Journal of the Mexican Chemical Society
ISSN: 1870-249X
editor.jmcs@gmail.com
Sociedad Química de México
México

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Journal of the Mexican Chemical Society, vol. 54, núm. 1, 2010, pp. 51-58
Sociedad Química de México
Distrito Federal, México

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J. Mex. Chem. Soc. **2010**, *54(1),* 51-58
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ISSN 1870-249X

Spectrophotometric Determination of the First Hydrolysis Constant of Praseodymium (III)

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Received November 25, 2009; Accepted March 29, 2010

Abstract. The behavior of the trivalent ion praseodymium in 2M of NaCl at 303 K and in CO_2 free conditions, was studied. Spectrophotometric titrations of the soluble species were used, in order to obtain the value of the first hydrolysis constant of Pr(III). The data obtained were treated with both the program SQUAD and by a graphic method, respectively. The result obtained using SQUAD was $\log^*\beta_1 = -8.94 \pm 0.03$, while it was $\log^*\beta_1 = -8.77 \pm 0.03$, when calculated graphically. These results are similar to the value obtained previously with the potentiometric method.
Key words: Hydrolysis of Pr(III), Hydrolysis Constants, Spectrophotometric Titrations, SQUAD.

Resumen. Se estudió el comportamiento del ion trivalente praseodimio, en el medio 2M de NaCl a 303 K y en condiciones libres de CO_2. Para obtener el valor de la primera constante de hidrólisis del Pr(III), se empleó la titulación espectrofotométrica de las especies solubles. Los datos obtenidos fueron tratados con el programa de cómputo SQUAD y un cálculo gráfico, respectivamente. El valor obtenido con el programa de cómputo SQUAD fue $\log^*\beta_1 = -8.94 \pm 0.03$, en tanto que el calculado gráficamente fue $\log^*\beta_1 = -8.77 \pm 0.03$. Estos resultados para el valor de la primera constante de hidrólisis del praseodimio son similares al valor obtenido previamente con el método potenciométrico.
Palabras clave: Hidrólisis de Pr(III), constantes de formación, titulaciones espectrofotométricas, SQUAD.

Introduction

One of the most important problem area nuclear technologies is the safe handling and the storage of spent nuclear fuels [1]. The lanthanides, some of them are products of uranium nuclear fission, and are analogues of trivalent elements of actinides [2]. The praseodymium is analogue with the protactinium. Therefore, deposition of non-or radioactive wastes in subsurface repositories of salt beds or ocean has generated interest in the complexation of the REE ions in the various oxidation states with hydrophilic ligand in nearly neutral solution is especially needed because complexation strongly affects their mobility [1]. Essential information on actinide chemistry in ground water is lacking. The hydrolysis of praseodymium has been studied by several methods [3-12]. However, the data are different, because of experimental conditions employed such as different ionic strength, temperature, concentrations of the praseodymium and pH range. Spectrophotometric titrations can be required the use of a computer program to calculate the constants. One such program is SQUAD (stability quotients from absorbance data) [13] which considers only soluble species. SQUAD, a FORTRAN IV-based program is capable of calculating simultaneously, or individually, overall stability constants (of the concentration type) for any species formed in systems containing up to two metals and two ligands. The method is therefore capable of yielding, from appropriate absorbance data, acid association constants, metal-ion hydrolysis constants, and stability constants of simple and polynuclear complexes. The non linear least-squares method is based on the minimization of function U, given by equation (1):

$$U = \Sigma (\Delta F)^2 = \Sigma (F_{calculated} - F_{experimental})^2 \qquad (1)$$

The input file data for SQUAD includes the pH measured, the metal concentration, and a chemical model that includes stoichiometry and estimated values of formation constants of the species present during titrations. The program SQUAD utilizes the UV/Vis absorbance values. The program SQUAD provides the refined values of formation constants, as well as a very complete statistical analysis of the data.

The absorption spectra form the base for the quantitative determination of many of the individual elements in the lanthanoides series [14].

Spectrophotometry is fundamentally applied to species in solution, measuring the radiation that was absorbed by said species. There are two basic methods used for spectrophotometric analysis of the rare earth elements [15]: one uses the absorption spectrum of the colored ions and the other one is based upon the absorption spectrum developed by the formation of colored complexes. Those elements from the rare earths that produce colored complexes with non colored anions (like oxides, nitrates, chlorides and sulfates) show bands of absorp-

tion in the ultraviolet (UV, 200 to 400 nm) or visible (Vis, 400 to 750 nm) regions of the electromagnetic spectrum.

Various lanthanoid cations with 3^+ charges are colorful, generally green, pink, and yellow; these colors come from electronic transitions *f-f*, in analogue form to *d-d* transitions in transition metals. Nonetheless, compared to the latter, the lanthanoides 4*f* orbital have deeply penetrated the atom and the widening effect that comes from the vibrations of the ligands is minimal [14]. Besides, the absorptions come in very precise wavelengths, of the sort of line spectra with narrow bands, in contrast with the wide absorptions of transition metals. Praseodymium's absorption spectrum has particularly simple constitution [16]. Within the wavelength interval of 400 to 700 nm, it presents four absorption bands whose absorption maximum values are placed as follows: 444.5, 469.0, 482.2 and 588.5 nm.

In spectrophotometric titrations commonly the measured property is the absorbance in order to obtain titration curves, the equivalence points of titration reactions or stability constants of species in the solution's titration, because the nature and concentration of the absorbent species, change. Spectrophotometric titrations are carried out in recipients in whom the optical path length of monochromatic light is constant. The method is based in two simple relations or ideal absorption laws: absorbance is directly proportional to the concentration of the absorbent species (Beer-Lambert law) and the additivity of the absorption of the different absorbent species (Additivity law) [17]. Absorption in these regions involves transformations of the molecules in their external electrons, going from the fundamental to the excited state [18]. To accomplish this excited state, energy absorption is needed, UV-Vis radiations for example, these two being the ones that make electrons go to greater energy orbital [19,20].

Their most common oxidation state praseodymium is III [14]; type Pr_2O_3 oxides, and in aqueous solution the $Pr(H_2O)_n^{3+}$ = Pr^{3+} ions are formed [9,14] and are first hydrolyzed in water through the chemical equilibrium:

$$Pr(H_2O)_n^{3+} + H_2O \rightleftarrows Pr(H_2O)_{(n-1)}(OH)^{2+} + H_3O^+ \qquad (2)$$

Praseodymium (III) hydrolysis

The reaction of any metallic ion with water ions is called hydrolysis [3]; this reaction, along with the redox reactions, controls the behavior of lanthanoides in solution.

The hydrolysis of Praseodymium may be represented by the global formation equilibria, such as:

$$Pr(H_2O)_n^{3+} + jH_2O \rightleftarrows Pr(H_2O)_{(n-j)}(OH)_j^{3-j} + jH_3O^+ \qquad (3)$$

and taking the law of mass action into consideration, we can define their equilibrium constants as:

$$*\beta_j = \frac{[Pr(H_2O)_{(n-j)}(OH^-)_j^{(3-j)}][H_3O^+]^j}{[Pr(H_2O)_n^{3+}]} = \frac{[Pr(OH^-)_j^{(3-j)}][H^+]^j}{[Pr^{3+}]} \qquad (4)$$

Hydrolysis reactions are affected when the conditions in which they are carried out change. One of these conditions, which have not received enough attention, is ionic strength. There are only a few literature works about environments such as sea water, and others with higher ionic strength like brine (used in salt mines for radioactive waste storage); and that is the source of our interest in providing knowledge about hydrolysis constants in high ionic strength environments. Therefore, in this work the first hydrolysis constant of praseodymium was determined by spectrophotometric methods in the same condition with López-González, *et al*. [12] because the IUPAC [21] recommends using two methods or more.

With this panorama ahead of use, the aim this research was to know the behavior of the hydrolysis of Pr^{3+}, through the determination of the first hydrolysis constant in ionic strength of 2M of NaCl and at a temperature of 303 K by spectrophotometric technique using the program SQUAD [13]; as well as a graphic method [22].

Results and discussion

pC_H/pH relationship

Potentiometric calibration line was obtained on pH measurement of solutions containing defined amounts of H^+ or OH^-. The pH measurements were corrected by means of this equation: $pC_H = (1.070 \pm 0.003)pH + (0.180 \pm 0.009)$ (r = 0.9993) for 2M NaCl. The result confirms the influence of the ionic strength in the measurements of pH in accordance to the observations by Feldman [23].

UV-Vis spectrophotometric calibration curves

Figure 1 shows the absorption spectra of each of the Pr(III) solutions obtained in the range 200 to 700 nm in 2 M NaCl at pH 3 and 303K. Spectra of concentrations ranging was from 0.0001 to 0.65 M. It can be noted that in the UV region (200 to 400 nm) there is a wide band between 1×10^{-4}M ≤ [Pr(III)] ≤ 0.065M. For the absorption band of 215 nm (Figure 1), is to determine low concentration of praseodymium. Furthermore in this first region, the band between 0.065 M ≤ [Pr(III)] ≤ 0.65 M, at least one more absorption band appears in the region (250 to 400 nm). The band transitions described in the UV region might be due to electronic transitions of the ligands or charge transfer, different to *f-f*, because they are wide.

On the other hand, and in agreement with Treadwell [16], in the visible region three narrow absorption bands (443, 468, and 481 nm) are observed between 0.026 M ≤ [Pr(III)] ≤ 0.65 M. The absorption band of 589 nm and a shoulder at 596 nm (Figure 1) are interesting, because, we can determine high concentration of praseodymium.

Even more, the concentration interval of praseodymium for the achievement of Beer-Lambert law have been established. At the wavelength of 215 nm, was observed between 1×10^{-4} M ≤ [Pr(III)] ≤ 0.026 M. At the wavelengths of

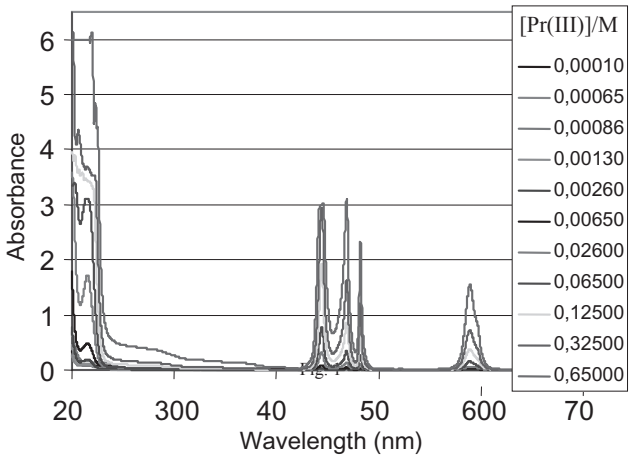

Fig. 1. UV-Vis absorption spectra for each one of the solutions of Pr (III) prepared in this work in 2M NaCl at pH 3 and 303 K.

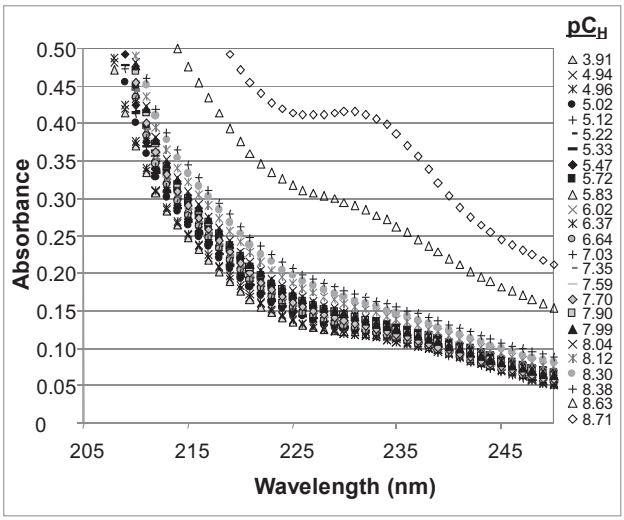

Fig. 2. Typical absorption UV spectra for the titration of [Pr(III)] 0.001M with NaOH in 2M NaCl at 303 K.

443 nm, 468 nm, and 481 nm the Beer-Lambert law follows between 0.0026 M ≤ [Pr(III)] ≤ 0.325 M. Finally, at 589 nm, the interval was 0.026 M ≤ [Pr(III)] ≤ 0.65 M. These results are shown in Table 1.

Determination of the first hydrolysis constant of Pr(III) in 2M NaCl by UV-Vis spectrophotometry

The value of the first hydrolysis constant of Pr(III) was determined using UV/Vis titration in a CO_2 free atmosphere at 303 K. In this work, absorption between 210 and 249 nm of the first band were chosen as the analytical wavelengths for the determination the first hydrolysis constant of praseodymium. This wavelength interval was chosen due to their best values of absorbance change with the pH. Figure 2 shows the UV/Vis absorption spectra of the titration of 0.00086 M Pr(III) with 0.005 M NaOH carried out in 2 M NaCl at different pH values. Each curve in Figure 2 represents the UV/Vis absorption spectrum of the Pr solution at each titration pH. The absorption values (in the range 210 to 449 nm) shown in Figure 2, the solution pH (in the range 3.91 to 8.71 pH), and the Pr(III) concentration were used to fed both the SQUAD program and the graphic method.

Determination of the first hydrolysis constant of praseodymium(III) by SQUAD

Figure 2 shows a bathochromic shift of the main UV transition, when pH becomes basic (from 210nm to 230nm), just before the precipitation of a solid, most probably $Pr(OH)_{3(s)}$. This behavior could be taken as an indicative of the formation of $Pr(OH_2)_5(OH)^{2+}$ (= $Pr(OH)^{2+}$) species.

The computer program SQUAD [13] was used to determine the first hydrolysis constant of Pr(III), as well as to compare it with the previously calculated with the potentiometric method [12]. The data range used as input for the program SQUAD was selected as follows: The initial point was taken after the excess acid was neutralized and the end point was selected just before $Pr(OH)_{3(s)}$ precipitation started, according to the first derivative Figure 3b and in range the absorbance values between 0.05 to 1.5. Several chemical models were

Table 1. Beer-Lambert law ranges of validity for the UV-Vis absorption bands of Pr(III) in 2M NaCl at pH 3.

	Wavelength regions of electronic transitions				
	200-250 nm		400-500 nm		560-620 nm
Concentration range of validity[a]	1×10^{-4}M ≤ C ≤ 0.026M		2.6×10^{-3} M ≤ C ≤ 0.325M		0.026 M ≤ C ≤ 0.65 M
Wavelength	215 nm	481 nm	468 nm	444 nm	589 nm
Calibration equations[a]	A = 64.65[Pr(III)]+0.04 r^2 = 0.9993	A=8.14[Pr(III)]+0.06 r^2 = 0.9976	A = 4.74[Pr(III)]+0.01 r^2 = 0.9999	A = 2.48[Pr(III)]+0.02 r^2 = 0.9988	A = 2.37[Pr(III)]-0.006 r^2 = 0.9986

[a] A = absorbance and [Pr(III)] = C = praseodymium (III) molarity.

used, but the better is showed here. SQUAD calculates overall stability constants values by mean of a nonlinear least-squares approach. The data for SQUAD calculations are UV/Vis absorption data, Pr(III) concentration, and a chemical model to describe the system (i.e. $Pr_{(aq)}^{3+} + H_2O \leftrightharpoons Pr(OH)^{2+} + H^+$). The first hydrolysis constant of Pr^{3+} obtained with the spectra of Figure 2, using SQUAD was $\log^*\beta_1 = -8.91 \pm 0.19$, and using SQUAD only with the absorbance data at 215 nm was $\log^*\beta_1 = -8.94 \pm 0.03$, as shown in Table 2.

Determination of the first hydrolysis constant of praseodymium(III) by graphic method

The absorbance-pC_H curves of praseodymium at 215, 230, 444, 468, 481, and 589 nm are show in Figure 3a. All the curves show that the absorbance of the praseodymium increase in the pH range of 8.4 to 8.8 and is constant below pH 8.4 and above pH 8.8 (including in the inset of the Figure 3a). At those wavelengths was calculated the first hydrolysis constant of praseodymium using the derivate graph, but, the Figure 3b shows the best absorbance/pC_H curve and the curve of its first derivative with the solid line, and the dashed line corresponds to the best fit to the experimental data with equilibrium constant and molar absorptivity coefficients at a wavelength of 215 nm obtained with SQUAD refinement. In principle, the maximum of the first derivative indicates an estimator of $\log^*\beta_1$ value [22], because it signals the inflection point of the sigmoid absorbance/pC_H curve. The estimator obtained by this graphic method is $\log^*\beta_1 = -8.77 \pm 0.03$. The parameters obtained for this refinement are shown in Table 2 and the molar absorptivity coefficients determined during the same refinement are shown in Figure 4. The great uncertainty for the $\log^*\beta_1$ and the shape of the molar absorptivity coefficient of $Pr(OH)^{2+}$ obtained with SQUAD may be due to the lack of information of the $Pr(OH)^{2+}$ species before the $Pr(OH)_{3(s)}$ precipitation. In fact, the spectra for pH 8.63 and 8.71 of the Figure 2 were not included in the SQUAD refinement (because the beginning of precipitation of $Pr(OH)_{3(s)}$ was observed for pH around 8.5); nevertheless these data are necessary to calculate the first hydrolysis constant from the first derivative method. This could be the reason why the estimator obtained with the first derivative is lower than that obtained with SQUAD.

Statistical comparison of the $-\log^*\beta_1$ estimators with the value obtained potentiometrically and reported in the literature by López-González *et al*. [12] are also shown, following Miller and Miller [24], at a significance level of 95% (Table 2).

The first hydrolysis constant value of the Pr(III) reported in scientific literature and that obtained in this work are presented in Table 3. As well as other rare earths, the authors that have obtained it may report different values. These differences may be attributed to the fact that most of the investigations were made with concentrated solutions of the element and in small pH intervals. The affinity of the lanthanoid ions for the carbonate ions were taken into account only in few cases. So far not all constants are known for a specific element, so a complete description of the hydrolytic behavior has not been achieved.

The reaction of Pr(III) with water has been studied in several works. The most usual method has been the potentiometric [4-6, 8-12]. Only one work has used solvent extrac-

Table 2. First hydrolysis constant obtained by spectrophotometry from selected data before precipitation of $Pr(OH)_{3(s)}$ in 2M NaCl and 303 K. $[Pr(III)]_{total} = 0.00086$ M. Statistical comparison of the $-\log^*\beta_1$ estimators with the value obtained potentiometrically and reported in the literature by López-González *et al*. [12] are also shown, following Miller and Miller [24], at a significance level of 95%.

		$-\log^*\beta_1$		
Formal species	Potentiometric methods [12]	SQUAD[a] (Fig. 2)	SQUAD[b] (Fig. 3b dashed line)	Graphic method[c] (Fig. 3b solid line)
$Pr(OH)^{2+}$	-8.76 ± 0.02	-8.91 ± 0.19	-8.94 ± 0.03	-8.77 ± 0.03
Sample size	20	720	20	5
F_{calc}	-	90.3 >	0.4 <	2.3 <
F_{crit}	-	2.2	2.2	2.9
H_o: variances equal		rejected	non-rejected	non-rejected
t_{calc}	-	17.91 >	22.15 >	0.91 <
t_{crit}	-	1.96	1.96	2.00
H_o: means equal		rejected	rejected	non-rejected

[a] 20 spectra were introduced in the $210 \leq l \leq 250$nm interval and 40 absorbance values of each spectra were introduced with a step of $\Delta\lambda = 1$nm and in the $3.9 < pC_H < 8.12$ range.

[b] estimated from the 20 data of absorbance/pC_H curve at 215nm in the $3.9 < pC_H < 8.12$ range, fixing the molar absorptivity coefficients (for Pr^{3+} 317 L mol^{-1} cm^{-1} and $Pr(OH)^{2+}$ 753 L mol^{-1} cm^{-1}), calculated in the refining described in (a).

[c] estimated from the first derivative of absorbance/pC_H curve at 215nm, probably deviated by precipitation of $Pr(OH)_{3(s)}$.

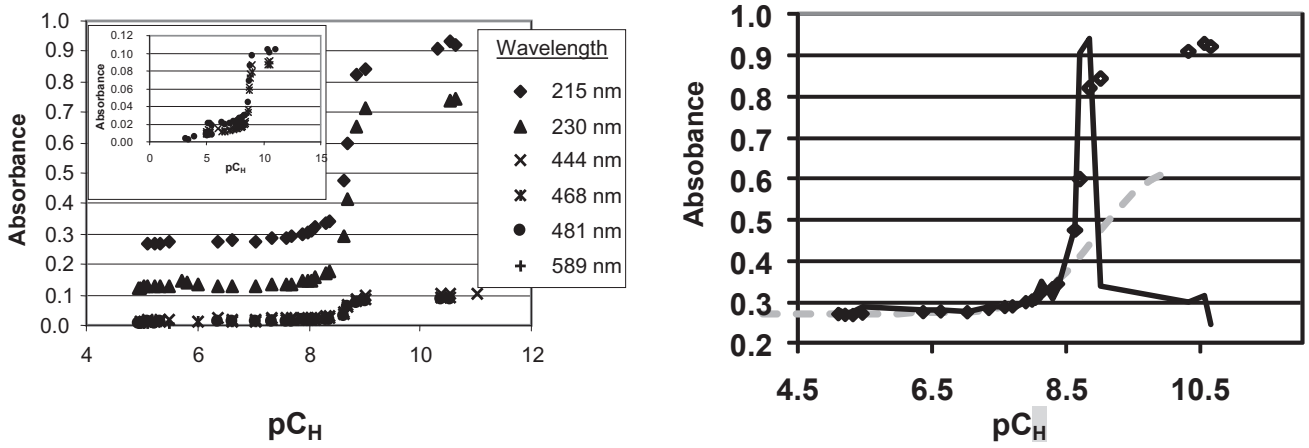

Fig. 3. a) Curves of absorbance as a function of pC_H, in 2M NaCl at 303 K, for several wavelengths. The detail shows for the absorbance band at 444, 468, 481 and 589 nm, respectively. b) Experimental absorbance values as a function of pC_H for a 215 nm wavelength are shown with markers. Fill markers represent points for solutions in absence of $Pr(OH)_{3(s)}$ and empty markers represent points for solutions in presence of $Pr(OH)_{3(s)}$. The first derivative of this curve is represented with the solid line while the dashed line corresponds to the best fit to the experimental data with equilibrium constant and molar absorptivity coefficients obtained with SQUAD.

tion methods [7] and the values reported in those papers are the lesser in Table 3. The Pr(III) concentrations in the first method were situated between 0.0001 M and 1M, while in the second method praseodymium concentration were in the order of 10^{-7} M. The ionic strength was studied in a wide interval 0.02-0.3 M, 3 M and 3 m, but many data are required to predict the influence of this parameter in the hydrolysis element's behavior. The differences between the values reported by Guillaumot *et al*. [7] and present work with the others is notorious, and might be due to the influence of the carbonate ions in those works.

The first hydrolysis constant of Pr(III) obtained using SQUAD [13] and potentiometric methods [12] are similar but statistically different, as shown in Table 2. No polynuclear species of this element are formed yet, in agreement with the expectations from the work of Ciavatta *et al*. [9].

Table 3. Comparison of the first hydrolysis constant of praseodymium for literature data and those obtained in this work.

Reference	Mehtod; (T,K)	I /M	[Pr(III)]	Medium	log*b_1
[4] Moeller, *et al*., 1946	P; 298	0.05	0.001-0.01 M	$Pr_2(SO_4)_3$	–9.0
[5] Tobias *et al*., 1956	P; 298	3	0.001-0.01 M	$NaClO_4/LiClO_4$	–8.5
[6] Frolova *et al*., 1966	P;298	0.3 0.02	0.004-0.009 M	$NaClO_4$ $Ba(OH)_2$	–9.45
[7] Guillaumont *et al*., 1971	SE; 298	0.1	1×10^{-7} M	$LiClO_4$	–7.1
[3] Baes and Mesmer, 1976	ER; 298	0	0.001-0.01 M	-	–8.1
[8] Burkov *et al*., 1982	P; 298	3	0.2-0.8 M	$NaClO_4$	–9.56 ± 0.03
[9] Ciavata *et al*., 1989	P; 333	3	0.03-1 m	$LiClO_4$	–8.74 ± 0.01
[10] Klungness *et al*., 2000	P;298	0.7	0.01 M	$NaClO_4$	–8.62 ± 0.06
[11] Ramírez-García *et al*., 2003	P; 303	1	1×10^{-4} M	NaCl	–8.58 ± 0.02
[12] López-González *et al*., 2005	P; 303	2	1×10^{-4} M	NaCl	–8.76 ± 0.02
This work	SP-G; 303	2	8.6×10^{-4} M	NaCl	–8.77 ± 0.03
This work	SP-SQUAD at 215nm; 303	2	8.6×10^{-4} M	NaCl	–8.94 ± 0.03
This work	SP-SQUAD; 303	2	8.6×10^{-4} M	NaCl	–8.91 ± 0.19

P: Potentiometric, ER: Empiric Relationship, SE: Solvent Extraction,
SP-G: Spectrophotometric Graphic Method, SP-SQUAD: Spectrophotometric processed by SQUAD.

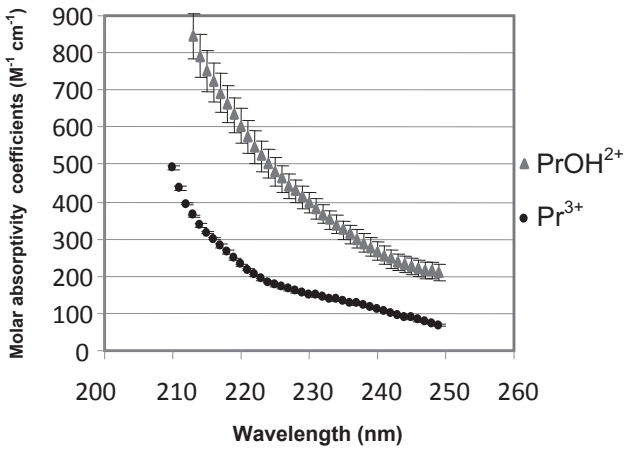

Fig. 4. Molar absorptivity coefficients as a function of wavelength, for Pr^{3+} and $Pr(OH)^{2+}$ species determined with the program SQUAD.

Conclusions

The $\log^*\beta_1$ value for the first hydrolysis of Pr(III) has been determined spectrophotometrically at 303 K in NaCl 2M, both graphically and with the aid of program SQUAD. Although the value obtained graphically is statistically equal to that reported previously by the potentiometric method [12], in the conditions of the present paper we have evidence that there are some points with presence of the solid phase corresponding to $Pr(OH)_{3(s)}$. The refined value obtained with SQUAD is statistically different by 0.17 units but it has been obtained in the absence of the solid. Then, it is necessary to obtain the first hydrolysis value with other methods, as suggested by IUPAC, in order to confirm the better estimator that could be recommended.

Experimental

Instrumentation

The reagents used were of analytical grade. To prepare the solutions and rinse the laboratory material, distilled water was used (1.3 Micromohs, obtained from a US BARNSTEAD equipment); particularly, just boiled for the sodium hydroxide solutions.

A Radiometer TIM900 Titrilab potentiometer was used, with a combined electrode for pH measurements, a 20mL Radiometer ABU901 automatic burette with a minimum addition volume of 0.2% and a water bath temperature controller Cole Parmer Polystat, model 12105-30 with a precision of 0.1 K units. The potentiometer's uncertainty is of 0.001 in pH. Before each of the experiments, the electrodes were calibrated with certified commercial solutions with pH of 4 ± 0.01 and 7 ± 0.01 (Radiometer).

To carry out the spectrophometric titrations, a Perkin Elmer UV-Vis Lambda 10 spectrophometer was used with quartz cells of 1cm optical path length.

Preparation of HCl solutions

For the preparation of the hydrochloric acid solutions, we started from HCl 1M (Merck, titrisol). Starting from this solution, all the others were prepared by dilution.

Preparation of NaOH solutions

To obtain the carbonate ion free NaOH solutions, the followed procedure was to prepare a NaOH solution at 50% weight/volume. This solution was centrifuged to separate the aqueous phase from the precipitate (sodium carbonate, insoluble) [19, 25] and later, in a glove box with an atmosphere of N_2 (Praxair, 99.99%) at ambience temperature, an aliquot part of the supernatant liquid was taken (carbonate free aqueous solution) and it was diluted at 1 liter with distilled water, boiled and cold, in a volumetric flask. This caustic soda solution was titrated with potassium hydrogen phthalate (99.95%, Aldrich) and the solutions needed for the experiments were prepared from it.

Determination of the pC_H/pH relationship at NaCl 2M

The relation between the pH and the pC_H ($pC_H = -\log[H^+]$) was determined by the TIM900 potentiometer. For that, 10^{-1}, 10^{-2}, 10^{-3}M HCl and same concentrations of NaOH solutions were prepared, in cold boiled water and all in the 2M NaCl medium. The potentiometric measurements of these solutions are the ones considered as pH values. The alkaline solutions were prepared inside the glove box and were divided in aliquot parts, which were kept sealed until they were measured. During measurements a constant flux of nitrogen was applied over the solution. Each of these solutions was measured three times the same day they were prepared and the three days that followed. All measurements were made at 303K. The obtained data were averaged out and a graphic relating the hydrogen ion (pC_H) concentration in both environments with the experimental pH was traced.

Solutions of praseodymium

The praseodymium stock solution was prepared starting from Pr_6O_{11} (99.9%, Aldrich Chemical). This compound is a mixture of Pr^{3+} and Pr^{4+} oxides and forms only Pr^{3+} in aqueous solutions [9]. The oxide was calcined according to recommendations in literature [26]. Once calcined and cold, a known quantity of Pr_6O_{11} was weighed, this sample was dissolved in 15 mL of concentrated solution of HCl (36.5-38%, Merck); this solution was evaporated almost to dryness, moved away from the heat in the last part and letting it evaporate by itself at room temperature, to obtain praseodymium chloride ($PrCl_3$). This procedure, from the addition of 15 mL of concentrated

solution of HCl, should be repeated by three times. Finally, the $PrCl_3$ obtained was dissolved and diluted adequately with 1×10^{-3}M HCl solution (initial pH = 3). The nominal concentration of the praseodymium (III) stock solution was 0.65 M.

When the stock praseodymium solution is prepared starting from its oxide, evaporation to dryness must be avoided, because then praseodymium hydroxide would form, which would stop subsequent evaporations from being carried out, since it's not water soluble.

The praseodymium in the standard solution was determined by titration [27,28] with a 0.025 M EDTA solution (Baker) at pH 7.2 adjusted with ammonia hydroxide solution. Three drops of pyridine and three drops of xylenol orange (Aldrich) were also added. The praseodymium concentration in the standard solution was 0.65 M. Starting from this solution, other solutions were made by dilution to obtain the calibration curves of praseodymium solutions by UV-Vis Spectrophotometry and for spectrophotometric titration.

Calibration curves of praseodymium solutions by UV-Vis spectrophotometry

To determine the absorption calibration curves, 10-cm^3 solutions of 0.0001, 0.00065, 0.0086, 0.0013, 0.0026, 0.0065, 0.026, 0.065, 0.125 and 0.325 M, all at pH 3 and with 2 M NaCl were prepared using the 0.65 M Pr standard solution. The absorbance vs. wavelength profiles of the resulting solutions were obtained in the range of 200-700 nm using a Perkin-Elmer UV/Vis Lambda 10 spectrophotometer .

The data treatment was processed with an Excel worksheet (Microsoft), to determine the relation absorbance in function to the wavelength.

First hydrolysis constant determination of praseodymium (III)

The photometric titrations were obtained by following a previously described methodology [22]. Briefly, a determined volume of the 0.65 M Pr solution was transferred to a titration cell containing 20 cm^3 of the 2 M NaCl solution (initial pH = 3). The transferred volume was enough to obtain a final Pr concentration of 10^{-3} M. The mixture was stirred for 7 minutes after which the solution's pH was recorded. Subsequently, an aliquot of 4 cm^3 was taken from the reaction cell to determine the UV/Vis absorption, and the volume obtained was returned to the titration cell. After that, a known volume of the 5×10^{-3} M NaOH in 2 M NaCl was added to the titration cell. After equilibration for 7 minutes, another aliquot was taken to determine the new pH and absorbance. The absorbance vs. wavelength profiles of the resulting solutions were obtained in the range of 200 to 700 nm. The addition of the NaOH solution, pH, and absorbance measurement was repeated until the pH was about 12. A nitrogen flux was maintained on the solution during the experiments. At least two experiments were performed under the same conditions to obtain reproducibility.

The pH measurements were carried out with a combined electrode (glass-AgCl/Ag), which has low interference coefficients for alkali ions. A pH-meter (Radiometer TIM900 Titrilab, France) together with an automatic burette (Radiometer ABU901, France), a double wall cell, and a constant-temperature circulator (Polyscience Circulator 12101-10, Perkin Elmer, Hayward, CA) with a precision of 0.001 pH units were used. All the experiments were carried out at 303 ± 0.1 K and a nitrogen flux was kept in the reaction cell to avoid the environmental CO_2. The pH of the NaCl stock solutions was adjusted to 3 with HCl in order to prevent Pr hydrolysis before the experiments began. The experimental values of the pH, absorbance, and volumes of NaOH added in each titration point were analyzed using the SQUAD [13] and graphic method [22]. The absorbance versus pC_H data were plotted using the Excel program of MS Office 2000®.

Acknowledgements

ARH want to acknowledge the support of CONACyT for a sabbatical leave in FESC-UNAM during 2009.

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