at least acceptable for practical application.

The diffusion coefficient for the chlorate ion, D_{ch}, was calculated for $NaClO_3$ solution without supporting electrolyte. From the equivalent conductance of $NaClO_3$ solutions and from D_{ch} in infinite dilution, i.e. $1.72 \times 10^{-9}\,m^2\,s^{-1}$ [11] and assuming the same concentration effect on the mobilities of both ions, viz Na^+ and ClO_3^-, it was calculated that $D_{ch} = 1.67 \times 10^{-9}\,m^2\,s^{-1}$ at 25° C for a 0.0376 M $NaClO_3$ solution. A 0.0376 M $NaClO_3$ solution containing a high concentration of $NaClO_4$ was used for the determination of the mass transfer coefficient for the chlorate ion at an oxygen-evolving electrode in perchlorate solution. Results of this work will be published separately.

Assuming the effect of the supporting electrolyte on the factor $D\eta$ for $Fe(CN)_6^{4-}$ and ClO_3^- are equal, it can be deduced, that for a $NaClO_3$ solution containing $NaClO_4$ as supporting electrolyte,

$$\frac{D_{ch}\eta}{(D_{ch}\eta)_0} = 1 + 0.48x_{pe} \tag{5}$$

This relation shows the factor $D_{ch}\eta$ as a function of the mass fraction of sodium perchlorate.

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