Mutual diffusion coefficients in systems containing the nickel ion

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Mutual diffusion coefficients of nickel chloride in water have been measured at 293.15 K and 303.15 K and at concentrations between 0.020 mol dm^{-3} and 0.100 mol dm^{-3}, using a conductimetric cell. The experimental mutual diffusion coefficients are discussed on the basis of the Onsager–Fuoss model. The equivalent conductances at infinitesimal concentration of the nickel ion in these solutions at those temperatures have been estimated using these results.

In addition, from these data, we have estimated some transport and structural parameters, such as limiting diffusion coefficient, ionic conductance at infinitesimal concentration, hydrodynamic radii and activation energy, contributing this way to a better understanding of the structure of these systems and of their thermodynamic behavior in aqueous solution at different concentrations.

1. Introduction

The diffusion of electrolytes in aqueous solutions and its impact on biological systems is of great interest, not only for fundamental purposes, but also for many technical fields, such as studies of corrosion in biological systems, desalination, dissolution and crystallization [1,2]. However, to our knowledge, there are only a few publications devoted to the study of diffusion in aqueous electrolyte solutions. We have been particularly interested in data about this property for chemical systems involving nickel ions in different aqueous media [3–5]. This work has been motivated by the fact that the nickel ion is one of the most mobile and bioavailable heavy metal ions present in different sources (e.g., drinking water, food, active pharmaceutical ingredients and excipients, and dental casting alloys), and by the possibility that the diffusion of nickel salts could produce substantial coupled flows of other dissolved salts. As far as the authors know, only data on mutual diffusion coefficients of nickel salts at 310.15 K and 298.15 K, have been published. Thus, because of their importance, including practical applications in fields as diverse as anticorrosion or therapeutic purposes, we tried to get a deeper insight into the understanding of their structure with increasing the range of temperatures for the same concentrations.

In this work, the open ended capillary cell are used to measure binary mutual diffusion coefficients for systems NiCl$_2$–water at different temperatures and at concentrations of 0.020 mol dm^{-3}, 0.050 mol dm^{-3}, 0.080 mol dm^{-3}, and 0.100 mol dm^{-3}. From these data, we have estimated some transport and structural parameters, such as limiting diffusion

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coefficient, ionic conductance at infinitesimal concentration, and hydrodynamic radius. These values are acceptable within the imprecision limits of the diffusion measurements ($< 3\%$).

2. Experimental

2.1. Reagents and solutions

Nickel chloride (Merck $> 97\%$ purity) was used without further purification. The solutions for the diffusion measurements were prepared in calibrated volumetric flasks using bi-distilled water. The solutions were freshly prepared and de-aerated for about 30 min before each set of runs.

2.2. Open-ended conductimetric capillary cell

An open-ended capillary cell, which has been used to obtain mutual diffusion coefficients of a wide variety of electrolytes, is described in great detail in previous papers (e.g., [2,6–10]). Basically, this consists of two vertical capillaries, each one closed at one end by a platinum electrode and positioned one above the other with the open ends separated by a distance of about 14 mm. The upper and lower tubes, initially filled with solutions of concentrations $0.75c$ and $1.25c$, respectively, are surrounded with a solution of concentration c. This ambient solution is contained in a glass tank $200 \times 140 \times 60$ mm immersed in a thermostatic bath. Perspex sheets divide the tank internally and a glass stirrer creates a slow lateral flow of ambient solution across the open ends of the capillaries. Experimental conditions are such that the concentration at each one of the open ends is equal to the ambient solution value c, that is, the physical length of the capillary tube coincides with the diffusion path. This means that the required boundary conditions described in the literature [12] to solve Fick's second law of diffusion are applicable. Therefore, the so-called Δl effect [12] is reduced to negligible proportions. In our manually operated apparatus, diffusion is followed by measuring the ratio $w = R_t/R_b$ of resistances R_t and R_b of the upper and lower tubes by an alternating current transformer bridge. In our automatic apparatus, w is measured by a Solartron digital voltmeter (DVM) 7061 with 6 1/2 digits. A power source (Bradley Electronic Model 232) supplies a 30-V sinusoidal signal at 4 kHz (stable to within 0.1 mV) to a potential divider that applies a 250-mV signal to the platinum electrodes in the top and bottom capillaries. By measuring the voltages V' and V'' between the top and bottom electrodes and a central electrode at ground potential in a fraction of a second, the DVM calculates w.

In order to measure the differential diffusion coefficient D at a given concentration c, the "bulk" solution of concentration c is prepared by mixing 1 L of the "top" solution with 1 L of the "bottom" solution, measured accurately. The glass tank and the two capillaries are filled with the c solution, immersed in the thermostat, and allowed to come to thermal equilibrium. The resistance ratio $w = w_\infty$ measured under these conditions (with solutions in both capillaries at concentration c) accurately gives the quantity $\tau_\infty = 10^4/(1 + w_\infty)$.

The capillaries are filled with the "top" and "bottom" solutions, which are then allowed to diffuse into the "bulk" solution. Resistance ratio readings are taken at various recorded times, beginning 1000 minutes after the start of the experiment, to determine the quantity $\tau = 10^4/(1 + w)$ as τ approaches τ_∞. The diffusion coefficient is evaluated using a linear least-squares procedure to fit the data and, finally, an iterative process applied using 20 terms of the expansion series of Fick's second law for the present boundary conditions. The theory developed for the cell has been described previously [12].

3. Results and discussion

Mutual diffusion coefficients, D, of $NiCl_2$ in aqueous solutions at 293.15 K and 303.15 K obtained by conductimetric technique are shown in Fig. 1 and Table 1. D is the mean value of, at least, three independent measurements. The reproducibility of these results was, in general, usually within $\pm(1$–$3)\%$. Concerning the effect of temperature on diffusion, an increase in the experimental D values is found in all nickel chloride concentrations. Also, the decrease of the diffusion coefficient was obtained when the concentration increased.

The following polynomial in c was used to fit the data by a least squares procedure,
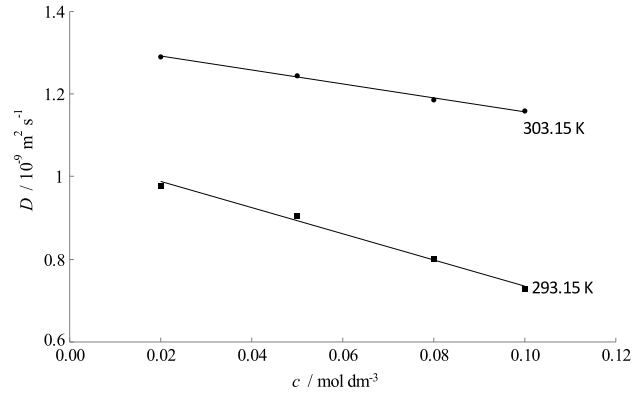
$$D/\left(10^{-9}\ \mathrm{m^2\,s^{-1}}\right) = a_0 + a_1 c \tag{1}$$

where the coefficients a_0 and a_1 are fitting parameters (Table 2). These may be used to calculate values of diffusion coefficients at specified concentrations within the range of the experimental data shown in Table 1. The goodness of the fit (obtained with a confidence interval of 98%) can be assessed by the excellent correlation coefficients, R^2 and the low percentage of standard deviation ($< 1\%$).

Assuming that the above D^0 values coincide with the Nernst values (Eq. (2)) for different temperatures [1,11,12] from

$$D^0 = \frac{RT}{F^2} \frac{|Z_{Ni^{2+}}| + |Z_{Cl^-}|}{|Z_{Ni^{2+}} Z_{Cl^-}|} \frac{\lambda^0_{Ni^{2+}} \lambda^0_{Cl^-}}{\lambda^0_{Ni^{2+}} + \lambda^0_{Cl^-}} \tag{2}$$

where $\lambda^0_{Cl^-}$ is the limiting equivalent conductance of Cl^- at infinitesimal concentration given in the literature [12,13], $Z_{Ni^{2+}}$ and Z_{Cl^-} represent the algebraic valences of a cation and of an anion, respectively, we have estimated the limiting equivalent

Fig. 1. Experimental mutual diffusion coefficients, D, as a function of solute concentration, c, at 293.15 K (■) and 303.15 K (●). The curves are a fit through the data using the empirical equation $D/(10^{-9}\ \mathrm{m^2\ s^{-1}}) = a_0 + a_1 c$.

Table 1
Experimental diffusion coefficients, D^a, of NiCl$_2$ in aqueous solutions at various concentrations, c, at $T = 293.15$ K and $T = 303.15$ K.

$c/\mathrm{mol\,dm^{-3}}$	$D^a \pm S_D{}^b/10^{-9}\ \mathrm{m^2\,s^{-1}}$	
	$T = 293.15$ K	$T = 303.15$ K
0.020	0.979 ± 0.020	1.290 ± 0.024
0.050	0.906 ± 0.010	1.244 ± 0.022
0.080	0.801 ± 0.022	1.187 ± 0.021
0.100	0.728 ± 0.006	1.159 ± 0.008

[a] D is the mean diffusion coefficient for 3 experiments.
[b] S_D is the standard deviation of that mean.

Table 2
Fitting coefficients (a_0 and a_1) of Eq. (1) to the mutual differential diffusion coefficients for nickel chloride in aqueous solutions at $T = 293.15$ K and $T = 303.15$ K.

T/K	a_0	a_1	R^2
293.15	1.051	−3.158	0.992
303.15	1.324	−1.671	0.997

Table 3
Some transport and structural parameters at different temperatures, T, in aqueous solutions: Self-diffusion of nickel ion at infinitesimal concentration, $D^0_{\mathrm{Ni^{2+}}}$, limiting equivalent conductance of nickel ion $\lambda^0_{\mathrm{Ni^{2+}}}$, and hydrodynamic radius of nickel ion, r_h.

T/K	$D^0/(10^{-9}\ \mathrm{m^2\,s^{-1}})$	$D^0_{\mathrm{Ni^{2+}}}/(10^{-9}\ \mathrm{m^2\,s^{-1}})$	$\lambda^0_{\mathrm{Ni^{2+}}}/(10^{-4}\ \mathrm{S\,m^2\,mol^{-1}})$	r_h/nm
293.15	1.051[a]	0.545	41.83	0.39
298.15	1.256[b]	0.713	53.57	0.34
303.15	1.324[a]	0.745	55.05	0.37
310.15	1.399[b]	0.782	56.50	0.42

[a] Values obtained from Eq. (1) (Table 1).
[b] Published data [3].

conductances of the nickel ion, $\lambda^0_{\mathrm{Ni^{2+}}}$, at 293.15 K and 303.15 K by using the Nernst relation for a singly charged species (Eq. (3) and Table 3) [11], that is:

$$\lambda^0_{\mathrm{Ni^{2+}}} = \frac{D^0_{\mathrm{Ni^{2+}}} Z F^2}{RT} \tag{3}$$

From the limiting tracer coefficients of the nickel ion, $D_{\mathrm{Ni^{2+}}}$, for different temperatures, and applying the well-known Stokes–Einstein equation (Eq. (4)), for spherical particles [14], which assumes that the particles are perfectly spherical and are solely subject to solvent friction [14]:

$$D^0_{\mathrm{Ni^{2+}}} = \frac{k_\mathrm{B} T}{6\pi \eta^0 r_\mathrm{h}} \tag{4}$$

k_B and η^0 being the Boltzmann constant and the water viscosity at temperature T [15], respectively, the hydrodynamic radius (r_h) of ionic nickel has also been estimated (Table 2).

The decrease of the diffusion coefficient, when the concentration increases, may be interpreted on the basis of species resulting from the eventual formation of ion pairs, increasing with concentration [3]. In relation to the effect of temperature on diffusion, an increase in the experimental D values was found at all nickel chloride concentrations (Table 1 and Fig. 1).

The variations of r_h with temperature (Table 3), including the data for the others temperatures, are, in general, relatively small (± 0.05), which is within the precision of the diffusion measurements. Although his relation can only be considered as an approximated one (mainly arising from the fact that the structure of both the solute kinetic species and the solvent are disregarded), it can be used to derive some valuable information on the relation between the size of nickel ion, its shape and the self-diffusion coefficient at infinitesimal concentration.

4. Concluding remarks

Diffusion coefficients have been measured for aqueous solutions of nickel chloride, providing transport and structural parameters necessary to model the diffusion for various purposes, such as chemical, medical, and pharmaceutical applications.

Acknowledgements

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