J. Mex. Chem. Soc. **2008**, *52(1)*, 47-53
© 2008, Sociedad Química de México
ISSN 1870-249X

Equilibrium Constants Determination of the Species Formation in the Al(III)-H_2O System by Integration of ^{27}Al-NMR Signals and Fitting with Species Fractions

Alberto Rojas-Hernández,[1]* Julio César Botello,[1,2] Ma de Lourdes Pacheco-Hernández,[1] Atilano Gutiérrez,[1] José Manuel Domínguez,[3] Gabriela Espinosa,[3] and María Teresa Ramírez-Silva[1]

[1] Universidad Autónoma Metropolitana-Iztapalapa, Departamento de Química, Área de Química Analítica, Apdo. Postal: 55-534, 09340 México D. F., México. e-mail: suemi918@xanum.uam.mx
[2] Facultad de Estudios Superiores Cuautitlán (UNAM), Sección Química Analítica, Campo 1, Av. 1º de Mayo s/n, 54740 Cuautitlán-Izcalli, Estado de México, México.
[3] Instituto Mexicano del Petróleo, Programa de Ingeniería Molecular, Eje Central L. Cárdenas 152, 07730 México D. F., México.
*Author to whom correspondence should be sent

Recibido el 11 de septiembre del 2007, aceptado el 30 de enero del 2008

Abstract. A quantitative methodology to determine formation constants that takes into consideration the ^{27}Al-NMR signals of Al(III)-H_2O systems has been analyzed, where area fractions beneath the peaks recorded were associated with the corresponding species fractions. The values of the formation constants were compared with the model obtained by potentiometric studies. In agreement with previous reports, the -log*β values obtained by NMR and potentiometry, at 0.020 M ≤ $[Al(III)]_{total}$ ≤ 0.500 M are 12.96 ± 0.02 for $Al(OH)_3$, 13.50±0.02 for $Al_3(OH)_4^{5+}$, and 109.70±0.09 for $Al_{13}(OH)_{32}^{7+}$, by assuming that $Al(OH)^{2+}$ has a value of 5.29. Additionally the equilibrium constant values obtained allowed fitting of the conductimetry titrations in the 6.00(10^{-3}) M ≤ $[Al(III)]_{total}$ ≤ 0.120 M. The algorithm presented in this work gives a support to establish that the area fractions of NMR signals are proportional to the species concentration fractions.

Key words: ^{27}Al-NMR, hydrolysis of Al^{3+}, formation constants, potentiometric titrations, conductometric titrations.

Resumen. Una metodología para determinar constantes de formación por medio de señales de ^{27}Al-NMR para sistemas Al(III)-H_2O se aplicó, en donde las fracciones de área bajo los picos se asoció con las fracciones de las especies correspondientes. Los valores de constantes de formación obtenidos de esta forma se compararon con los obtenidos con estudios potenciométricos. Los valores obtenidos de -log*β obtenidos por NMR y potenciometría a partir de sistemas con 0.020 M ≤ $[Al(III)]_{total}$ ≤ 0.500 M son 12.96 ± 0.02 para $Al(OH)_3$, 13.50 ± 0.02 para $Al_3(OH)_4^{5+}$, y 109.70 ± 0.09 para $Al_{13}(OH)_{32}^{7+}$, considerando que $Al(OH)^{2+}$ tiene un valor de 5.29, y concuerdan con reportes previos. Además, estos valores de constantes de equilibrio permiten ajustar curvas de valoración conductimétricas, en las cuales 6.00(10^{-3}) M ≤ $[Al(III)]_{total}$ ≤ 0.120 M. Este algoritmo da fundamento para establecer que las fracciones de área de las señales de NMR son proporcionales a las fracciones de concentración de las especies.

Palabras clave: ^{27}Al-NMR, hidrólisis de Al^{3+}, constantes de formación, titulaciones potenciométricas, titulaciones conductimétricas

Introduction

The aluminum species in solution have been extensively studied in the last twenty five years by using different techniques, due to the widespread use of this element and its various alloys in human activities, their poluting potential and known toxicity [1-2]. Complexation of the Al^{3+} ion is widely employed in order to detect or sequestrate it. Often, the formation of these complexes is followed by ^{27}Al-NMR [3-9].

For the Al(III)-H_2O system several potentiometric studies have been developed [9-16] to determine the species and their hydrolysis constants, using data processing software like SUPERQUAD [17] or OPIUM [18], and only few studies have been undertaken by analysis of the signal variations of ^{27}Al-NMR as a function of the solution pH [8, 9, 19-21]. Those studies have allowed establishing the chemical ambience and the chemical shift that the different aluminum species exhibit during hydrolysis. To the best of our knowledge, only Bottero *et al.* [20], and Marklund and Öhman [21] have proposed the quantitative treatment of the observed ^{27}Al-NMR signals during the hydrolysis of the Al(III), using thermodynamic models, in order to calculate the formation constants of the species.

Considering the previous remarks, it is thought relevant to establish that the purpose of the present work is to apply an algorithm, developed previously by us for the speciation of the system B(III)-H_2O [22], with the aim to determine the chemical model and the hydrolysis constants of Al(III)-H_2O system and to compare the results with those obtained by potentiometric studies.

Experimental

Potentiometric Studies

Aqueous solutions of Al(III) in the 0.010 M to 2.000 M concentration range were prepared from $AlCl_3$ (Aldrich, 99.9%) or $Al(NO_3)_3{\cdot}9H_2O$ (Sigma/ACS 99.1%), using deionized water Type I (Millipore Milli-Q Gradient quality) in all cases.

At least two samples of each solution were titrated with aqueous NaOH and the pH variations were recorded with a pH-meter Radiometer-Tacussel LPH430T (ΔpH = 0.005), fitted with a combined electrode (glass sensor with internal reference of saturated $KCl/AgCl_{(s)}/Ag_{(s)}$, used to measure

0-14 pH values). The temperature of the systems was maintained at 25ºC (ΔT = 0.1 °C) during all titrations, with a water bath (VWR, model 12101-10) and a glass titration cell with a double jacket.

To avoid carbonates formation in the system, a nitrogen (Praxair) flow was maintained over the solution during whole experiments and pH values measured were corrected by efficiency of the cell, as was explained in our previous work [23], before processing them with SUPERQUAD [17] in order to obtain the formation constants of Al(III) species with hydroxide ions.

^{27}Al-NMR Studies

An Al(III) 0.500 M solution and an hydrolyzed Al(III) 1.000 M to OH/Al ratio of 0.5 was diluted successively with water, until reaching a 0.001 M concentration, were prepared from $AlCl_3$ (Aldrich, 99.9%) or $Al(NO_3)_3 \cdot 9H_2O$ (Sigma ACS 99.1%). The hydrolysis of these systems was achieved by addition of aqueous NaOH standardized solutions until reaching the OH/M ratio desired, registering the pH values for each hydrolyzed solution. Deionized water Type I was used (Millipore Milli-Q Gradient quality) in all cases.

The ^{27}Al-NMR spectra were obtained with a Bruker DMX-500 spectrometer, at 25 ºC, employing $Al(NO_3)_3$ in 1M aqueous HNO_3, as reference of chemical shift. The excitation frequency used for Aluminum nuclei was equal to 130.32 MHz. D_2O (30 μL D_2O/ 500 μL sample) was added to the system for locking the signal of external magnetic field. The uncertainty percent for observed chemical shifts ($\%(\Delta\delta/\delta_o)$) was no greater than 1%. The uncertainty percent ($\%(\Delta A/A)$) for area integration beneath the peaks may be as great as 2% or up to 5% when deconvolution algorithms are applied.

Conductometric Studies

The conductometric titrations of at least two Al(IIII) solutions with NaOH standardized solutions were performed, obtaining at least 50 conductivity measurements of each titration with a Radiometer Copenhagen CDM230 conductimeter, equipped with a Radiometer Copenhagen CDC865 conductivity fourpole cell, equipped with 4 platinum rings. The temperature of the titration cell was fixed at 25.0 °C (ΔT = 0.1 °C) by means of a VWR PolyScience water bath and with a Radiometer Copenhagen T201 sensor. A constant high purity nitrogen (Praxair) flow was kept over the solutions during the titrations.

Component and species fractions

When several mononuclear and polynuclear species are formed by hydrolysis the chemical equilibria associated may be represented by Equation 1:

$$\begin{gathered} iM^{q} + jH_2O = M_i(OH)_j^{qi-j} + jH^{+} \\ {}^{*}\beta_{ij} = \frac{\left[M_i(OH)_j^{qi-j}\right]\left[H^{+}\right]^{j}}{\left[M^{q}\right]^{i}} \end{gathered} \tag{1}$$

For such systems, Equation 2 defines the well known molar fractions distribution used in chemical literature [22]. These fractions establish the ratio of the M component amount found in each species, which in this work will be called component fractions (F_{ij}).

$$F_{ij} = F_{M_i(OH)_j^{qi-j}} = \frac{i\left[M_i(OH)_j^{qi-j}\right]}{\left[M_{total}\right]} = \frac{i\left[M_i(OH)_j^{qi-j}\right]}{\sum_i\left(\sum_j\left\{i\left[M_i(OH)_j^{qi-j}\right]\right\}\right)} \tag{2}$$

However, it is also important to establish that in systems where polynuclear species are present, the distribution of the species concentration therein, is given by the concentration ratio of the species [22]. Then the species fractions (f_{ij}) may be defined by Equation 3.

$$f_{ij} = f_{M_i(OH)_j^{qi-j}} = \frac{\left[M_i(OH)_j^{qi-j}\right]}{\Sigma_M} = \frac{\left[M_i(OH)_j^{qi-j}\right]}{\sum_i\left(\sum_j\left[M_i(OH)_j^{qi-j}\right]\right)} \tag{3}$$

The comparison of equations 2 and 3 shows clearly that the component fractions are different and that the overall concentration of component M ($[M_{total}]$) is greater than the simple sum of species concentrations (Σ_M) and are only equal among them for systems without polynuclear species. On the other hand, is clear that both sets of fractions can be represented as a function of global formation constants and the components concentration [24].

Fitting area fractions using component or species fractions

It seems obvious to consider that for a quantitative NMR spectrum the area fractions beneath each peak must be equal to the component fraction of one or several species [19-21]. Nevertheless, this has not been demonstrated for systems with several species present in chemical equilibrium: in that sense, we have proved for each peak in the B(III)-H_2O system that the area is equal to the sum of the species fractions of several species [22, 24].

Considering the aforementioned, it was thought appropriate to fit in this work the experimental area fractions of each NMR peak signals with the calculated component fractions in the first place (with the aid of MEDUSA [29] and the values of equilibrium constants proposed) and subsequently to fit the experimental area fractions with the calculated species fractions (the latter calculated using MEDUSA, the values of equilibrium constants proposed and a worksheet). In both cases, it was considered that the response factors of the observed signals are equal for all nuclei of the same element in all chemical ambiences.

Results and discussion

Potentiometric studies of Al(III)-H_2O systems

Several titration curves of Al(III) were performed at different concentrations, with aqueous solutions of standardized NaOH suitable for each (Fig. 1). In this figure it is observed the acidity of the system increases as the $[Al(III)]_{total}$ does so as expected, because HCl is formed on dissolving $AlCl_3$ in water. All titrations shown in Fig.1 were finished before precipitation. Table 1 shows the best fit obtained by refining the data with SUPERQUAD [17] for the system with $[Al(III)]_{total}$ = 0.020 M, considering formation constants for species, in agreement with Equation 4.

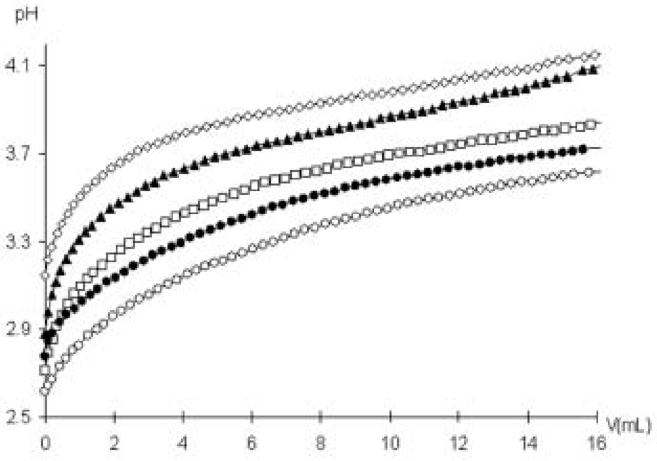

Fig. 1. Typical potentiometric titrations, with standardized NaOH, of Al(III)-H_2O system for different $[Al(III)]_{total}$ values: ◊ 0.100 M, ▲ 0.200 M, □ 0.300 M, ● 0.400 M, **O** 0.500 M.

$$iAl^{3+} + jH_2O = Al_i(OH)_j^{3i-j} + jH^+$$

$$*\beta_{ij} = \frac{\left[Al_i(OH)_j^{3i-j}\right]\left[H^+\right]^j}{\left[Al^{3+}\right]^i} \qquad (4)$$

It should be mentioned that, in spite of the chemical model proposed by Öhman and Forsling [16] and by Domínguez *et al.* [25], and the good agreement obtained for the formation constant values shown in Table 1 (for $Al(OH)^{2+}$, $Al_3(OH)_4^{5+}$ and $Al_{13}(OH)_{32}^{7+}$ species) with that previously reported in the same references, the significant difference is that in the present work it was possible to determine a value for the formation constant of $Al(OH)_3$. Few authors have reported a value for this formation constant and, in general, it has been considered an insoluble or colloidal species [20, 26, 27].

^{27}Al-NMR studies of Al(III)-H_2O systems

Fig. 2 shows the ^{27}Al-NMR spectra obtained for a solution with $[Al(III)]_{total}$ = 0.500 M and several NaOH additions. Fig. 2a exhibits the characteristic signals of these spectra in acidic media at pH = 3.89. In order to assign suitable structures in the present work, the papers of Akitt and Greenwood [19] and that of Akitt and Elders [28] have been considered. In the cited works, the peak near to 0 ppm has been assigned to the Al(III) nucleus in octahedral geometry while the peak near 5 ppm has been associated to the Al(III) nucleus pertaining to an oligomer. This has been previously reported as a dimer [19] but afterwards as a trimer [28]. The latter interpretation has been adopted for the present studies because it is consistent with the potentiometric studies presented above. The peak appearing near 63 ppm has been assigned to the Al(III) tetrahedral nucleus alone residing in the center of a tridecamer with Keggin structure; then the tetrahedral nucleus is surrounded by twelve aluminates with a central Al(III) in octahedral ambience. It has been claimed before that these twelve octahedral nuclei are not visible in ^{27}Al-NMR [19]. In agreement with the report of Akitt and Greenwood report [19], the present work does report not finding a signal near 80 ppm in acidic media, as has been claimed by Bottero *et al.* [20].

Table 1. Best refinement values for the formation constants determined from potentiometric data by SUPERQUAD. $[Al(III)]_{total}$ = 0.020 M.

Species	Formal species	-log*β	Statistical[a] Parameters
$Al(OH_2)_5(OH)^{2+}$	$Al(OH)^{2+}$	5.29[b]	σ = 1.120
$Al(OH_2)_3(OH)_3$	$Al(OH)_3$	12.96 ± 0.02	U = 108.03
$Al_3O(OH)_2(OH_2)_{11}^{5+}$	$Al_3(OH)_4^{5+}$	13.50 ± 0.02	χ^2 = 7.45
$Al_{13}O(OH)_{24}(OH_2)_{12}^{7+}$	$Al_{13}(OH)_{32}^{7+}$	109.70 ± 0.09	

[a]. 89 points were introduced to SUPERQUAD. [b] This value was maintained constant during refinement.

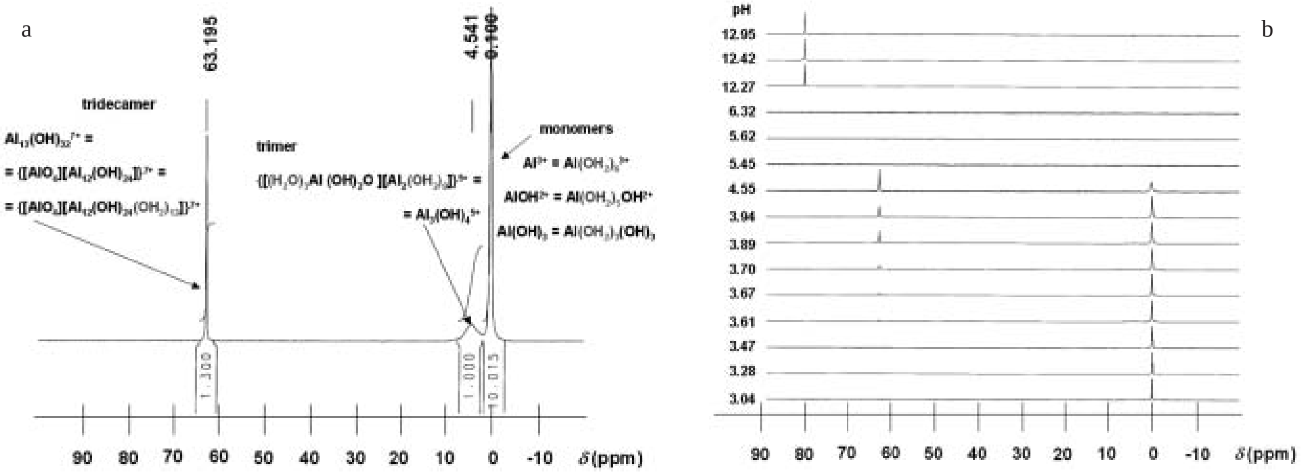

Fig. 2. Typical ^{27}Al-NMR spectra for Al(III)-H_2O system with $[Al(III)]_{total} = 0.500$ M. (a) Spectrum for a pH = 3.89 showing chemical shifts, integration of signals and species assigned to each signal (see text for explanation of these assignations). (b) Variation of NMR spectrum with pH. It should be noticed the inversion of area ratio ($A_{tridecamer}/A_{monomers}$, from a value less than unit to another greater than unit) for 63 ppm and 0 ppm signals, when pH changes from 3.94 to 4.55. Also, it is remarkable the great broadening and weakening for the 0 ppm signal at the same pH values.

Fig. 2b shows the ^{27}Al-NMR spectra as a function of pH, where, it can be observed that in the $3.04 \leq pH \leq 4.55$ range there is a 0 ppm signal, that in the present work has been assigned to the Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_3$ species, since the Al(III) nucleus in all of them exhibits practically the same octahedral geometry and the signal is broadened as the pH increases. Additionally, another signal appears at 5 ppm in the $3.47 \leq pH \leq 3.94$ range that has been assigned to $Al_3(OH)_4^{5+}$. Furthermore, in the $3.61 \leq pH \leq 4.55$ range the signal at 63 ppm has been related with $Al_{13}(OH)_{32}^{7+}$. The disappearance of all the signals in the $5.45 \leq pH \leq 6.32$ range could be explained by the formation of species of very low symmetry or by a practically complete precipitation of the $Al(OH)_{3(s)}$, although the second explanation seems more feasible. Finally, the signal at 80 ppm that appears in the $12.27 \leq pH$ range has been assigned to the $Al(OH)_4^-$ species, where the Al(III) nucleus are in tetrahedral geometry.

For each spectrum shown in Fig. 2b the area beneath each peak was obtained by simple integration, to obtain the experimental area fractions calculated as the ratio of peak area (A_{peak}) divided by the total peaks area (A_{total}), A_{peak}/A_{total}, as explained in a previous work [22]. Component and species fractions were calculated with the aid of MEDUSA [29], by using formation constants near to that presented in Table 1. Addition of component or species fraction of Al^{3+} $Al(OH)^{2+}$ and $Al(OH)_3$ was achieved in order to compare these grouped fractions with the experimental area fraction of the 0 ppm signal. The experimental area fraction of the 5 ppm signal has been compared with component or species fraction of $Al_3(OH)_4^{5+}$ and the experimental area fraction of 63 ppm signal has been compared with component or species fraction of $Al_{13}(OH)_{32}^{7+}$.

Fig. 3a presents the comparison between experimental area fractions and component fractions (F_i), showing a very poor fitting. On the other hand, Fig. 3b shows the comparison between experimental area fractions and species fractions (f_i), showing a much better fitting. Table 2 shows the data used for the fitting observed in Fig. 3b: note that the values presented on it are similar to those shown on Table 1, which may be due to the different ionic strength of the systems. The spectrum obtained for pH = 4.55 is noteworthy, because the area fraction of the 63 ppm signal is greater than the area fraction of 0 ppm and 5 ppm signals. In this work, this behavior is taken as a confirmation that, at least for this $[Al(III)]_{total} = 0.0500$ M, the twelve octahedral Al(III) nuclei in the tridecamer are not visible for the kind of perturbation used in these ^{27}Al-NMR experiments. This explanation is consistent with all the information previously reported for chemical shifts of octahedral Al(III) nuclei (that are observed in the range of 0 ppm to 20 ppm) [8, 9, 19-21].

Previously, Bottero *et al.* [20], have identified the experimental area fractions beneath the peaks with the component fractions, but its fit is better when they use a log $*\beta_{13,36}$ = -105.5 value. This result may be erroneous, by the observed signal at 80 ppm in the acidic media, that was assigned there to a dimer $Al_2(OH)_x^{(6-x)}$ and that, consequently, influences the fitting of the area fractions.

Afterwards, Marklund and Öhman [21] have followed the same line of thought to fit the area fractions of the spectra obtained, for a system with $[Al(III)]_{total} = 0.01$ M in aqueous NaCl 0.6 M. Their results fit with a $\log*\beta_{13,32} = -105.5$, and they claim that this value also agrees with potentiometric studies carried out in that same work. Unfortunately, the authors do not give details of the ^{27}Al-NMR spectra obtained or on

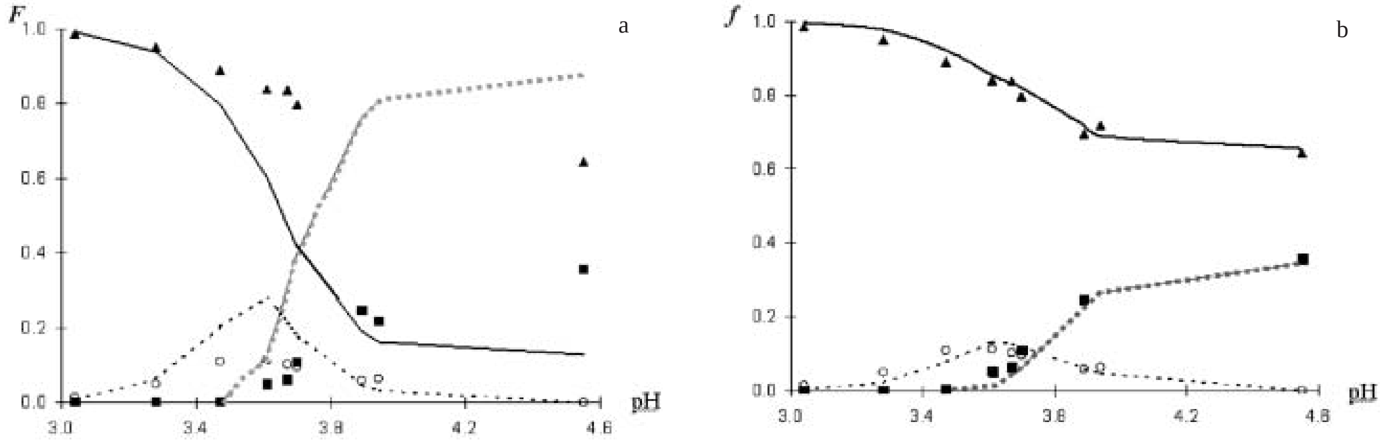

Fig. 3. Comparison of fractions determined with the model calculated by SUPERQUAD and area fractions obtained by ^{27}Al-NMR. ▲ 0ppm, **O** 5 ppm, and ■ 63 ppm experimental fractions. — monomers, - - - trimer, and ▪▪▪ tridecamer estimated fractions. (a) Component fractions. (b) Species fractions: It should be noticed that the fit is accomplished, practically, over the corresponding species distribution diagram.

Table 2. Formation constants calculated by ^{27}Al RMN data (Fig. 2b) in the acid media –before precipitation of $Al(OH)_{3(s)}$. $[Al(III)]_{total}$ = 0.500 M.

Species	**Formal species**	-log*β
$Al(OH_2)_5(OH)^{2+}$	$Al(OH)^{2+}$	5.29
$Al(OH_2)_3(OH)_3$	$Al(OH)_3$	12.06
$Al_3O(OH)_2(OH_2)_{11}{}^{5+}$	$Al_3(OH)_4{}^{5+}$	14.10
$Al_{13}O(OH)_{24}(OH_2)_{12}{}^{7+}$	$Al_{13}(OH)_{32}{}^{7+}$	110.60

the calculations of the experimental area fractions or on the algorithm used for the fit. Additionally, the obtained value for log*$\beta_{13,32}$ differs respect to that reported previously by Öhman and Forsling [16] with potentiometric methods (log*$\beta_{13,32}$ = -109.2) in the same conditions of $[Al(III)]_{total}$ and ionic strength, but in the presence of carbonates. In the present work it has been shown that a good agreement may be obtained between experimental area fractions and calculated species fractions for observed ^{27}Al-NMR signals, obtaining formation constants similar to those determined by potentiometry. This is in agreement with a previous work [22], so that we can establish that the area beneath the ^{27}Al-NMR signals are proportional to the species fractions and in this way it is possible to achieve quantitative studies and to determine formation constants, not only to determine the geometry and chemical environment of Al nuclei.

Conductometric studies of Al(III)-H_2O systems

In order to validate the chemical model proposed in this work, conductometric titrations of Al(III) solutions with NaOH were performed, before $Al(OH)_{3(s)}$ precipitation.

Fig. 4 shows the conductometric titrations for the Al(III) system, within the 6.0(10^{-3}) M $\leq$ $[Al(III)]_{total}$ $\leq$ 2.8(10^{-2}) M concentration range (Fig. 4a), where the conductivity remains almost constant, until [OH]/[Al(III)] = 2.5; after this value precipitation takes place. Further, for a concentration of 0.12 M the conductivity increases with the hydrolysis degree (Fig. 4b).

The graphical fit of the experimental data was achieved by calculating conductivity values by means of Equation 5, where $z_{Al_i(OH)_j^{3i-j}}$ represents the charge of the corresponding aluminum species; the component fractions of Al(III) species were calculated by means of the program MEDUSA using the formation constants shown in Table 1, $[Na^+]$ was calculated by means of the amount of NaOH added; $[NO_3^-]$ was obtained from the initial amount of $Al(NO_3)_3$; while the concentration of H^+ and OH^- were determined from the experimental pH (*i.e.* corrected by the cell efficiency). The values for the equivalent conductivities (λ) were estimated by iteration. Table 3 shows the estimated values for the equivalent ionic conductivities.

$$\kappa = \lambda_{Na^+}\left[Na^+\right] + \lambda_{NO_3^-}\left[NO_3^-\right] + \lambda_{H^+}\left[H^+\right] + \lambda_{OH^-}\left[OH^-\right] + \sum \left| z_{Al_i(OH)_j^{3i-j}} \right| \lambda_{Al_i(OH)_j^{3i-j}} F_{Al_i(OH)_j^{3i-j}} \left[Al(III)\right]_{total} \tag{5}$$

The fittings achieved for the experimental conductivity data with the calculated values are also shown in Fig. 4, as solid lines. Fig. 4 also shows a good agreement between the experimental conductivity and the estimated values, which confirms the validity of the model obtained for Al(III)-H_2O system. As expected, the λ values increase as the sepecies concentration diminish [30].

Conclusions

This work gives support to establish that the algorithm used to explain the NMR signals leads to obtaining quantitative

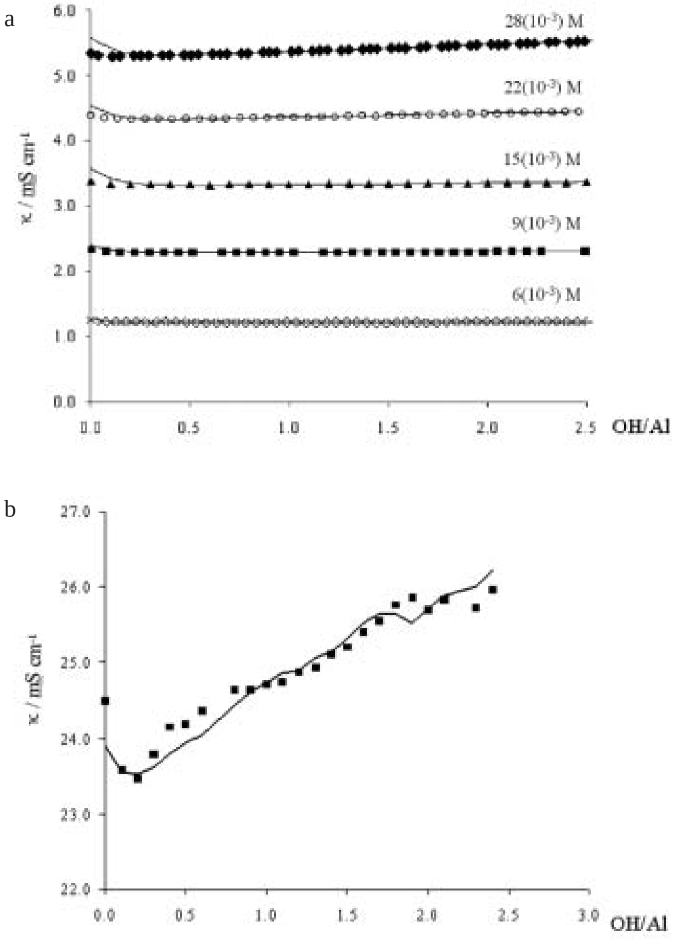

Fig. 4. Conductometric titrations curves for the Al(III)-H_2O system with different $[Al(III)]_{total}$ values. The solid lines represent the conductivity estimated using the model obtained by means of the SUPERQUAD program. The markers represent the experimental conductivity values. (a) $6.00(10^{-3})M \leq [Al(III)]_{total} \leq 28.0(10^{-3})M$. (b). $[Al(III)]_{total} = 0.12M$.

evidence about the species for the Al(III)-H_2O system and to determine the formation constants, associating the area fractions of signals to the species fractions, as was explained in our previous work for the B(III)-H_2O system [22]. The consistence obtained in this work between the results observed by the quantitative NMR analysis with potentiometric and conductometric results gives validity to the algorithm suggested.

On the other hand, this work supports the idea that the NMR signals are associated with the thermodynamic distribution of species in solution and probably a generalization of Beer's law could be extended to NMR.

It is remarkable to consider the good explanation achieved for different techniques with the same species set, for a great range of overall concentration of Al(III). The different values of equilibrium constants refined may be due to the different inonic strength values of the studied solutions.

Table 3. Equivalent conductivity values estimated by fitting of conductivity titrations for the Al(III)-H_2O system.

Species	Formal species	λ [a] /mS cm^2 $equivalent^{-1}$
$Al(OH_2)_6^{3+}$	Al^{3+}	3.5-15
$Al(OH_2)_5(OH)^{2+}$	$Al(OH)^{2+}$	10
$Al(OH_2)_3(OH)_3$	$Al(OH)_3$	0
$Al_3O(OH)_2(OH_2)_{11}^{5+}$	$Al_3(OH)_4^{5+}$	8
$Al_{13}O(OH)_{24}(OH_2)_{12}^{7+}$	$Al_{13}(OH)_{32}^{7+}$	42-47
	Na^+	8.6-18
	NO_3^-	50-70.1

[a] The lower limit corresponds to higher $[Al(III)]_{total}$ and the upper limit corresponds to lower $[Al(III)]_{total}$

Acknowledgements

The authors wish to acknowledge CONACYT for the grants given to JCBP, and MLPH to undertake their postgraduate studies. Thanks are also given to PEMEX and IMP (through the project FIES-96-31-III) for partial financing support. The authors are indebted to Dr I. Puigdomenech and Prof. Josef Havel for the copy of the program MEDUSA, as well as to Dr A. Vacca and Dr P. Gans for the copy of the program SUPERQUAD and, finally, to Dr. Mario A. Romero-Romo and to Prof. William F Reynolds for helpful comments.

References

1. Valente, J. V.; Buntine, M. A.; Lincoln, S. F.; Ward, A. D. *Inorg. Chim. Acta*. **2007**, *360*, 3380-3386.
2. Desroches, S.; Daydé, S.; Berton, G. *J. Inorg. Biochem*. **2000**, *81*, 301-312.
3. Kinrade, S. D.; Swaddle,T. H. *Inorg. Chem*. **1989**, *28*, 1952-1954.
4. Yokoyama, T.; Kinoshita, S.; Wakita, H.; Watanabe, T. *Anal. Sci*. **1991**, 7. Suppl., 429-430.
5. Caravan, P.; Orvig, Ch. *Inorg. Chem*. **1997**, *36*, 236-248.
6. Djurdjevic, P.; Cvijovic, M.; Vesna, Z. *Spectrosc. Lett*. **2005**, *38*, 617-634.
7. Tossell, J. A. *Geochim. Cosmochim. Ac*. **2001**, *87*, 115-124.
8. Perry, C. C.; Shafran, K. L. *J. Inorg. Biochem*. **2001**, *87*, 115-124.
9. Djurdjevic, P.; Cvijovic, M.; Zakrzewska, J. *J. Coord. Chem*. **2005**, *58*, 1615-1629.
10. Ratomir, M. J.; Ljubinka, G. J.; Djurdjevic, P. T. *J. Solution Chem*. **2005**, *34*, 1235-1261.
11. Frink, C. R.; Peech, M. *Inorganic Chemistry.* **1963**, *3*, 473-478
12. Brown P. L.; Sylva, R. N. *J. Chem. Soc. Dalton Trans*. **1985**, 1967-1970
13. Sillén, L. G. Polynuclear Complexes in Solution, in *Coordination Chemistry*. Martell, A. E., Ed, Van Nostrand Reinhold, New York, **1971**.
14. Öhman, L. O.; Sjöberg, S.; Ingri, N. *Acta Chem. Scand*. **1983**, *A37*, 561-568
15. Letterman, R. D.; Asolekar, S. R. *Wat. Res*. **1990**, *24*, 931-939
16. Öhman, L. O.; Forsling, W. *Acta Chem. Scand*. **1981**, A35, 795-802
17. Gans, P.; Sabatini, A.; Vacca., A.*J. Chem. Soc. Dalton Trans*. **1985**, 1195-1200

18. M. Kývala and I. Lukeš, International Conference, Chemometrics ’95, Pardubice, Czech Republic, 1995, p. 63; a full version of “OPIUM” is available (free of charge) on http://www.natur.cuni.cz/~kyvala/opium.html , accessed in January, **2008**
19. Akitt, J.W.; Greenwood, N. N.; Khandelwal, B. L.; Lester, G. D. *J. Chem. Soc. Dalton Trans*. **1972**, 604-610
20. Bottero, J. Y.; Cases, J. M.; Fiessinger, F.; Poirier, J. E. *J. Phys. Chem*. **1980**, *84*, 2933-2939
21. Marklund, E.; Öhman, L. O. *Acta Chem. Scand*. **1990**, *44*, 228-234
22. Botello, J. C.; Morales-Domínguez, E.; Domínguez, J. M.; Gutiérrez, A.; Rojas-Hernández, A.; Ramírez, M. T. *Spectrochimica Acta Part A*. **2003**, *59*, 1477-1486
23. Gómez-Zaleta, B.; Ramírez-Silva, M. T.; Gutiérrez, A.; González-Vergara, E.; Güizado-Rodríguez, M.; Rojas-Hernández, A. *Spectrochimica Acta Part A*. **2006**, *64*, 1002-1009
24. Rojas-Hernández, A.; Moya-Hernández, R.; Rueda-Jackson, J. C.; Ramírez-Silva, M. T.; in Emerging Fields in Sol-Gel Science and Technology; López, T. M.; Avnir, D.; Aegerter, M. Eds. Kluwer, Boston, **2003**, 354-380
25. Domínguez, J. M.; Botello-Pozos, J. C.; López-Ortega, A.; Ramírez, M. T.; Sandoval-Flores, G.; Rojas-Hernández, A. *Catalysis Today*. **1998**, *43*, 69-77
26. Nazarenko, V. A.; Biryuk, E. A. *Zhur. Neorg. Khim*. **1974**, *19*, 632-635
27. Bourcier, W. L.; Knauss, K. G.; Jackson, K. J. *Geochim. Cosmochim. Ac*. **1993**, *57*, 747-762
28. Akitt , J. W.; Elders, J. M. *J. Chem. Soc. Dalton Trans*. **1988**, 1347-1355
29. Puigdomenech, I. MEDUSA (Making Equilibrium Diagramas Using Sophisticated Algorithms) http://www.kemi.kth.se/medusa/, accessed in January, **2008**
30. Castellan, G. W. Physical Chemistry, Addison-Wesley, Reading, **1983**, Chapter 31