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ABSTRACT

The hydrolysis of the Dysprosium (III) (Dy^{3+}) ion has been investigated at 25°C in 1, 2 and 3 molal $(Na)ClO_4$ medium through a combined potentiometric–coulometric methodology. At each perchlorate concentration the formation constants of the complexes $DyOH^{2+}$, $Dy_2(OH)_2^{4+}$ and $Dy_5(OH)_9^{6+}$ have been determined. The values have then been extrapolated to zero ionic strength by using the Specific Interaction Theory. Analogies with the hydrolysis mechanism of other lanthanides are pointed out.

This paper is just the first to be reported of a series of studies undertaken with the aim to prove that a single mechanism of hydrolysis applies to all the trivalent lanthanides and probably to the corresponding actinides, too radioactive to be investigated directly.

Keywords: Dy^{3+} ion; hydrolysis; potentiometry; coulometry; Specific Interaction Theory.

INTRODUCTION

The greatest part of the studies so far devoted to the chemistry of lanthanides (Kagan, 2002) concerns their catalytic activity in organic synthesis and in the site-selective hydrolysis of nucleic acids (Roigk *et al*.,1998; Kuzuya *et al.*, 2002) and mononucleotides (Zhu *et al.*, 1997), as well as in the preparation of new materials. In fact, the regular decrease in the ionic radius along the series makes these elements particularly adequate to investigate the possible correlation's between the thermodynamic quantities and the charge density of the ions. Similarities have also been found between the chemistry of trivalent lanthanides and actinides having nearly the same ionic radius (Yang *et al.*, 2002), a topic of high relevance in safety assessment studies of nuclear plants and in the radioactive wastes management. Thus it looks as a paradox that, despite the many experimental efforts, the hydrolysis pattern of the Ln^{3+}

ions is still an open question (Pettit *et al.*, 1999). Among the hydrolysis products the mononuclear $LnOH^+$ species is the hardest to determine; recently the influence of temperature and ionic strength on the stability of this complex has been the subject of extensive investigations (Klungness and Byrne, 2000). On the other hand, there seems to be still a large uncertainty on the stoichiometry and the formation constants of the polynuclear complexes (Luo *et al.*, 1990), which may be thought to represent intermediate soluble species in the formation process of solid lanthanide hydroxides. Actually, less than 2% of the total Ln(III) may be transformed into hydrolysis products before the formation of a solid phase, at pH values close to neutrality (Baes and Mesmer, 1986). As a consequence, the univocal interpretation of the data, in terms of composition and stability constants of the hydrolysis products is very arduous, unless extremely accurate procedures are adopted. In the present work the hydrolysis of the Dy^{3+} ion is investigated by using combined potentiometric-coulometric methodology. The ionic strength effects are evaluated by using the Specific Interaction Theory (Biedermann, 1975).

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METHODOLOGY

Notations

All the concentrations are expressed as mol/kg water, *molality*, indicated by m.

h: molal concentration of (free) protons ;

H: (total) analytical proton excess on the *zero level* represented by Dy^{3+}, ClO_4^- and water;

b: molal concentration of (free) Dy^{3+} ion;

B: (total) analytical concentration of Dy(III);

I: ionic strength $= 1/2\Sigma\ z_i^2\ m_i$; z_i represents the charge of the ion i and m_i its concentration. For univalent electrolytes the value of the ionic strength coincides with its concentration.

$c_{p,q}$: molal concentration of the $Dy_p(OH)_q^{(3p-q)+}$ complexes formed according to the general reaction (1)

$$pDy^{3+} + qH_2O = Dy_p(OH)_q^{(3p-q)+} + qH^+ \qquad (1)$$
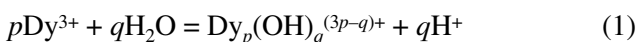
The hydrolysis of the Dy^{3+} ion has been studied at 25°C in 1, 2 and 3 molal (Na)ClO_4, as the ionic medium. The experiments have been performed as potentiometric titrations at constant total metal ion concentrations B. Each experiment started by weighing into a titration vessel V_0 cm³ of the test solution

TS: B m Dy^{3+}, H_0 m H^+, $(I-H_0-3B)$ m Na^+, I m ClO_4^-

the analytical acidity of which, H_0, was set high enough to suppress the hydrolysis of the Dy^{3+} ion. Traces of $CO_2(g)$ were removed from TS by means of a continuous stream of high-purity argon. The total acidity of the test solutions was decreased stepwise through constant-current coulometry, by producing *in situ* OH⁻ ions at the Pt cathode of the coulometric circuit (I)

$$(+)\ AE\ /\ TS\ /\ Pt\ (-) \qquad (I)$$
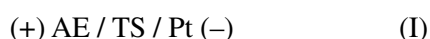
in which

AE: I m $NaClO_4$ / 0.050 m $Hg_2(ClO_4)_2$, $(I-0.100)$ m $NaClO_4$, Hg

is an auxiliary electrode. The intensity of current in the electrolysis circuit was measured from the potential drop at the ends of a calibrated resistance; the current density was set at about 1 mA/cm². After each coulometric addition, which produced the neutralisation of μ_T micromoles of H_3O^+ ions, the electromotive force, E, at the ends of the galvanic cell (II)

$$GE\ /\ TS\ /\ RE \qquad (II)$$

was measured, with a precision of 0.01 mV. In the cell (II) GE represents a glass membrane electrode and

RE: I m $NaClO_4$ / 0.010 m $AgClO_4$, $(I-0.010)$ m $NaClO_4$ / AgCl,Ag

is an Ag,AgCl reference electrode, external to the cell, but in electrical contact with it through a salt bridge. When the potential E of cell (II) did not change more then ±0.02 mV for at least 15 minutes, we assumed that true equilibrium had been attained. In all the experiments the titration continued until the formation of an amorphous solid, often invisible, which has not been identified. In order to test the reversibility of the hydrolytic equilibria in some experiments the polarities of the circuit (I) were inverted in order to perform a backward titration which proved to coincide with the forward one. In addition, some titrations were also repeated under the same experimental conditions. The measurements were performed at constant perchlorate levels, namely 1 m, 2 m and 3 m; the primary data $E(\mu)_B$ are reported in Tables 1, 2 and 3. They constitute the basis for the computerised calculations which are reported below.

Reagents

Double-distilled water was employed throughout for the preparation of the solutions. *Perchloric acid* solutions were prepared from $HClO_4$ 65% (Carlo Erba, p. a.) and standardised with both $KHCO_3$ and Tl_2CO_3 (Carlo Erba p. a.) as the primary standards, using methyl red as indicator. Analyses agreed within 0.1%. *Dysprosium perchlorate* solutions were prepared from Dy_2O_3 (99.99%, Aldrich Chemical Co.) and perchloric acid; the oxide was heated in a furnace oven at 1100°C for 12 hours in order to eliminate carbonate impurities. A slight excess of the solid on the stoichiometric amount was added stepwise to a hot $HClO_4$ solution; this suspension, stirred under nitrogen for a week, was filtered to remove colloidal particles of hydroxides. The resulting solution appeared clear at the UV light and was acidified up to pH = 4 with $HClO_4$. The lanthanide content was determined, with an accuracy of ±0.2%, trough EDTA titrations, both volumetric, using xylenol orange as indicator, and conductometric. *Sodium perchlorate* stock solutions were prepared and titrated (with an accuracy of ±0.05%) as reported by Ciavatta *et al.* (1981). The perchloric acid excess was determined through coulometric titrations. Highly pure Argon (99.999%) from cylinders was bubbled through the test solution after passing through two washing bottles containing, respectively, double-distilled water and a solution of I molal $NaClO_4$. The last one has the function of pre-saturating the gas at the same water pressure of the test solution.

Instrumentation

All the experiments have been performed into a home-made air box thermostat, large enough to accommodate

Table 1 Primary potentiometric data on the hydrolysis of the Dy^{3+} ion in 3 molal $(Na)ClO_4$ at 25°C in the form $Z(-\log h)_B$

B = 0.9467 m

$Z \times 10^3(-\log h)$: 0.069(4.740); 0.22(4.904); 0.37(5.00); 0.53(5.073); 0.68(5.127); 0.84(5.171); 0.99(5.208); 1.15(5.240); 1.30(5.269); 1.46(5.295); 1.62(5.317); 1.77(5.338); 1.93(5.356); 2.08(5.374); 2.24(5.390); 2.40(5.404); 2.55(5.418); 2.71(5.432); 2.86(5.444); 3.02(5.455); 3.18(5.477); 3.33(5.477); 3.49(5.487); 3.64(5.493); 3.80(5.500); 3.95(5.507); 4.11(5.514); 4.27(5.520); 4.42(5.527); 4.58(5.534); 4.73(5.541); 4.89(5.547); 5.04(5.554); 5.20(5.560); 5.35(5.567); 5.51(5.573); 5.67(5.579); 5.82(5.585); 5.98(5.591); 6.13(5.597); 6.29(5.603); 6.44(5.609); 6.60(5.615); 6.75(5.620); 6.91(5.626); 7.07(5.631); 7.22(5.636); 7.38(5.641); 7.53(5.646); 7.69(5.651); 7.84(5.656); 8.00(5.661); 8.15(5.666).

B = 0.3038 m

$Z \times 10^3(-\log h)$: 0.091(4.051); 0.53(5.245); 1.23(5.495); 1.93(5.630); 2.64(5.711); 3.35(5.773); 4.05(5.821); 4.76(5.857); 5.47(5.889); 6.18(5.917); 6.89(5.946); 7.59(5.968); 8.30(5.988); 9.01(6.005); 9.72(6.026); 10.42(6.040); 11.13(6.053); 11.84(6.065); 12.55(6.077); 13.32(6.087); 14.96(6.097); 14.67(6.106); 15.38(6.115); 16.09(6.122); 16.79(6.129); 17.50(6.137).
$Z \times 10^3(-\log h)$: 18.37(6.149); 17.66(6.147); 16.95(6.140); 16.24(6.133); 15.54(6.125); 14.83(6.115); 14.12(6.105); 13.41(6.093); 12.70(6.082); 12.06(6.069); 11.29(6.054); 10.58(6.039); 9.87(6.023); 9.17(6.005); 8.46(5.986); 7.75(5.965); 7.04(5.944); 6.34(5.921); 5.63(5.895); 4.92(5.863); 4.21(5.830); 3.51(5.787); 2.80(5.735); 2.09(5.661); 1.39(5.555); 0.69(5.341).

B = 0.1008 m

$Z \times 10^3(-\log h)$: 6.83(6.097); 7.44(6.119); 8.06(6.139); 8.67(6.156); 9.29(6.172); 9.90(6.187); 10.51(6.201); 11.13(6.213); 11.74(6.225); 12.36(6.237); 12.97(6.247); 13.58(6.256); 14.20(6.266); 14.81(6.274); 15.43(6.284); 16.04(6.292); 16.66(6.300); 17.27(6.305); 17.88(6.311); 18.50(6.318); 19.11(6.324); 19.73(6.329); 20.34(6.335); 20.95(6.340); 21.57(6.345); 22.18(6.350); 22.80(6.354); 23.41(6.359); 24.03(6.364); 24.64(6.368); 25.25(6.371); 25.87(6.374); 26.48(6.377).
$Z \times 10^3(-\log h)$: 25.57(6.377); 24.95(6.375); 24.34(6.372); 23.72(6.370); 23.11(6.366); 22.50(6.363); 21.88(6.358); 21.27(6.354); 20.65(6.349); 20.04(6.344); 19.42(6.338); 18.81(6.332); 18.20(6.327); 17.58(6.320); 16.97(6.313); 16.35(6.305); 15.74(6.300); 15.12(6.289); 14.51(6.281); 13.90(6.272); 13.28(6.260); 12.67(6.249); 12.05(6.238); 11.44(6.225); 10.83(6.215); 10.21(6.203); 10.01(6.198); 9.80(6.194); 9.60(6.189); 9.39(6.185); 7.34(6.124).
$Z \times 10^3(-\log h)$: 0.19(4.518); 0.61(5.444); 1.28(5.686); 1.96(5.805); 2.64(5.885); 3.31(5.944); 4.01(5.989); 4.69(6.027); 5.38(6.058); 6.06(6.085); 6.75(6.111); 7.43(6.132); 8.12(6.148).

Table 2 Primary potentiometric data on the hydrolysis of the Dy^{3+} ion in 2 molal $(Na)ClO_4$ at 25°C in the form $Z(-\log h)_B$

B = 0.6664 m

$Z \times 10^3(-\log h)$: 1.25(5.369); 1.28(5.381); 1.34(5.394); 1.43(5.411); 1.56(5.431); 1.72(5.454); 1.90(5.478); 2.12(5.503); 2.37(5.527); 2.66(5.554); 2.97(5.578); 3.31(5.603); 3.69(5.627); 4.10(5.651); 4.54(5.674); 5.01(5.696); 5.51(5.718); 6.04(5.739); 6.61(5.758); 7.20(5.776); 7.83(5.794); 8.49(5.815); 9.18(5.827); 9.90(5.842); 10.66(5.856); 11.44(5.870); 12.26(5.883); 13.10(5.896); 13.98(5.908); 14.89(5.920); 15.83(5.931); 16.81(5.942); 17.81(5.953); 18.84(5.963); 19.91(5.973); 21.01(5.982); 22.14(5.990); 23.30(5.998); 24.49(6.006); 25.71(6.013); 26.97(6.020).
$Z \times 10^3(-\log h)$: 23.10(6.012); 21.94(6.002); 20.81(5.990); 19.71(5.861); 18.65(5.968); 17.61(5.957); 16.61(5.941); 15.63(5.928); 14.69(5.913); 13.78(5.898); 12.90(5.883); 12.06(5.866); 11.24(5.849); 10.46(5.832); 9.70(5.814); 8.98(5.795); 8.29(5.776); 7.63(5.759); 7.00(5.740); 6.41(5.722); 5.84(5.702); 5.31(5.681); 4.81(5.660); 4.34(5.639); 3.90(5.617); 3.49(5.595); 3.11(5.573); 2.77(5.549); 2.46(5.524); 2.17(5.498); 1.92(5.473); 1.70(5.449); 1.52(5.423); 1.36(5.396); 1.23(5.377); 1.14(5.363); 1.08(5.354); 0.95(5.330); 0.83(5.303); 0.70(5.273); 0.58(5.234); 0.45(5.197); 0.33(5.146); 0.20(5.081); 0.081(4.995); 0.039(4.862).

B = 0.3063 m

$Z \times 10^3(-\log h)$: 0.215(5.132); 0.74(5.436); 1.22(5.558); 2.03(5.678); 2.97(5.763); 4.05(5.829); 5.26(5.888); 6.62(5.935); 8.10(5.971); 9.72(6.004); 11.48(6.033); 13.37(6.059); 15.40(6.083); 17.56(6.105); 19.85(6.126); 22.29(6.144); 24.85(6.161); 27.55(6.177); 30.39(6.192); 33.36(6.205); 36.47(6.218); 39.71(6.230); 43.09(6.241); 46.60(6.255); 50.25(6.264); 54.03(6.273); 57.94(6.282); 61.99(6.287).

B = 0.09794 m

$Z \times 10^3(-\log h)$: 2.69(5.654); 3.78(5.868); 5.14(5.993); 6.78(6.080); 8.69(6.145); 10.88(6.195); 13.34(6.236); 16.07(6.260); 19.08(6.289); 22.37(6.318); 25.92(6.338); 29.75(6.359); 33.85(6.379); 38.23(6.396); 42.88(6.413); 47.81(6.429); 53.01(6.443); 58.48(6.457); 64.23(6.469); 70.25(6.481); 76.54(6.491); 83.11(6.501); 89.95(6.500).

the whole measuring system (cell, bridges, burettes, *etc*.), capable of keeping the temperature of the test solutions at (25.00 ± 0.02)°C. Both the glass and the reference electrodes were Metrohm products (models 6.0123.100 and 6.0729.100, respectively). Platinum electrodes had a surface of about 1 cm^2 and were cleaned, before each experiment, with hot aqueous nitric acid ($HNO_3{:}H_2O = 1{:}1$). The coulometric circuit was based on a potentiostat-galvanostat Amel 2051 and a 100 Ω resistor having a precision of ±0.03% (from H. Tinsley & Company). The titrations were carried out around the clock by using a fully automated data acquisition system Agilent 34970A, governed by the software TITPOT developed by InLab (www.inlab.it).

Table 3 Primary potentiometric data on the hydrolysis of the Dy^{3+} ion in 1 molal $(Na)ClO_4$ at 25°C in the form $Z(-\log h)_B$

B = 0.3333 m

$Z \times 10^3 (-\log h)$: 1.40(5.585); 1.45(5.603); 1.57(5.622); 1.75(5.648); 1.98(5.677); 2.28(5.713); 2.63(5.747); 3.05(5.779); 3.52(5.810); 4.05(5.842); 4.64(5.871); 5.29(5.899); 5.99(5.926); 6.76(5.954); 7.57(5.974); 8.44(6.011).
$Z \times 10^3 (-\log h)$: 19.23(6.186); 17.89(6.173); 16.61(6.160); 15.38(6.145); 14.22(6.129); 13.11(6.111); 12.07(6.093); 11.08(6.087); 10.15(6.061); 9.28(6.039); 8.47(6.017); 7.70(5.990); 6.99(5.967); 6.34(5.943); 5.74(5.920); 5.21(5.901); 4.74(5.878); 4.32(5.853); 3.97(5.837); 3.17(5.814); 3.43(5.803); 3.26(5.795); 3.14(5.791); 3.08(5.787).

B = 0.1001 m

$Z \times 10^3 (-\log h)$: 0.25(5.105); 2.13(5.860); 3.29(5.977); 4.66(6.057); 6.21(6.119); 7.96(6.168); 9.91(6.204); 12.05(6.235); 14.38(6.260); 16.91(6.283); 19.63(6.304); 22.55(6.323); 25.67(6.340); 28.97(6.356); 32.48(6.372); 36.17(6.387); 40.06(6.400); 44.15(6.412); 48.43(6.424); 52.90(6.435); 57.57(6.446); 62.44(6.455); 67.50(6.465); 72.75(6.473); 78.20(6.481).

RESULTS

In order to determine at each perchlorate concentration, *I*, the equilibrium constants (2)

$$^*\beta_{p,q}^{(I)} = c_{p,q} h^q b^{-p} \qquad (2)$$

of the prevailing $Dy_p(OH)_q^{(3p-q)+}$ complexes formed, according to the general reaction (1), values of *h* and *H* were calculated from the primary $(E, \mu_T)_B$ data. For each experimental point, the equilibrium protons concentration, *h*, could be evaluated from the measured *E* by using the Nernst equation (3) for cell(II)

$$E = E_0 + 59.16 \cdot \log h \qquad (3)$$

provided the constant term E_0 is known. The evaluation of E_0 was performed in the first stage of each titration, when the hydrolysis of the metal ion is negligible, and thus eq.(4) holds

$$h = H = (\mu_0 - \mu_T) / w_0 \qquad (4)$$

in eq.(4) μ_0 are the micromoles of strong acid initially present in the w_0 milligrams of water contained in the volume of TS placed in the titration vessel. Thus, by using the method of Gran (1952) both μ_0 and E_0 could be determined with an uncertainty lower than 0.1 % and 0.02 mV, respectively. The data collected in the presence of detectable amounts of hydrolytic species ($h > H$) were used to determine the stoichiometric composition and the formation constants of the complexes. The analytical quantities *H* and *B*

$$H = h - \Sigma\,\Sigma\, qc_{p,q} - K_w h^{-1} = h -$$
$$\Sigma\,\Sigma\, q\, ^*\beta_{p,q}^{(I)} b^p h^{-q} - K_w h^{-1} \qquad (5)$$

$$B = b + \Sigma\,\Sigma\, pc_{p,q} = b + \Sigma\,\Sigma\, p\, ^*\beta_{p,q}^{(I)} b^p h^{-q} \qquad (6)$$

were combined with *h* in order to derive the *formation function Z*, eq. (7)

$$Z = (h - H - K_w h^{-1}) / B \qquad (7)$$

which depends on $-\log h$, the values of the $^*\beta_{p,q}^{(I)}$ constants, but also on the analytical Dy(III) concentration. Thus the non-coincidence of the $Z(-\log h)_B$ curves at different *B* indicate the existence of polynuclear complexes. This is the case for the Dy^{3+} ion, as it is evident from Figure 1, in which *Z* vs $-\log h$, collected for different *B* values at *I* = 3 molal, are reported. In order to determine the stoichiometric composition and the values of the hydrolysis constants, the data were processed by means of the programs Letagrop-ETITR (Brauner *et al.*, 1969) and HYPERQUAD (Gans *et al.*, 1996).

The results obtained are entirely compatible although by the former the analytical acidity of the solutions was minimized, whereas the residual square sum of the emf data was minimized through the latter. Several models were tested, including different combinations of polynuclear complexes. The best fit was, however, obtained by assuming the formation of the species $DyOH^{2+}$, $Dy_2(OH)_2^{4+}$ and $Dy_5(OH)_9^{6+}$, with the values of the formation constants reported in Table 4.
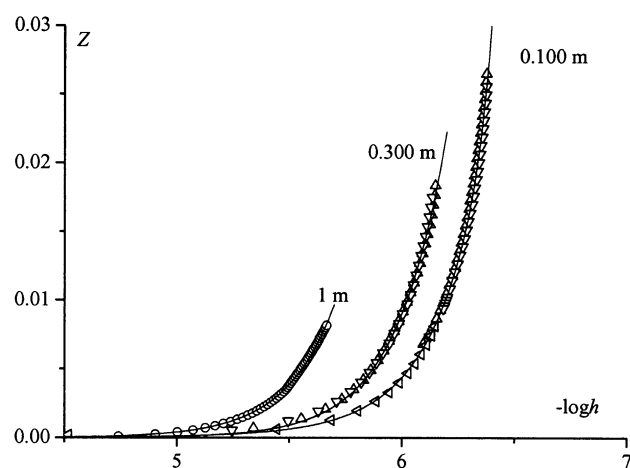

Figure 1 Plot of the formation function Z vs $-\log h$ at different total Dy(III) concentrations, B, in 3 molal $(Na)ClO_4$ at 25°C. At each B value, different symbols represent backward titrations. The full curves have been calculated by using the $^*\beta_{p,q}$ values reported in Table 6.

Table 4 Survey of the formation constants of the hydrolysis complexes of the Dy^{3+} ion at different (Na)ClO$_4$ concentrations, at 25°C. The errors reported are three times the standard deviation on the constant

Constant	Letagrop-Etitr	Hyperquad	Proposed value
(Na)ClO$_4$ 3 molal			
$\log*\beta_{1,1}$	−9.16 ± 0.04	−9.18 ± 0.07	−9.18 ± 0.07
$\log*\beta_{2,2}$	−13.76 ± 0.07	−13.76 ± 0.07	−13.76 ± 0.07
$\log*\beta_{5,9}$	−56.66 ± 0.03	−56.62 ± 0.05	−56.63 ± 0.06
(Na)ClO$_4$ 2 molal			
$\log*\beta_{1,1}$	−8.4 ± 0.1	−8.47 ± 0.05	−8.4 ± 0.1
$\log*\beta_{2,2}$	−13.76 ± 0.04	−13.76 ± 0.05	−13.76 ± 0.05
$\log*\beta_{5,9}$	−56.8 ± 0.2	−56.8 ± 0.2	−56.8 ± 0.2
(Na)ClO$_4$ 1 molal			
$\log*\beta_{1,1}$	−8.6 ± 0.2	–	−8.6 ± 0.2
$\log*\beta_{2,2}$	−13.76 ± 0.07	−13.80 ± 0.04	−13.76 ± 0.08
$\log*\beta_{5,9}$	–	−57.1 ± 0.1	−57.1 ± 0.1

DISCUSSION

In Table 5 the percent abundance of each hydrolytic complex, relative to the total Dy(III) concentration, is reported as a function of −log$h$. The quantities have been calculated by using the equilibrium constants valid in 3 molal (Na)ClO$_4$. It appears evident that also in the most concentrated solutions, the total amount of the $DyOH^{2+}$ and $Dy_5(OH)_9^{6+}$ complexes does not exceed few micromoles. This makes the values of their formation constants more uncertain than the one relative to the dimer, $Dy_2(OH)_2^{4+}$, whose particular stability is certainly due to the formation of two double hydroxo bridges. The equilibrium constants, determined at each perchlorate concentration, were extrapolated to zero ionic strength by using the Specific Interaction Theory (SIT). It is easy to demonstrate that, applying the SIT and separating the known from the unknown terms eq. (8) is obtained.

$$F_{p,q} = \log*\beta_{p,q}^{(0)} + (\Delta\epsilon)_{p,q} \cdot I = \log*\beta_{p,q}^{(I)} + [9p - q - (3p - q)^2] \cdot D - q \log a_w \quad (8)$$

in which $(\Delta\epsilon)_{p,q}$ is defined in eq.(9)

Table 5 Percentage of each hydrolytic complex on the total Dy(III) for different B values. The quantities have been calculated by using the equilibrium constants valid in (Na)ClO$_4$ 3 molal

B, m	% DyOH^{2+}	% Dy$_2$(OH)$_2^{4+}$	% Dy$_5$(OH)$_9^{6+}$
1.00	0.04	0.68	7×10^{-4}
0.30	0.10	1.60	0.06
0.10	0.17	1.67	0.13
0.01	0.72	2.84	6.02

$$(\Delta\epsilon)_{p,q} = p\epsilon_b - q\epsilon_h - \epsilon_{p,q} \quad (9)$$

which is an algebraic sum of the following *interaction coefficients,* taken from Biedermann, 1975: $\epsilon_b = \epsilon(Dy^{3+},ClO_4^-) = (0.50 \pm 0.03)$ m^{-1}, $\epsilon_h = \epsilon(H^+,ClO_4^-) = (0.14 \pm 0.02)$ m^{-1} and $\epsilon_{p,q} = \epsilon(Dy_p(OH)_q^{(3p-q)+},ClO_4^-)$. In eq. (8), D represents the *Debye term,*

$$D = 0.5107 I^{1/2}/(1+1.5 I^{1/2}) \quad (10)$$

and depends, at a given temperature, on the ionic strength I of the test solution, while the water activity may be expressed (Robinson and Stokes, 1955) by eq. (11)

$$\log a_w = -0.01565 (I - B) \Phi \quad (11)$$

where Φ represents the molal osmotic coefficient of TS. Plots of $F_{p,q}$ vs. I can be obtained on the basis of the proposed values of the equilibrium constants. The results are presented in Table 6. From the $(\Delta\epsilon)_{p,q}$ values reported in Table 6 it may be evaluated $\epsilon_{1,1} = \epsilon(DyOH^{2+},ClO_4^-) = (0.36 \pm 0.05)$ m^{-1}, which is in close agreement with the interaction coefficients of other mononuclear hydroxo complexes of tripositive ions: $\epsilon(AlOH^{2+},ClO_4^-) = 0.31$ m^{-1} (Hedlund, 1988); $\epsilon(FeOH^{2+},ClO_4^-) = 0.38$ m^{-1} (Spahiu, 1983); $\epsilon(AmOH^{2+},ClO_4^-) = (0.39 \pm 0.04)$ m^{-1} (Silva *et al.*, 1995). Concerning the $Dy_2(OH)_2^{4+}$ dimer, it must be noticed that, as expected from the SIT treatment, there is no dependence of its formation constant from the ionic strength of TS (the *Debye terms* cancel each other); furthermore, while $(\Delta\epsilon)_{2,2} = 0$, one has $\epsilon_{2,2} = \epsilon(Dy_2(OH)_2^{4+},ClO_4^-) = 2 \epsilon_{1,1} = (0.72 \pm 0.05)$ m^{-1}, to be compared with (Spahiu, 1983) $\epsilon(Fe_2(OH)_2^{4+},ClO_4^-) = 0.82$ m^{-1}. Also the constant of the $Dy_5(OH)_9^{6+}$ complex is independent from ionic strength variations; from the linear plot of $F_{5,9}$ vs. I reported in Figure 2, a value was obtained for $(\Delta\epsilon)_{5,9}$ from which it follows $\epsilon_{5,9} = (1.0 \pm 0.2)$ m^{-1}. This value is not absurd if one takes into account the linear dependence of the interaction coefficients with the ion charge. In Figure 3 the average values of $\epsilon(M^{z+}, ClO_4^-)$ for species having charges ranging from 1 to 6, taken from the compilations (Grenthe I. and Puigdomenech I., 1997), are reported *versus z*. As we can see a good linear correlation is

Table 6 Survey of the equilibrium constants of the hydrolytic complexes of Dy^{3+} at 25°C and zero ionic strength, obtained extrapolating the data through the SIT. The errors reported are three times the standard deviation

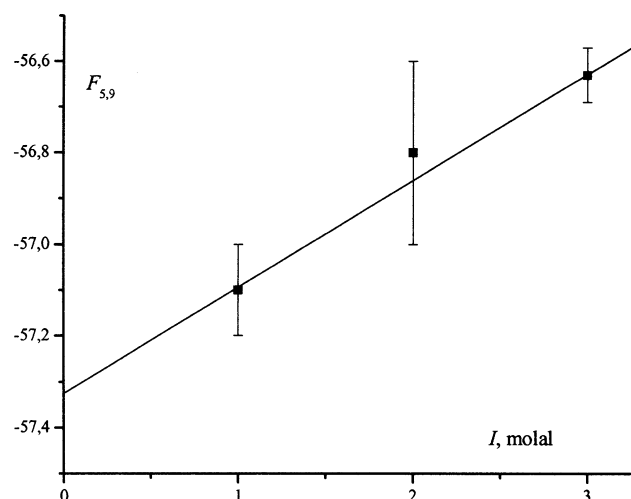| Species	$\log*\beta_{p,q}^{(0)}$	$(\Delta\epsilon)_{p,q}$, KgH$_2$O/mol
DyOH^{2+}	−7.5 ± 0.5	0
Dy$_2$(OH)$_2^{4+}$	−13.76 ± 0.08	0
Dy$_5$(OH)$_9^{6+}$	−57.3 ± 0.1	0.23 ± 0.05

Figure 2 *Extrapolation of the log *$\beta_{5,9}$ applying the SIT. The intercept on the ordinate gives log $^0\beta_{5,9}$ and the slope allows to calculate $(\Delta\epsilon)_{5,9}$ defined in eq.(9).*
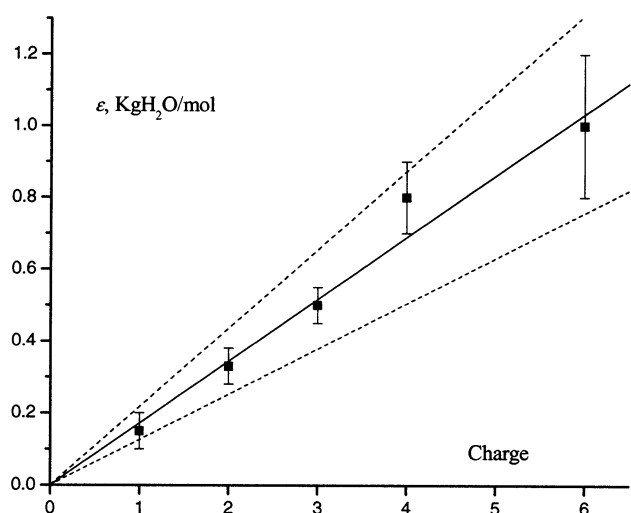

Figure 3 *Plot of the interaction coefficient, ϵ, vs the charge of the species considered. The squares represent the average values of ϵ taken from the tables reported in (Grenthe and Puigdomenech 1997). A linear correlation is shown, indicating that ϵ may often be predicted if the charge of the species is known.*

obtained, indicating that ϵ may be predicted, within narrow confidence limits, if the charge of the species is known.

CONCLUSIONS

The present work has demonstrated the existence of a hydroxo bridged dimer of Dy^{3+}, $Dy_2(OH)_2^{4+}$, which has a stoichiometric composition largely diffuse among hydrolytic species of tripositive ions (Baes and Mesmer, 1986). The double OH bridge enhances the

stability of the complex with respect to the mononuclear $DyOH^{2+}$ species, as it is suggested by the equilibrium constant; K_D, of the dimerization reaction (12)

$$2\ DyOH^{2+} = Dy_2(OH)_2^{4+} \qquad (12)$$

$\log K_D = 4.6$. This means that further stability is brought about by any single OH bridge and equals 2.3 in 3M $NaClO_4$. We found, long ago (Biedermann and Ferri, 1982), that the dimerization constant of some trivalent metal ions amount to $\log K_D = 3.8 \pm 0.4$, regardless of the acidity of the metal ion. This observation suggests that the dimerization is a property of oxygen independently of the metal ion taken into consideration. Our preliminary data on several lanthanides point in the same direction.

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