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Diffusion Coefficients in Aqueous Solutions of Cobalt Chloride at 298.15 K

Ana C. F. Ribeiro, Victor M. M. Lobo,* and J. J. S. Natividade

Department of Chemistry, University of Coimbra, 3004−535 Coimbra, Portugal

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Differential diffusion coefficients of cobalt chloride in water at 298.15 K, and at concentrations from 8×10^{-3} mol dm^{-3} to 3×10^{-1} mol dm^{-3}, have been measured using a conductometric cell and an automatic apparatus to follow diffusion. The cell uses an open ended capillary method and a conductometric technique is used to follow the diffusion process by measuring the resistance of a solution inside the capillaries, at recorded times. The results are discussed on the basis of the Onsager−Fuoss and Gordon models.

Introduction

No data for diffusion coefficients of cobalt chloride in aqueous solutions are reported in the literature.[1] The present paper is intended to fill this gap and reports those experimental data at 298.15 K obtained by an open-ended capillary cell. This conductometric technique follows the diffusion process by measuring the ratio of electrical resistances of the electrolyte solution in two vertically opposed capillaries as time proceeds. The method has previously given us reasonably precise and accurate results.[2−7]

The data are discussed on the basis of the Onsager−Fuoss[8] and Gordon models.[9] Cobalt compounds in aqueous solutions originate complex ions,[10] and these species affect the viscosity and consequently their diffusion in the solvent.

Experimental Section

The apparatus assembled for use with the open-ended capillary cell in this laboratory is essentially the same as previously reported.[2] The cell has two vertical capillaries, each 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 0.75*c* and 1.25*c*, respectively, are surrounded with a solution of concentration *c*. This ambient solution is contained in a glass tank (200 × 140 × 60) mm immersed in a thermostat at 298.15 K. The tank is divided internally by Perspex sheets 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 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 or, in other words, the boundary conditions described in ref 2 to solve Fick's second law of diffusion are applicable. Therefore, the so-called Δl-effect[2] is reduced to negligible proportions. In a manual apparatus, diffusion is followed by measuring the ratio of resistances of upper and lower tubes by an alternating current transformer bridge. In an automatic apparatus $w = R_t/R_b$ is measured by a Solartron digital voltmeter (DVM) 7061 to $6^1/_2$ digits. A power source Bradley Electronics Model 232 supplies a 30 V sinusoidal signal of 4 kHz (stable up to 0.1 mV) to a potential divider that applies a 250 mV signal to the platinum electrodes at the top and bottom capillaries. By measuring the voltages V' and V'' from top and bottom electrodes to the central electrode at ground potential, in a fraction of a second, the DVM calculates $w = R_t/R_b$.

To measure the differential diffusion coefficient *D* at a given concentration *c*, a "top" solution of concentration 0.75*c* and a "bottom" solution at 1.25*c* are prepared, each in a 2 L volumetric flask. The "bulk" solution of concentration *c* is prepared by mixing 1 L of "top" solution with 1 L of "bottom" solution, accurately measured. The cobalt chloride solutions were prepared from pro analyse Merck reagent. The glass tank and the two capillaries are filled with *c* solution, immersed in the thermostat, and allowed to come to thermal equilibrium. $\text{TRinf} = 10^4/(1 + w)$, where $w = R_t/R_b$ is the electrical resistance (*R*) ratio of the top (t) and bottom (b) diffusion capillaries at infinite time (when their solutions are *c*), is now measured very accurately. $\text{TR} = 10^4/(1 + w)$ is the equivalent, at any time *t*.

The capillaries are then filled with "top" and "bottom" solutions and allowed to diffuse into the "bulk" solution. Resistance ratio readings are taken at recorded times, beginning 1000 min after the starting of an experiment. The diffusion coefficient is finally evaluated using a linear least-squares procedure to fit the data and subsequently an itterative process by using 20 terms of the expansion series of the solution of Fick's second law for the present boundary conditions. The theory developed for this cell has already been described.[2]

Results and Discussion

The results of diffusion experiments in solutions 3×10^{-1} mol dm^{-3} $CoCl_2$ at 298.15 K are shown in Table 1. They are in good agreement and indicate the precision of the method for measuring differential diffusion coefficients. Measurements in 0.1 mol dm^{-3} KCl solutions by this method agree with those of Miller within 0.1%.[7] Table 2 shows the results with cobalt chloride solutions from 8×10^{-3} mol dm^{-3} to 3×10^{-1} mol dm^{-3} at 298.15 K. These results are the average of four experiments performed in consecutive days. The reproducibility of the results is good,

* Corresponding author. E-mail: vlobo@ci.uc.pt. Fax: +351 239 827703.

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Table 1. Diffusion Experiments with 3 × 10^{-1} M $CoCl_2$ in Aqueous Solutions at 298.15 K

10^9D $m^2\ s^{-1}$	TRinf[a]
1.083	5053.0
1.085	5053.1
1.088	5053.0
1.087	5053.0

[a] TRinf = $10^4/(1 + w)$, where $w = R_t/R_b$ is the resistance ratio of top and bottom capillaries.

Table 2. Diffusion Coefficients, *D*, of $CoCl_2$ in Aqueous Solutions at 298.15 K at Different Concentrations, *c*

c mol dm^{-3}	mean value of D in 4 experiments $10^{-9}\ m^2\ s^{-1}$	TRinf[a]	$10^9\sigma_{av}$[b] $m^2\ s^{-1}$	10^9D_{OF}[c] $m^2\ s^{-1}$	10^9D_G[d] $m^2\ s^{-1}$
8 × 10^{-3}	1.290	5040.0	0.001	1.175	1.182
1 × 10^{-2}	1.269	5030.5	0.002	1.172	1.178
5 × 10^{-2}	1.217	5005.0	0.008	1.171	1.155
8 × 10^{-2}	1.209	5056.0	0.008	1.179	1.145
1 × 10^{-1}	1.108	5008.0	0.002	1.185	1.140
2 × 10^{-1}	1.091	5030.0	0.001	1.211	1.114
3 × 10^{-1}	1.086	5053.0	0.001	1.235	1.090

[a] See Table 1. [b] σ_{av} is the standard deviation of the mean of four experiments. [c] D_{OF} represents the diffusion coefficient calculated by the Onsager–Fuoss theory.[8] [d] D_G represents the diffusion coefficient calculated by the Gordon equation.[9]

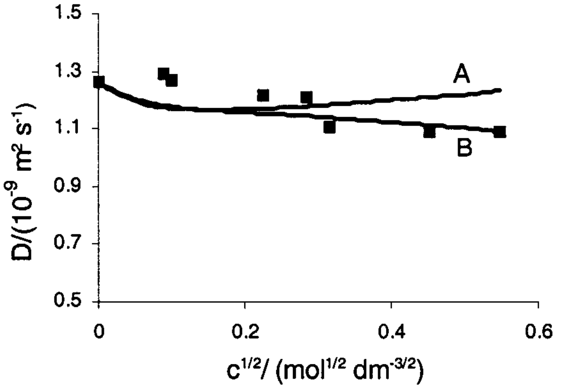

Figure 1. Comparison of diffusion coefficients of $CoCl_2$ calculated by Onsager–Fuoss[8] and Gordon [9] models (curves A and B, respectively), using $a = 8.1 \times 10^{-10}$ m for the ion size parameter,[11] and our results (■) at 298.15 K.

as shown by the standard deviation of the mean, σ_{av}. Previous papers reporting data obtained with our conductoimetric cell support our view that the uncertainty of our results is not larger than 1–2%. The uncertainty in the temperature T is close to ± 0.01 °C and in the concentrations c is close to ± 0.001%.

Figure 1 compares experimental results with calculations on the basis of Onsager–Fuoss[8] and Gordon models.[9] The Onsager–Fuoss equation for an electrolyte of this type is often written

$$D_{OF} = 2000RT\frac{\bar{M}}{c}\left(1 + c\frac{\partial(\ln y_{\pm})}{\partial c}\right) \tag{1}$$

where

$$\frac{\bar{M}}{c} = 1.0741 \times 10^{-20}\,\frac{\lambda_1^0\lambda_2^0}{|z_1|\nu_1\Lambda^0} + \frac{\Delta\overline{M'}}{c} + \frac{\Delta\overline{M''}}{c} \tag{2}$$

In (2), the first- and second-order electrophoretic terms are given by

$$-\frac{\Delta\overline{M'}}{c} = \frac{2(|z_2|\lambda_1^0 - |z_1|\lambda_2^0)}{|z_1z_2|(\Lambda^0)^2(\nu_1\nu_2)}\,\frac{3.132 \times 10^{-19}}{\eta_0(\epsilon T)^{1/2}}\,\frac{c\sqrt{\Gamma}}{(1 + ka)} \tag{3}$$

and

$$\frac{\Delta\overline{M''}}{c} = \frac{({z_2}^2\lambda_1^0 + {z_1}^2\lambda_2^0)^2}{(\Lambda^0)^2}\,\frac{9.304 \times 10^{-13}c^2}{\eta_0(\epsilon \mathrm{T})^2}\phi(ka) \tag{4}$$

where $\Gamma = \sum c_iz_i^2$ is the ionic strength, η_0 is the viscosity of the solvent, k is the "reciprocal of average radius of ionic atmosphere", a is the mean distance of approach of ions, $\phi(ka) = |e^{2ka}Ei(2ka)/(1 + ka)^2|$ has been tabulated by Harned and Owen,[12] and the other letters represent well-known quantities.[12] $\lambda^0_{Co^{2+}}$ and $\lambda^0_{Cl^-}$ are given in the literature[13] as 54.0 × 10^{-4} m^2 S mol^{-1} and 76.3 × 10^{-4} m^2 S mol^{-1}, respectively.

Gordon's equation[9] for the calculation of the diffusion coefficient D_G is

$$D_G = D_{OF}\left(\frac{\eta_0}{\eta}\right) \tag{5}$$

where η is the viscosity of the solution. For the Onsager–Fuoss and Gordon curves, shown in Figure 1, the value used for the ion size parameter a is 8.1 × 10^{-10} m calculated by the sum of the hydrated ionic radii (diffraction methods).[11]

For c = 0.08 mol dm^{-3}, the results predicted from the above models differ from experimental observation between 3% and 10%. This is not surprising if we take into account the formation of complexes between Co^{2+} and Cl^- and the variety of ion pairs eventually formed, factors not taken into account in Onsager–Fuoss (eqs 1–4) and Gordon (eq 5) equations.

At higher concentrations ($c > 0.08$ mol dm^{-3}), the results predicted from the Onsager–Fuoss model differ significantly from experimental observation. This is understandable if we take into account the change with concentration of parameters such as viscosity, dielectric constant and hydration, which are not taken into account in the Onsager–Fuoss model. In this context, taking only in consideration the effect of the viscosity on diffusion of this electrolyte in Gordon equation,[9] we obtain results closer to experimental data. We can conclude that the behavior of this electrolyte depends strongly on the viscosity change in the solution. Taking into account the effect of the hydration on diffusion of the same system (using Agar's model[14]), for the same interval of concentrations ($c > 0.08$ mol dm^{-3}), we obtain more significant differences between these results and our data. When we use different values of the hydration number (h = 1, 6, and 12[14,15]) this deviation increases from 4% to −10%, and so the hydration factor seems to have a negligible role on the diffusion of this salt.

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