Investigation of the Self-Diffusion Coefficients of Trivalent Gd^{3+} in aqueous solutions: The Effect of Hydrolysis and nitrate ion association

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Abstract: In recent work, we have deduced that berkelium and gadolinium, which have 4f and 5f with half-filled configurations, also display similar diffusion properties. Results, using self-diffusion coefficients to study thermodynamic properties, show very similar behavior, which is understood given their similarities in charge, ionic size, mobility, conductance, and hydration number. In this paper we undertook a study of Gd^{3+} as an aid for deducing the thermodynamics properties of the Bk^{3+} .

In first part we compare magnitudes of transport (self-diffusion coefficient) of the trivalent aquo ions of Gd III for two concentrations, $C_1 = 2\ 10^{-4}$ mol.L^{-1}, $C_2 = 10^{-3}$ mol.L^{-1} , and in perchlorate and nitrate media . In second part, we studied the variation of D with the medium's pH. Self-diffusion coefficients, D, of the trivalent f-elements aqua ions have been determined in an aqueous electrolyte support of Gd(NO$_3$)$_3$ and Nd(ClO$_4$)$_{3\ and}$ at a pH=2.5. (HNO$_3$, HClO$_4$) and at 25 °C using the open-end capillary method (O.E.C.M.).
The variation of D versus pH shows three zones

We changed the NO$_3^-$ counter ion with ClO$_4^-$,and found that measurements must be carried in perchloric acid medium so as to avoid pairing phenomena. Using association constants between Gd^{3+} and NO$_3^-$, and a hydration constant, we estimated self-diffusion coefficients for Gd(NO$_3$)$^{2+}$ and Gd(OH)$^{2+}$.

The results justified our choice of working at pH = 2.5 which constitute an optimum condition to avoid hydrolysis and pairing phenomena. Our results were confirmed by mobility measurements using an electro migration technique.

Key words: Self-diffusion coefficient, 4f, 5f, trivalent ions, Gadolinium, hydrolysis, Pairing.

Introduction

The chemistry of f-element ions have recently been explored by a large number of studies on physicochemical properties of their trivalent oxidation states. It would appear to be an important area of investigation[1,2]. In our recent work[3,4-9] we have deduced that for the Bk and Gd, which have half-filled electronic configurations (4f and 5f), that their self-diffusion coefficients provide a method, as a meth to study the thermodynamic properties, show a same behavior, explained by similarity of charge, size[1], mobility[5], conductance[10], and hydration number. In this paper, we project to study behavior of Gd^{3+} as a help for deducing the thermodynamics properties of $Bk3^{+}$ [11].

The measurements of self-diffusion coefficients, D, were done with the tracer [153]Gd (III), by using the open end capillary method (O.E.C.M) as described by Anderson[12], developed by Mills[13], and adapted by Chemla et al[14-15]. At constant temperature, this method allows the study of the variation of the diffusion coefficients versus ionic strength of supporting electrolytes such as $Gd(NO_3)_3$ with added HNO_3 to adjust the pH. At a first step, ionic self-diffusion coefficients for [153]Gd (III) data are reported as a function of pH solutions for two concentrations of a supporting electrolyte on gadolinium (III) nitrate solutions ($2.10^{-4}M$ and $10^{-3}M$) at 25°C. This study permits a comparison with hydrolysis observed by Kepal et al[16] for [144]Ce(III) ,[147]Pm (III) and [155]Eu (III) ions for pH > 3 and hydrolysis constants established by M'Halla et al[17] for the lanthanides La (III), Eu (III), Gd (III) and Lu (III) chloride by conductimetric measurements. Also, we add that by a transient conductivity method of, Schmidt et al[18] have determined hydrolysis constants of the metal cations, Eu (III), Yb (III) and UO_2 (II) in aqueous media by exploiting the pH dependence on asymptotic conductivity change in rare earth perchlorate solutions.

Lindqvist-Reis et al[19-20] and Skanthakumar et al[21] have also studied the ground-state and excited-state crystal field splitting of 8-fold-coordinate Cm(III) in several crystals using laser spectroscopy and have analyzed single-crystal X-ray diffraction data to understand the hydration of Cm(III) in solution. In the same context, the stability constant of europium nitrate[22], berkelium nitrate[23] and lanthanides complex[24] were estimated.

In this paper, we will justify our choice of using a pH value of 2.50 in order to avoid hydrolysis of trivalent 4f and 5f ions and to minimize the formation of ion pairs or complexes[6-7, 25-28]. In dilute solutions, the hydrodynamic theory of Onsager may be used for the evaluation and interpretation of transport parameters[29] as a function of the ionic composition of the solution. The ionic strength was used in preference to the molar concentration of gadolinium nitrate, owing to the presence of nitric acid in all the solutions. The limiting coefficient value, D_0, obtained by extrapolation of the measured values as a function of the ionic strength I, is compared to the limiting coefficient at infinite dilute solution taken from published conductimetric measurements[17,30] using the Nernst expression. In solution at pH 2.50, the diffusion data show that there is a similarity between [153]Gd (III) and some trivalent actinide ions, such as [241]Am (III), [244]Cm (III) and [249]Bk (III) in the ionic transport process[6-7, 25]. Therefore, it may be argued that [153]Gd (III) and the trivalent actinide ions have essentially the same degree of hydration as a tripositive ion of comparable ionic radii in the absence of hydrolysis, ion pairing or complexing at pH 2.50[31]. For dilute solutions, the variation of D with the square root of the supporting electrolyte solution concentration is not linear[5,7, 25-27].

Divergence from the Onsager limiting law[27,29] begins around 10^{-3}M; the limiting self-diffusion coefficient, D_0, of the trivalent lanthanide ^{153}Gd(III) is $(6.04 \pm 0.07)10^{-6}$cm^{2}s^{-1}. We proposed[27] and discussed[31] an extension (valid up to about 0.3 M) to the Onsager model, with one adjustable ion-size parameter b'.

Experimental method
Stock Solutions and sample preparation

Stock solutions were prepared from rare earth salts supplied by Merck and Johnson Matthey Co as the gadolinium (III) nitrate hexahydrate, and were used without further purification. Those concentrated solutions obtained by weighing, with a resolution of 0.1 mg, were used to prepare more dilute solutions by mass dilution (molal concentration). The molar concentration was determined with precision by measuring the density. Densities, d, were measured with a digital precision densitometer DMA46 (PAAR, Graz; Austria), type vibrating tube densitometer operating at room temperature. Calibration were performed with water and with air at room conditions, with the solution's temperature being controlled to $\pm$ 0.01°C. Assuming that concentrations of our stock solutions are known to a 0.05%, the uncertainty in density is about 1.5 10^{-4}g.cm^{-3} or less. The solvent used was de-ionized and double-distilled water having a specific conductivity of about 10^{-6} Ohm^{-1}.cm^{-1}. The pH of aqueous solutions was controlled by addition of nitric acid (Fluka) and measured with a digital pH-meter (model BE 105 "BICASA") after equilibrium with carbon dioxide of atmosphere.

Measurement of self-diffusion coefficient

Self-diffusion coefficients D of ^{153}Gd (III) in different solutions were measured by the open end capillary method (O.E.C.M.)[12,14,15] at constant temperature (T= 25.00 $\pm$ 0.01°C). Gadolinium (III) nitrate aqueous solutions were labeled with the tracer ^{153}Gd (III) supplied by (Amersham, U.K). Radioactive solutions were prepared by dissolving ^{153}Gd (III) chloride in hydrochloric acid at 0.1 M. The length of the quartz capillaries (l $\approx$ 3 cm) was measured with a travelling microscope. These capillaries were filled with an electrolyte solution (at concentration c) labeled with the tracer as indicated above. Radioactive solutions were kept in contact with an inactive solution, which has the same composition, ensuring that concentration gradients did not exist in the system. We denote by A_0 the total activity in the capillary tube at initial time (t = 0). It was measured in the absence of diffusion (reference tube) by means average of a Packard-Tricarb liquid scintillation spectrometer model (33200). The gamma emitter of ^{153}Gd (III) could be counted directly in the glass tube. After a diffusion time t (about 4 days), the final average activity will be A_t. By solving Fick's equation:

$$\partial c / \partial t = \text{div} (D . \text{grad } c) \qquad (1)$$

With the proper limiting boundary, the ratio Γ ($\Gamma = A_t / A_0$) can be related to the self-diffusion coefficient D by the following equation:

$$\Gamma = \Sigma_o 8 / (\pi^2(2n+1)^2). \exp(-\pi^2(2n+1)^2 D.t / 4l^2) \qquad (2)$$

Generally, only the first term (Eq. 3) of this rapid converging series (the second term is less than 10^{-3} compared to the first one) is required:

$$D = (4l^2 / \pi^2.t) \text{Log} (8 / \pi^2\Gamma). \qquad (3)$$

For accurate measurement [25], we stop the diffusion where Γ is approximately equal to 0.5 (optimal value). The reported self-diffusion coefficients are the average values of 16 separate measurements; we estimate the precision of our diffusion data to be $\pm$ 1%.

Theory
Self diffusion variation with ionic strength
Linear Onsager limiting law (Eq.4) is based on the dielectric relaxation effect at very dilute solutions and relates self diffusion coefficient, D_i, with ionic strength I and self diffusion coefficient limit at I=0. A_{Ons} is an variable coefficient depending to concentration and mobility of species in solution.

$$D_i \;=\; D°_i.[1 \,-\, A_{Ons}.\sqrt{I}\,] \tag{4}$$

According to the calculations based on the theory of strong electrolytes, when ionic strength can be written:

$$I \;=\; 1\,/\,2\; \Sigma\; c_i.z_i^2 \tag{5}$$

Where c_i is the concentration of the ith diffusing specie and z_i its charge, we can write :

$$D_i \;=\; k_B T\,/\,|z_i|\; \{1 - |z_i|^2|e^2\,/\,(3\,\varepsilon\,k_B\,T).\chi.(1\,-\,\sqrt{d_i}\,)\} \tag{6}$$

Where k_B is Boltzmann's constant, T is the absolute temperature and χ_i is the characteristic distance defined by :

$$\chi_i \;=\; \sqrt{\{8\pi N_A e^2\,/\,(1000\,\varepsilon\,k_B\,T).I\}} \tag{7}$$

e is the elementary electric charge; ε is the dielectric constant of water while d_i is a quantity depending on the mobilities and valences of all present ions.

If a solution of tracer ion i containing different ions j is considered and $\lambda°_j$ are their limiting equivalent conductivities, we can write:

$$d_i \;=\; 1\,/\,(2\,I).\Sigma_j\,[\,c_j\,|z_j|\,\lambda°_j)\,/\,(\lambda°_j\,/\,|z_j| + \lambda°_i\,/\,|z_i|)] \tag{8}$$

According to the Nernst-Einstein expression at infinite dilute solution,

$$D°_i \;=\; k_B\,T\,\lambda°_i\,/\,(|z_i|\,N_A e^2) = 2.661\,10^{-7}\,\lambda°_i\,/|z_i| \qquad \text{(at 25°C)} \tag{9}$$

where N_A is the Avogadro number, (Eq.6) can be rewritten at 25°C :

$$D_i \;=\; D°_i\,[1\,-\,0.7816\;z_i^2\,(1\,-\,\sqrt{d_i})\,\sqrt{I}] \tag{10}$$

However, when only two kinds of ions are present (i.e. those of the main binary electrolyte like $Gd(NO_3)_3$ in pure water) and tracer-species i is $^{153}Gd(III)$, (Eq.8) is reduced to:

$$d_i = |z_i|\,/\,(|z_2| + |z_3|)\,[\,|z_1|\lambda°_1\,/\,(\,|z_i|\,\lambda°_1 + |z_3|\lambda°_i) + |z_2|\lambda°_2\,/\,(\,|z_i|\lambda°_2 + |\,z_2|\lambda°_i\,)] \tag{11}$$

and becomes independent of concentrations c_j. In this case, d_i becomes constant and the limiting law (Eq.10) takes a linear form expressed by (Eq.4).

The negative deviation of Onsager law, can be reduced by an extension for the precedent model (Eqs. 4,10) when we add an adjustable parameter b' (Eq. 12)

$$D \;=\; D°_i\,[1\,-\,A_{Ons}.I\,/\,(1 + b'.I)] \tag{12}$$

This model [27,31] is in excellent agreement with experimental data up to concentration 0.114 M in $Gd(ClO_4)$: See (Table 2 – figure 1) and $Gd(NO_3)_3$.

b' can be estimated in first order approximation when we partially consider the ion-solvent interaction into the short-range interaction between ions. This effect is well described when we take into account the ionic cloud resulting from finite sized ion; we have added a denominator to (Eq. 4) and (Eq.10):

$$1 + \chi . a° = 1 + B^{DH} a° \sqrt{I} \tag{13}$$

This term is chosen by analogy to the ion interaction theory treated by Debye-Hückel and Stokes [30,36], where χ is expressed by (Eq.7) and

$$B^{DH} = 50.29 \, (\varepsilon.T)^{-1/2} = 0.329 \tag{14}$$

The quantity a° (Å) is the distance of the closest approach of two ions and can be taken equal to the sum [24] of radii of solvated ions calculated from Stokes law (Eq.15)

$$r_{st} = k_B T / 6 \pi D \eta \tag{15}$$

$$a° = r_{Gd(III)} + r_{NO3-} \approx 5.6 \, \text{Å} \tag{16}$$

$$b' \approx B^{DH}. a° \approx 1.84 \, l^{3/2}mol^{-1/2} \tag{17}$$

b' for $Gd(ClO_4)_3$ is almost same of b' for $Gd(NO_3)_3$. The magnitude of b'_{cal} calculated from these radii near the experimental b'_{exp}, suggests that this coefficient depends at least in part, on the hydration phenomenon and the other short-range interactions. Note that this simple semi-empirical correction includes implicitly the activity coefficient introduced in order to take into account some different interactions. Numerical applications of this adjustment give an excellent agreement (Table 2) with experimental values of self-diffusion coefficients D (Figure 1) in dilute aqueous solutions.

Table 1: The terms of the equation 8

Present charged species	Gd^{3+}	$GdOH^{2+}$	NO_3^-	OH^-	H^+	ClO_4^-
Number j in Eq.8	1	2	3	4	5	3
Ionic limiting equivalent conductivity $\lambda°_j$ (Scm^2mol^{-1})	68.09	39.1	71.46	198.3	349.8	67.4
ion charge (valency) z_j	3	2	1	1	1	1

Hydrolysis studies

When hydrolysis is considered, the ionic self-diffusion coefficient, D_{exp}, as measured is an average coefficient of different diffusion entities in the solution. In case of Gd(III) aqueous solutions, there are principally four diffusion entities such as: Gd^{3+}, $GdOH^{2+}$, $Gd(OH)_2^+$ and $Gd(OH)_3$ which D_0, D_1, D_2 and D_3 are respectively their self-diffusion coefficients. The mean experimental coefficients D_{exp} is in relation to the individual coefficients D_i by the following equation:

$$D = \Sigma_0 D_i [Gd(OH)_i^{3-i}] / [Gd^{3+}]_0 = \{(D_0 + \Sigma_1 D_i ß_i [OH^-]^i / (1 + \Sigma_1 ß_i [OH^-]^i\} \tag{18}$$

The symbol [...] indicates the molar concentration, and $[Gd^{3+}]_0$ is the total concentration of Gd used in the solutions ($2 \cdot 10^{-4}$M or 10^{-3}M). The conditional constant $ß_i$ of hydrolysis (Eq. 19) is in principle calculated according to the knowledge of hydrolysis constants of different steps.

$$ß_i = [Gd(OH)_i^{3-i}] / ([Gd(OH)_{i-1}^{4-i}].[OH^-]) \tag{19}$$

In this case, we must resolve an equations system of seven unknowns: D_0, D_1, D_2, D_3 and $ß_1$, $ß_2$, $ß_3$ at a given concentration in $Gd(NO_3)_3$. Owing to the deficiency of experimental data of D at seven different concentrations of rare earth salt $Gd(NO_3)_3$, we cannot solve the Eqs.18-19 related to conditional constants of hydrolysis, $ß_i$. So, we proceed to some approximations in order to examine the limitations of Onsager theories for the asymmetrical electrolytes 3:1. In the literature, investigators[7,16-18] consider that in pure water, trivalent lanthanide ions are weakly

hydrolysable (approximately 1%) and their first hydrolysis constants vary from 10^{-10} up to 10^{-6}. When the pH increases progressively, we can restrict, in first approximation, to the first hydrolysis:

$$Gd(III) \ + \ H_2O \quad === \quad Gd(OH)^{2+} \ + \ H^+ \tag{20}$$

When the first hydrolysis constant K_{h1} can be written:

$$K_{h1} = \ [Gd(OH)^{2+}].[H^+] \ /[Gd^{3+}] \ = ß_1.K_w \tag{21}$$

where K_w is the ionic water product.

Two kinds of tracers diffusing then simultaneously, $^{153}Gd^{3+}$ and $^{153}Gd(OH)^{2+}$ in the following charged species Gd^{3+}, $Gd(OH)^{2+}$, NO_3^-, OH^- and H^+ (Table 1), (Eq.18) is restricted as following:

$$D_{exp} \ = \ \alpha \ D_{hi} \ + \ (1-\alpha) \ D_{fi} \tag{22}$$

where D_{fi} is the self-diffusion coefficient (noted D_0 in Eq. 18) of free ions Gd (III), D_{hi} the self-diffusion coefficient (noted D_1 in Eq. 18) of hydrolysable ion $Gd(OH)^{2+}$ and α, is the hydrolysis degree.

In the absence of data for equivalent limiting conductivity of $Gd(OH)^{2+}$ in the literature, in the beginning we estimate λ°_2 by considering that $Gd(OH)^{2+}$ having the same mobility with Gd^{3+} and after we correct it until convergence . Finally, $\lambda^\circ_2 \approx 39,1 \ Ohm^{-1}cm^2mol^{-1}$

Indexes 1,2,3,4 and 5 are conformed to numbers (j) of Table 1.

The hydrolysis degree is calculated from hydrolysis constant $2.2 \ 10^{-8} \ mol.l^{-1}$ determined by conductimetric measurements[17]. Considering Eqs. 8, 10 and 22, we can write:

$$D_{exp}=\alpha D^\circ_{hi}[1-0.7816z_2^2(1-d_{hi})\sqrt{I}]+(1-\alpha)D^\circ_{fi}[1-0.7816z_1^2(1-d_{fi})\sqrt{I}] \tag{23}$$

where D°_{fi} and D°_{hi} are limiting self-diffusion coefficients of D_{fi} and D_{hi} used in (Eq.22) at zero ionic strength. Also, using (Eq. 23) we estimate a value of ($D^\circ_{hi} \approx 5.2 \ 10^{-6} \ cm^2s^{-1}$) , value lower than that of D°_{fi} ($6.04 \ 10^{-6}cm^2s^{-1}$) for free ions.

In fact, when contact ion pairs are formed by direct contact of OH^- anion and Gd (III) cation, the hydration shell, initially possessed by the free ions, is destroyed and the water molecules are set free and they return to the bulk water. Using limit values for D°_{exp} in water ($c \rightarrow 0$) and D°_f deduced from self diffusion in perchlorate medium at pH=2.5 , we will deduce $D^\circ_{hi} \approx 5.2 \ \pm 0.1 \ 10^{-6} \ cm^2s^{-1}$

Results and Discussion
Onsager law extension

In the beginning we studded self-diffusion coefficient variation of Gd^{3+} in perchloric acid at pH=2,5 with square root ionic strength $\sqrt{I}$. This study will serve us later since we will assume that in these circumstances we have no pair formation or hydrolysis. In this case, the measured self-diffusion coefficient skills considered one of Gd^{3+} we call free. We used and extended Onsager's law. Comparison of D measured and calculated by equations 10 and 12 summarized in following table. D_{Gd3+} is experimental self-diffusion coefficient of Gadolinium. D_{10} and D_{12} are values calculated using equations 10 and 12.

Table 2: Experimental and calculated self-diffusion coefficient of Gadolinium with O*nsager law.*

C (mol.l^{-1})	D $_{Gd3+}$ (10^{-6} cm^{2}s^{-1})	I (mol.l^{-1})	d (Onsager term)	D$_{10}$ calculated	D$_{12}$ calculated
0,0050	5,85	0,0332	0,5889	5,8416	5,8423
0,0080	5,75	0,0512	0,5794	5,7569	5,8085
0,0300	5,69	0,1832	0,5669	5,3496	5,6929
0,0500	5,65	0,3032	0,5650	5,1150	5,6435
0,1140	5,57	0,6872	0,5633	4,6541	5,5642
Deviation σ =				0,248	0,0007

D$_{12}$ gives a good fitting with better deviation σ = 0,0007. D$_{10}$, D$_{12}$ and D are plotted in the following graph .
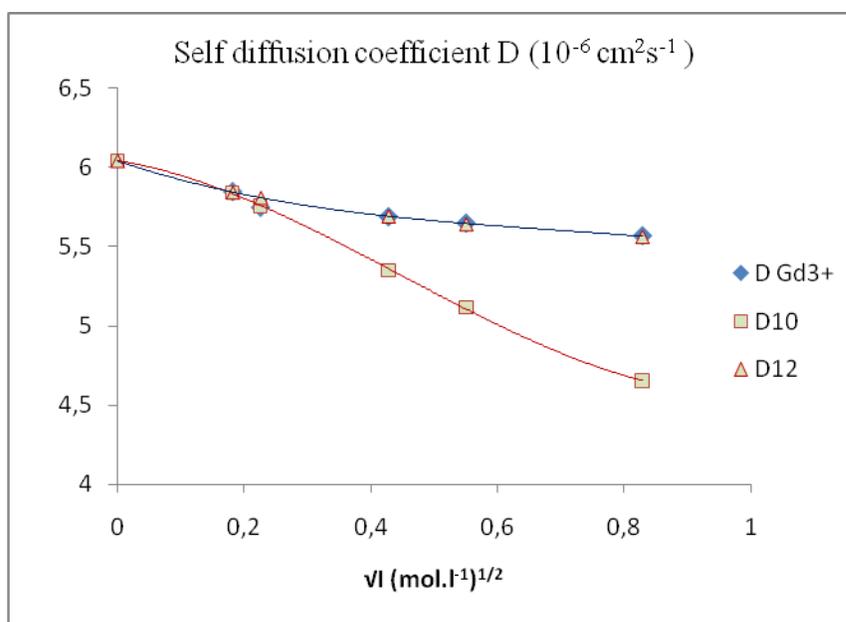
Figure 1: Plot of experimental and calculated self-diffusion coefficient of Gadolinium with Onsager law.

pH dependence of D (self-diffusion coefficient)

In first part we compare magnitudes transport (self-diffusion coefficient) of the trivalent aquo ions for Gd III , in three types of solutions : gadolinium nitrate in water ; gadolinium nitrate in acid solution of HNO$_3$ at pH=2,5 and gadolinium perchlorate in acid solution of HClO$_4$ at pH=2,5. Results are summarized in following table, and plotted in the graph.

Table 3: Self-diffusion coefficients measured in different type of solutions.

C mol.L^{-1}	$\sqrt{I}$ (mol.L^{-1})$^{1/2}$	D (Gd^{3+}) in Gd(ClO$_4$)$_3$ pH=2,5	D (Gd^{3+}) in Gd(NO$_3$)$_3$ pH=2,5	D (Gd^{3+}) in Gd(NO$_3$)$_3$ aqueous
0	0	6,04	5,96	5,86
0,0001	0,0244949			5,57
0,0002	0,0346410			5,42
0,0001	0,0613374		5,84	5,39
0,0002	0,0774596		5,82	5,28
0,001	0,1353682		5,7	
0,005	0,1821051	5,85	5,68	
0,008	0,2261909	5,75	5,66	
0,01	0,2449490			4,97
0,03	0,4279746	5,69	5,62	
0,05	0,5479416	5,65	5,58	
0,114	0,8289511	5,57	5,36	

* D (10^{-6} cm^{2}s^{-1})
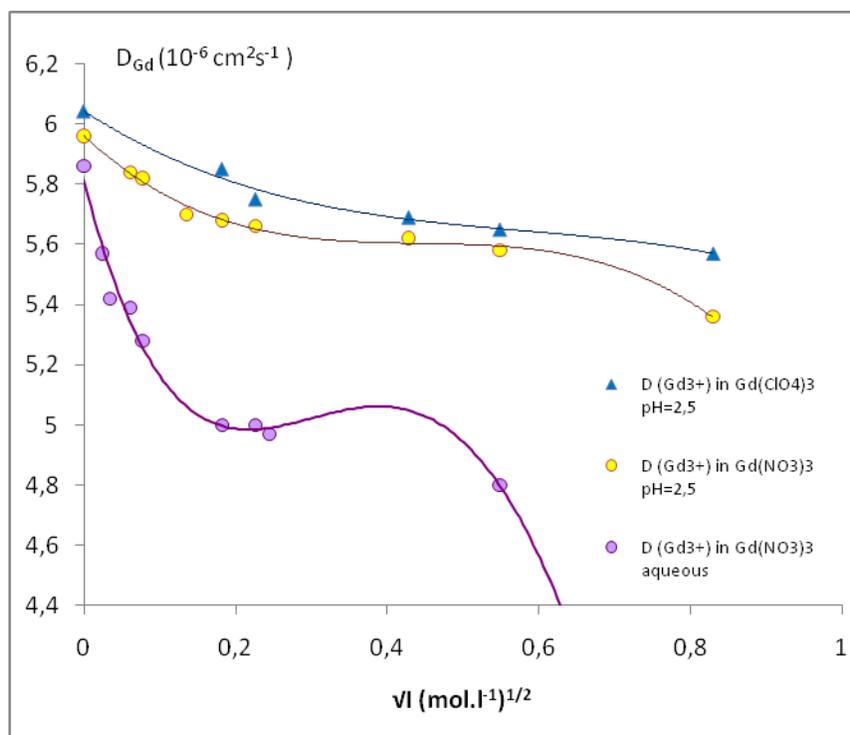
Figure 2: Variation of self-diffusion coefficients of Gd(III) in different type of solutions.

Figure 2 shows that in perchlorate (blue curve) the self-diffusion coefficients of gadolinium are significantly higher than in nitrate and in aqueous media. We can have a first deduction: nitrate ions that are more complexing than perchlorates. Similarly, in acid medium, the hydrolysis phenomenon was stopped.

In second part, we study variation of D with pH for two concentrations: $C_1 = 2\ 10^{-4}$ mol.l^{-1}, $C_2 = 10^{-3}$ mol.l^{-1}.

Table 4: Variation of self-diffusion coefficients of Gd(III) in nitric acid at different pH.

pH	$C_1 = 2\ 10^{-4}$ mol.L^{-1}		$C_2 = 10^{-3}$ mol.L^{-1}	
	I (mol.L^{-1})	D (10^{-6} cm^{2}s^{-1})	I (mol.L^{-1})	D (10^{-6} cm^{2}s^{-1})
1.50	3.2819 10^{-2}	5,72	3.7605 10^{-2}	5,63
2.50	4.2819 10^{-3}	5,82	9.1447 10^{-3}	5,70
3.50	1.2819 10^{-3}	5,80	6.2986 10^{-3}	5,71
4,50	1.2819 10^{-3}	5,81	6.0140 10^{-3}	5,67
5,50	1.2819 10^{-3}	5,71	5.9856 10^{-3}	5,54
6,50	1.2819 10^{-3}	5,42	5.8926 10^{-3}	5,28
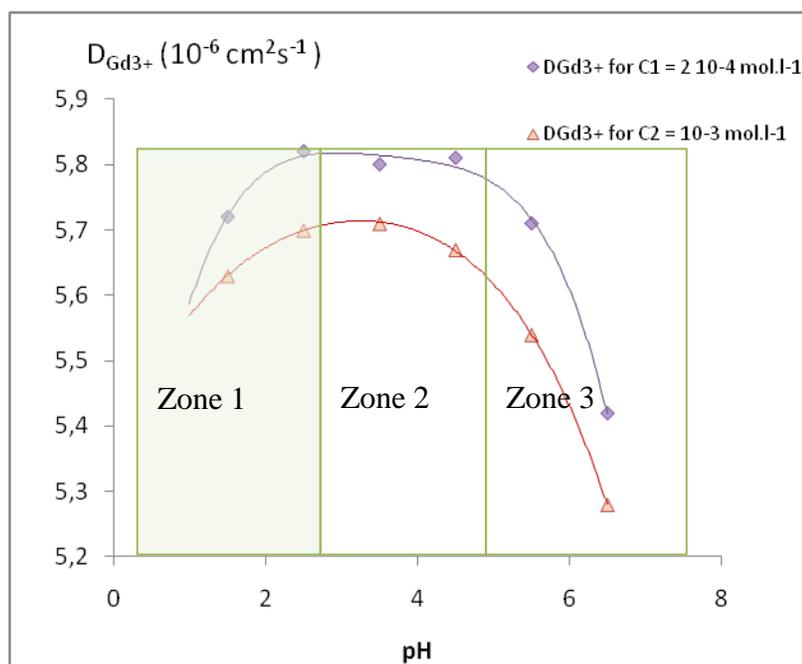
Figure 3 : Variation of self-diffusion coefficients of Gd(III) in nitric acid at different pH

The variation of D versus pH shows three zones : Zone 1 :pH $\leq$ 2 where the acid is majority (likelihood of association with NO_3^-). Zone 2 : $2 < pH < 3$-4, D is constant and Zone 3 : pH > 5. D decreases strongly showing a phenomenon of hydrolysis.
We change counter ion NO_3^- by ClO_4^- , we find that measurements must be carried in perchloric acid medium so as to avoid pairing phenomena. Using association constant between Gd^{3+} and NO_3^- , and hydration constant, we estimate self-diffusion coefficient for $Gd(NO_3)^{2+}$ and $Gd(OH)^{2+}$ and we correct self-diffusion coefficient D° , at infinite dilution, for Gd^{3+} taking account hydrolysis and pairing phenomena.

Study of Gadolinium hydration

In this part we will estimate self diffusion coefficient for ion pair $Gd(OH)^{2+}$ at infinite dilution D°_{hi} . We suppose that in perchlorate medium and at pH= 2,5 there are no hydrolysis and no pairing formation, so Di extrapolated to I=0 is D°_{fi} self diffusion coefficient for free ions Gd^{3+} at I=0 : (D°_{fi} = 6,04 10^{-6} cm^2s^{-1})

Taking account of variation of activity coefficient of species present for reaction, the Hydration constant, K_h°, was recalculated at Ionic strength null (I=0) with following relation :

$$Log\ (K_h^{\circ}) = log\ (K_h)\ -0,511.\Delta Z^2(\sqrt{I}/(1+\sqrt{I})\ -0,3I) \qquad (24)$$

K_h at I = $1,8.10^{-3}$ M have a value of $2,2.10^{-8}$ M [37] so K_h° = $2,6613.10^{-8}$ M .
At pH = 2.5 the ratio $[Gd(OH)^{2+}]$ /$[Gd^{3+}]$ $\approx 6.10^{-6} \approx 0$ (no hydrolysis) and at infinite dilution pH = 7 and so the ratio $[Gd(OH)^{2+}]$ /$[Gd^{3+}]$ = 0,26613 and α = 0,2102 using (eq.16) we have:
$$D^{\circ}_{exp}\ =\ \alpha\ D^{\circ}_{hi}\ +\ (1-\alpha)\ D^{\circ}_{fi}$$

D°_{exp} = 5,86 10^{-6} cm^2s^{-1} and D°_{fi} = 6,04 10^{-6} cm^2s^{-1} we deduce
D°_{hi} = 5,2 ± 0,1 10^{-6} cm^2s^{-1}

And so, using Einstein Relation we can calculate the conductibility equivalent for $Gd(OH)^{2+}$ $\lambda^{\circ}_2 \approx 39,1$ $Ohm^{-1}cm^2mol^{-1}$ and stokes radius Rst = 4,713 Å with following relation:

$$Rst = k_B\ T\ /(6\ \pi\eta D) \qquad (25)$$

And radius corrected by :
$$R = 2,613 + 0,636.Rst -0,0808.Rst^2 + 0,01071.Rst^3 \qquad (26)$$

$R(Gd(OH)^{2+})$ = 4,94 Å , with the same way $R(Gd^{3+})$ = 4,58 Å . Unlike the volumes of the two species is exactly the amount of OH^- (Δv = 102 $Å^3$) $R(OH^-)$ hydrated = 2,9 Å . We conclude that OH^- is the ninth-site solvation shell without any disturbance. It is as if the site was empty before hydrolysis.

Study of Gadolinium association with nitrate ion

In this part we estimate self diffusion coefficient for ion pair $Gd(NO_3)^{2+}$ at infinite dilution, D°_{pi} .We assume that in perchlorate medium and at pH= 2,5 there is no hydrolysis and or pairing formation, so Di extrapolated to I=0 is D°_{fi} , the self diffusion coefficient for free ions Gd^{3+} at I=0 : (D°_{fi} = 6,04 10^{-6} cm^2s^{-1})

Taking account of variation of activity coefficient of species present for reaction, association constant K_p° was recalculated at Ionic strength null (I=0) with Davies equation[37]:

$$Log\ (K_p^{\circ}) = log\ (K_p)\ -0,511.\Delta Z^2(\sqrt{I}/(1+\sqrt{I})\ -0,3I) \qquad (27)$$

K_p at I = 0,35 M have a value of 2,38 M [38] so K_p° = 15,6 M . At infinite dilution and pH = 2,5 [NO_3^-]= $10^{-2,5}$M and so the ratio [$Gd(NO_3)^{2+}$] /[Gd^{3+}] = 0,04933 and α = 0,0470 using (eq.16) we have:

$$D_{exp}^\circ = \alpha D_{pi}^\circ + (1-\alpha) D_{fi}^\circ$$

$D_{exp}^\circ = 5,96 \cdot 10^{-6}$ cm^{2}s^{-1} and $D_{fi}^\circ = 6,04 \cdot 10^{-6}$ cm^{2}s^{-1} we deduce
$$\mathbf{D_{pi}^\circ = 4,34 \cdot 10^{-6} \; cm^2s^{-1}}$$

This result is unclear because the coefficient of dissociation is low. To refine calculation of D_p° , we calculate for different ionic strength D_p and conclude graphically after plotting variation of D_p with √I . Results are summered in following table.

Table 5: Calculus of D_p for different ionic strength I.

C (mol.l^{-1})	pH	I (mol.l^{-1})	√I	Kp	α	D_f^a (10^{-6} cm^{2}s^{-1})	D_p (10^{-6} cm^{2}s^{-1})
10^{-3}	1,5	0,0376	0,18374	5,0809	0,13843	5,818	4,46
8 10^{-3}	2,5	0,0512	0,22619	4,740	0,00852	5,75	3,34
5 10^{-2}	2,5	0,30024	0,54794	2,428	0,019337	5,65	2,03
0,114	2,5	0,68716	0,82895	2,733	0,050526	5,57	1,414

a: *Values of D_f are calculated from variation of self diffusion of Gd in perchlorate at pH=2,5*

Variation of D_p was plotted in following graph:
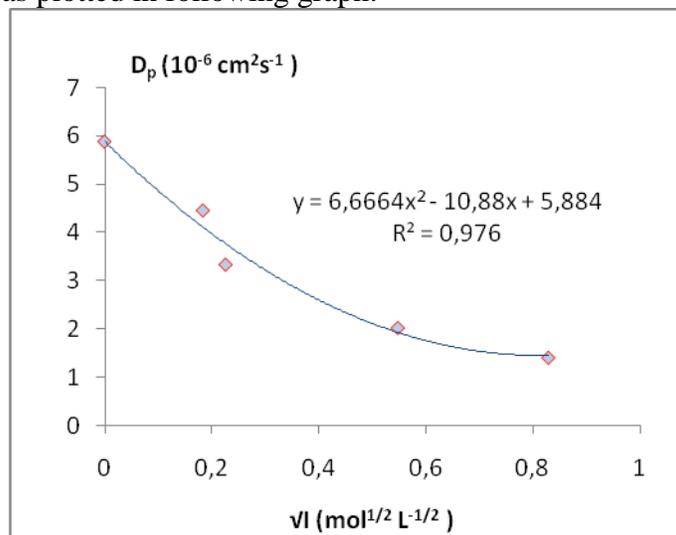
Figure 4: Plot of D_p for different ionic strength I.

We deduce **$D_{pi}^\circ = 5,88 \pm 0,1 \cdot 10^{-6}$ cm^{2}s^{-1}**. And using Einstein Relation we can calculate the conductibility equivalent for $Gd(NO_3)^{2+}$ $\lambda_2^\circ \approx 44,2$ Ohm^{-1}cm^{2}mol^{-1} and radius R = 4,64 Å .
Variation between ionic volumes of Gd^{3+} and $Gd(NO_3)^{2+}$ is close to 14,8Å^3 .We conclude that association phenomena of ion nitrate with Gd^{3+} is similar to hydrolysis, NO_3^- is the ninth-site solvation shell.

Conclusion

In this paper, we verify validity of Onsager's law up to an ionic strength of I = 0.7 M, and have observed hydrolysis phenomena when pH > 4 and association with ions nitrate for pH ≤ 2 and appreciable ratio nitrate/gadolinium. Self-diffusion of $Gd(NO_3)^{2+}$ and $Gd(OH)^{2+}$ are estimated and show that   in this case, association does not affect the hydration layer . NO_3^- is the ninth-site solvation shell. Our results are in perfect agreement with several works and several technical. Investigation of inner sphere coordination of trivalent lanthanides and actinides was studied by EXAFS spectroscopy[39,40]. Complexes with nitrate ions formed, may be interpreted in terms of outer-sphere, which may change the coordination number from 9 to 8 and increase the effective symmetry[38].

Acknowledgements

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