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Diffusion Coefficients of Chromium Chloride in Aqueous Solutions at 298.15 K and 303.15 K

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Mutual diffusion coefficients (interdiffusion coefficients) have been measured of chromium(III) chloride in water at 298.15 K and 303.15 K at concentrations between 0.005 mol·dm^{-3} and 0.05 mol·dm^{-3} using a conductometric cell. The experimental mutual diffusion coefficients are discussed on the basis of the Onsager−Fuoss model. The equivalent conductance at an infinitesimal concentration of the chromium(III) ion in these solutions at 303.15 K has been estimated using these results.

Introduction

The study of diffusion processes in electrolyte solutions is important both for fundamental reasons, helping to understand the nature of aqueous electrolyte structure, and for practical application in fields such as corrosion. We have been particularly interested in data on this property for chemical systems occurring in the oral cavity, to understand and resolve corrosion problems related to dental restorations in systems where data are not currently available. Oral restorations involve various dental metallic alloys.[1−6] For example, it is possible to have a metal-ceramic crown over a dental implant in the oral cavity that is in contact with an amalgam restoration made on an adjacent or antagonist tooth. This can act as an abutment for a partial removable denture made of a chromium−cobalt alloy. The oral cavity is a wet environment, providing favorable conditions for corrosion. The saliva acts as an electrolyte solution for different dental alloys, leading to an electrochemical reaction. One fundamental condition for metal materials used as dental amalgams in restorations is that they must resist completely the action of the corrosive media (e.g., saliva, bacterium plaque, and decomposition of food) and of fluctuations in temperature, changes in pH, or mechanical effects. Corrosion is said to be continuous in the mouth because the ions, produced from the surface of the alloy, are removed with the abrasion of foods, liquids, and brushing ("corrosion−erosion"). However, the properties and behavior of chemical systems in the oral cavity are poorly known, even though this is a prerequisite to obtain adequate understanding and solution of these wear and corrosion problems. This has provided the impetus for the present study of the diffusion of one of these ions, chromium(III) as its chloride, in aqueous solutions.

It is very common in the scientific literature to find misunderstandings concerning the meaning of the parameter frequently just denoted by D referred to as the "diffusion coefficient".[7−9] It is necessary to distinguish between two distinct processes (adequately defined in IUPAC's compendium of chemical terminology): self-diffusion, D^* (intradiffusion, tracer diffusion, single ion diffusion, and ionic diffusion) and mutual diffusion, D (interdiffusion, concentration diffusion, and salt diffusion).[7−10] Many techniques are used to study diffusion in aqueous solutions. Methods such as NMR, polarographic, and capillary-tube techniques with radioactive isotopes measure self-diffusion coefficients ("intradiffusion coefficients"). However, for bulk ion transport, the appropriate parameter is the mutual diffusion coefficient, D. Relationships derived between intradiffusion and mutual diffusion coefficients, D^* and D, have had limited success, and consequently, mutual diffusion coefficients are much needed.

As far as the authors know, no data on mutual diffusion coefficients of Cr(III) salts have been published.[11] In this study, mutual diffusion coefficients, D, (interdiffusion coefficients) are reported for aqueous solutions of chromium(III) chloride determined in the concentration range from (0.005 to 0.05) mol·dm^{-3} using an open-ended conductometric capillary cell.[12−27] These results are discussed on the basis of the Onsager−Fuoss model.[28−31] We are aware that, under the conditions used in this study, various complexed[32−34] and hydrolyzed[35] chromium(III) species may be present. No attempt is made at this stage to separate individual contributions to the mutual diffusion, since what is required in practical applications, such as the chemistry of the oral cavity, is knowledge on the global behavior.

Experimental Section

Reagents. Chromium(III) chloride (Riedel-de-Haen, Seelze, Germany, *pro analysi* > 97%) was used without further purification. Aqueous solutions were prepared using bidistilled water. All solutions were freshly prepared just before each experiment.

Open-Ended Conductometric Capillary Cell. An open-ended capillary cell, which has been used to obtain mutual diffusion coefficients of a wide variety of electrolytes,[12,13] is described in great detail in previous papers.[12−27] Basically, this consists of 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

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distance of ~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 × 140 × 60) mm^3 immersed in a thermostat bath at 25 °C. 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. The 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. 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'' from the top and bottom electrodes to a central electrode at ground potential in a fraction of a second, the DVM calculates w.

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 "top" solution with 1 L of "bottom" solution, measured accurately. The glass tank and the two capillaries are filled with 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 min 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]

pH measurements were carried out with a Radiometer pH meter PHM 240 with an Ingold U457-K7pH conjugated electrode; the pH was measured in fresh solutions, and the electrode was calibrated immediately before each experimental set of solutions using IUPAC-type 2 and 4 pH buffers. From pH meter calibration results a zero-pH of 6.897 ± 0.030 and a sensitivity higher than 98.7%.

Results

Mutual diffusion coefficients, D, of $CrCl_3$ in aqueous solutions at 298.15 K and 303.15 K are shown in Table 1, where D is the mean value of, at least, three independent measurements. The imprecision of these results was usually within ±1%. Previous papers reporting data obtained with our conductometric cell support our view that the inaccuracy of our results should not be much larger than the imprecision. That is, we believe that our uncertainty is not much larger than 1−2%.

For the purposes of our research, it was not necessary to extend the limits in concentration indicated in Table 1.

Table 1. Diffusion Coefficients, D,[a] of $CrCl_3$ in Aqueous Solutions at Various Concentrations, c

c/mol dm^{-3}	D/10^{-9} m^2·s^{-1} [a]	S_D/10^{-9} m^2·s^{-1} [b]
	T = 298.15 K	
0.005	1.326	0.010
0.008	1.200	0.010
0.01	1.170	0.016
0.02	1.096	0.017
0.03	1.060	0.008
0.05	1.026	0.005
	T = 303.15 K	
0.005	1.847	0.010
0.008	1.328	0.011
0.01	1.310	0.010
0.02	1.260	0.010
0.03	1.200	0.011
0.05	1.170	0.010

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

Table 2. Fitting Coefficients a_0−a_2 of the Polynomial Equation [D/(10^{-9} m^2 s^{-1}) = a_0 + a_1(c/mol dm^{-3}) + a_2(c/mol dm^{-3})^2] to the Mutual Differential Diffusion Coefficients for Chromium Chloride in Aqueous Solutions at 298.15 K and 303.15 K[a]

T/K	a_0	a_1	a_2	R^2 [b]
298	1.272	−10.88	119.5	0.992
303	1.393	−8.809	86.61	0.993

[a] These equations were fitted to experimental data, except for c = 0.005 mol·dm^{-3} at 298.15 K and 303.15 K (see Table 1). [b] See the second-to-last paragraph of the Results section.

The following polynomial in c was used to fit the data by a least-squares procedure

$$D = a_0 + a_1 c + a_2 c^2 \tag{1}$$

where the coefficients a_0, a_1, and a_2 are adjustable parameters. Table 2 shows the coefficients a_0−a_2 of eq 1. 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%).

pH measurements were made on some of the chromium chloride solutions to assist interpretation of these results. For 0.005 mol·dm^{-3} ≤ c ≤ 0.05 mol·dm^{-3} and T = 298.15 K, the pH values were in the range 2.87 ≤ pH ≤ 2.31, respectively, due to hydrolysis.

Discussion

To understand the transport process of this electrolyte in aqueous solutions, as a first approach, the experimental mutual diffusion coefficients at 298.15 K were compared with those estimated using the Onsager−Fuoss equation [eq 2 (Table 3)]

$$D = \bar{M}\left(\frac{|z_1| + |z_2|}{|z_1 z_2|}\right)\frac{RT}{c}\left(1 + c\frac{\partial \ln y_\pm}{\partial c}\right) \tag{2}$$

where D is the mutual diffusion coefficient of the electrolyte in m^2·s^{-1}, R is the gas constant in J·mol^{-1}·K^{-1}, T is the absolute temperature, z_1 and z_2 are the algebraic valences of a cation and of an anion, respectively, and the last term in parentheses is the activity factor, with $y_\pm$ being the mean

Table 3. Diffusion Coefficients of Chromium Chloride Calculated from the Onsager−Fuoss Theory, D_{OF}, at 298.15 K[29,31]

c/(mol dm^{-3})	D'_{OF}/(10^{-9} m^2·s^{-1}) ($a = 2 \times 10^{-10}$ m)[a]	$\Delta D/D'_{OF}$[b]/%	D''_{OF}/(10^{-9} m^2·s^{-1}) ($a = 5 \times 10^{-10}$ m)[c]	$\Delta D/D''_{OF}$[b]/%
0.000	1.266		1.266	
0.005	1.179	12.5	1.146	15.7
0.008	1.170	2.6	1.135	5.7
0.010	1.167	0.3	1.132	3.4
0.020	1.162	−0.1	1.133	−3.3
0.030	1.154	−8.1	1.133	−6.4
0.050	1.116	−8.1	1.146	−10.5

[a] Sum of the ionic radii (obtained from diffraction methods).[38] [b] $\Delta D/D'_{OF}$ and $\Delta D/D''_{OF}$ represent the relative deviations between D (Table 1) and D'_{OF} and D''_{OF} values, respectively. [c] Sum of hydrated ionic radii (obtained from diffraction methods).[38]

molar activity coefficient, c being the concentration in mol·m^{-3}, and $\bar{M}$, in mol^2·s·m^{-3}·kg^{-1} , given by

$$\bar{M} = \frac{1}{N_A^{\,2} e_0^{\,2}}\left(\frac{\lambda_1^{\,0}\lambda_2^{\,0}}{\nu_2|z_2|\lambda_1^{\,0} + \nu_1|z_1|\lambda_2^{\,0}}\right)c + \overline{\Delta M'} + \overline{\Delta M''} \quad (3)$$

In eq 3, the first- and second-order electrophoretic terms are given by

$$\Delta\overline{M'} = -\frac{c}{N_A}\frac{(|z_2|\lambda_1^{\,0} - |z_1|\lambda_2^{\,0})^2}{(|z_1|\nu_1\lambda_2^{\,0} + |z_2|\nu_2\lambda_1^{\,0})^2}\frac{\nu_1\nu_2}{\nu_1 + \nu_2}\frac{k}{6\pi\eta_0(1 + ka)} \quad (4)$$

$$\Delta\overline{M''} = \frac{(\nu_1|z_2|\lambda_1^{\,0} + \nu_2|z_1|\lambda_2^{\,0})^2}{(\nu_1|z_1|\lambda_2^{\,0} + \nu_2|z_2|\lambda_1^{\,0})^2}\frac{1}{(\nu_1 + \nu_2)^2}\frac{1}{N_A^{\,2}}\frac{\mathrm{k}^4\phi(ka)}{48\pi^2\eta_0} \quad (5)$$

where η_0 is the viscosity of the water in N·s·m^{-2}, N_A is Avogadro's constant, e_0 is the proton charge in C, ν_1 and ν_2 are the stoichiometric coefficients, λ_1^0 and λ_2^0 are the limiting molar conductivities of the cation and anion, respectively, in m^2·mol^{-1}·Ω^{-1}, k is the "reciprocal average radius of ionic atmosphere" in m^{-1} (see, e.g., ref 36), a is the mean distance of closest approach of ions in m, $\phi(ka) = |e^{2ka}Ei^{(2ka)/(1+ka)}|$ has been tabulated by Harned and Owen,[36] and the other letters represent well-known quantities.[36] In this equation, phenomena such as complexation and/or ion association[37] and hydrolysis[35] are not taken into consideration. There is no direct method for measuring the ion size parameter a, "mean distance of closest approach" from the Debye−Huckel theory, but it may be estimated from the data of Marcus (Table 13 of ref 38) using two approximations. First, the a values were estimated as the sum of the ionic radii, R_{ion}, reported by Marcus.[38] The R_{ion} values were obtained as the difference between the mean internuclear distance of a monatomic ion, or the central atoms of polyatomic ions, and the oxygen atom of a water molecule in its first hydration shells, $d_{ion-water}$, and the half of the mean intermolecular distance between two water molecules in liquid water, R_{water}. Briefly, $R_{ion} = d_{ion-water} - R_{water}$ and $a = R_{cation} + R_{anion}$. To account for the effect of the ion hydration shell on the a values, a second approximation considers the sum of the $d_{ion-water}$ values reported by Marcus.[38] In other words, in this approach, the a values are determined as $a = R_{cation-water} + R_{anion-water}$.

Comparing the calculated diffusion coefficients of $CrCl_3$, D_{OF} (Table 3), with the related experimental values at 298.15 K (Table 1), the experimental D value is higher in chromium chloride concentrations for 0.005 mol·dm^{-3}. This can be explained not only by the initial $CrCl_3$ gradient and the formation of complexes between chloride and chromium(III) but also by a further hydrogen ion flux, according to eq 6.

Chromium chloride aqueous solutions are acidic because of the hydrolysis of Cr(III)

$$x\mathrm{Cr}^{3+} + 2y\mathrm{H_2O} \leftrightarrow \mathrm{Cr}_x(\mathrm{OH})_y^{(3x-y)+} + y\mathrm{H_3O^+} \quad (6)$$

and the most prominent hydrolyzed species are $Cr(OH)^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_4^-$, and probably the neutral species $Cr(OH)_3$.[35] Consequently, as the hydrogen ion has a much higher mobility than Cl^- or Cr^{3+}, the whole flux of matter goes faster. The present conductometric technique is not capable of measuring these individual Dij values. However, it does measure D assuming the system to be pseudobinary, and for practical purposes for the diffusion of chromium(III) chloride in aqueous solution, this is the relevant value. At a more sophisticated level, the system is a multicomponent one and consequently the Dij coefficients would have to be measured to adequately describe the diffusion phenomena. However, this will involve a large number of species, and for 0.008 mol·dm^{-3} ≤ c ≤ 0.02 mol·dm^{-3}, a reasonable agreement is observed between the experimental data and this model. Moreover, the deviation between the limiting D^0 value calculated by extrapolating experimental data to $c \rightarrow 0$ (Table 2) and the Nernst value (Table 3) is also acceptable (0.5%). Given the similar deviations between the two theoretical and experimental curves, and the uncertainties in these estimations, the choice of the parameter a is irrelevant, within reasonable limits.

For $c > 0.02$ mol·dm^{-3}, the results predicted from the above model differ from experimental observation by (6−8)%. This is not surprising if we take into account the change with concentration of parameters such as viscosity,[36,39,40] dielectric constant,[36] and, above all, hydration,[36,40,41] which are not taken into account in the Onsager−Fuoss model. The decrease of the diffusion coefficient, when the concentration increases, may be interpreted on the basis of new species resulting from the hydrolysis and complexation of this salt. In fact, we may assume[35] that $Cr(OH)^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_4^-$, and probably the neutral species $Cr(OH)_3$, together with $CrCl^{2+}$ and $CrCl_2^+$, are predominant in those circumstances, with their concentration increasing as the concentration of $CrCl_3$ increases (though an estimate of their amounts is not possible). The decrease of $D_{(CrCl_3)}$ with increasing concentration may be explained assuming those species have a lower mobility than Cr^{3+} due to their size. The eventual formation of ion pairs, increasing with concentration, also may contribute to the decrease of $D_{(CrCl_3)}$ with concentration. Concerning the effect of temperature on diffusion, an increase in the experimental D values is found in all chromium chloride concentrations. Also, a decrease of the diffusion coefficient is obtained when the concentration increases. However, given the absence of the values of parameters for estimations of D_{OF}, only the diffusion coefficient of chromium chloride at infinitesimal concentration and the equivalent conductance of the chromium ion were estimated.

From the following equation for analysis of the data, shown in Table 2, we estimated the diffusion coefficient of chromium chloride at infinitesimal concentration as $D^0 = 1.393 \times 10^{-9}\ \mathrm{m^2{\cdot}s^{-1}}$. To estimate $\lambda^0_{\mathrm{Cr^{3+}}}$, we may assume that the above estimation of D^0 coincides with the Nernst value[29] from

$$D^0 = \frac{RT}{F^2}\,\frac{|Z_{\mathrm{Cr^{3+}}}| + |Z_{\mathrm{Cl^-}}|}{|Z_{\mathrm{Cr^{3+}}}Z_{\mathrm{Cl^-}}|}\,\frac{\lambda^0_{\mathrm{Cr^{3+}}}\lambda^0_{\mathrm{Cl^-}}}{\lambda^0_{\mathrm{Cr^{3+}}}\lambda^0_{\mathrm{Cl^-}}} \tag{7}$$

where $Z_{\mathrm{Cr^{3+}}}$ and $Z_{\mathrm{Cl^-}}$ represent the algebraic valences of a cation and of an anion, respectively. $\lambda^0_{\mathrm{Cl^-}}$ is the equivalent conductance of $\mathrm{Cl^-}$ at infinitesimal concentration, given in the literature[36,42] as $\lambda^0_{\mathrm{Cl^-}} = 84.2 \times 10^{-4}\ \mathrm{m^2{\cdot}\Omega^{-1}{\cdot}mol^{-1}}$. Therefore, from eq 7, we have $\lambda^0(^1/_3\mathrm{Cr^{3+}}) = 71.3 \times 10^{-4}\ \mathrm{m^2{\cdot}\Omega^{-1}{\cdot}mol^{-1}}$.

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