In Situ pH Probing of Hydrothermal Solutions by NMR

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An NMR method for pH probing of hydrothermal solutions is described. NMR tubes withstanding autogenous pressures at temperatures up to 200 °C are used in conventional NMR probe heads. After selection, several molecules stable in aqueous solutions up to 200 °C are shown usable as pH probes. Two amines, imidazole and 1,4-diazabicyclo[2.2.2]octane, are complementary pH indicators. Both together permit a range of about 9 pH units to be covered. Calibration of the amine ^{14}N chemical shift (δ) versus pH is established. The dependence on temperature of the amine parameters, K_{a_i} (dissociation constants) and δ_i (chemical shifts of the different protonation states), is investigated. Both amines present high NMR sensitivities to protonation changes, expressed as $d[\delta(^{14}N)]/d[pH]$, and have a very small sensitivity to medium effects. This pH determination method is successfully applied to follow the pH evolution during hydrothermal synthesis of aluminum hydroxide, and of $AlPO_4$−CJ2.

Introduction

High-temperature aqueous solutions are involved in many technologically important processes due to the unique dielectric, rheological, transport, and chemical properties of water. The usefulness of high-temperature/high-pressure water in chemical, geochemical, environmental, and biological processes is related to the drastic changes of its properties as a solvent from its properties in ambient conditions. The chemistry of high-temperature/high-pressure aqueous systems is dominated by protolytic processes including acid−base dissociation, hydrolysis, and solubility reactions. These phenomena are present in many areas of science and technology such as hydrothermal synthesis of ceramic or catalytic materials, hydrothermal crystal growth, thermal power generation, hydrothermal geochemistry, ore-forming processes, nuclear waste disposal, and oxidation of hazardous organics. If pH could be measured accurately in hydrothermal aqueous systems (T > 100 °C), our knowledge of protolytic phenomena would be increased, and this would greatly aid progress in all the areas of science mentioned above. There have been some reports of potentiometric pH measurements in high-temperature aqueous systems up to 300 °C using platinum−hydrogen electrodes;[1−7] a Au−hydrogen electrode has also been used in supercritical water.[8] More recently, an yttria-stabilized membrane sensor was demonstrated to be a primary pH electrode for potentiometric measurements in high subcritical and supercritical systems up to 450 °C.[2−6]

The formation mechanisms of materials such as molecular sieves and ceramics synthesized in hydrothermal conditions are still controversial. The understanding of synthetic pathways is often limited to the analysis of the final structure and rationalization of a plausible retrosynthesis. One should obtain critical information on the solid-phase formation steps from in situ characterization of the medium at high pressure and temperature. In situ measurements offer a substantial improvement over batch-mode techniques, in the rapidity with which data may be collected and in the evidence of phenomena actually taking place at high temperature, which may not be quenchable.

Hydrolysis and condensation reactions of metalate ions are essentially acidobasic reactions, which lead to the formation of higher molecular weight products. In water, it is well-known that the state of condensation of metalate ions obtained by hydrolysis of a metal salt is controlled by the pH of the medium.[9] pH is one of the main parameters that determines the stoichiometry of ligands in the coordination sphere of a cation $MO_x(OH)_y(H_2O)_z$. The formation reaction of aluminum oxyhydroxide (boehmite) by hydrolysis and polymerization of

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(1) Mesmer, R. E.; Palmer, D. A.; Wesolowski, D. J. In *Physical Chemistry of Aqueous Systems*; White, H. J., et al., Eds.; Begell House: New York, 1995; p 423.

(2) Macdonald, D. D.; Butler, P.; Owen, D. *Phys. Chem.* **1973**, *77*, 2474.

(3) Macdonald, D. D.; Hettiarachchi, S.; Lenhart, S. J. *J. Solution Chem.* **1988**, *17*, 719.

(4) Hettiarachchi, S.; Makela, K.; Song, H.; Macdonald, D. D. *J. Electrochem. Soc.* **1992**, *139*, L3.

(5) Macdonald, D. D.; Hettiarachchi, S.; Song, H.; Makela, K.; Emerson, R.; Haim, M. *J. Solution Chem.* **1992**, *21*, 849.

(6) Ding, K.; Seyfried, W. E. *Science* **1996**, *272*, 1634.

(7) Eklund, K.; Lvov, S. N.; Macdonald, D. D. *J. Electroanal. Chem* **1997**, *437*, 99.

(8) Ding, K.; Seyfried, W. E. *J. Solution Chem.* **1996**, *25*, 421.

(9) Baes, C. F. Jr.; Mesmer, R. E. *The hydrolysis of cations*; John Wiley & Sons: New York, 1976.

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hexaaquoaluminum cations at temperatures higher than 100 °C illustrates the pH change occurring during such a reaction: $Al(H_2O)_6^{3+} \rightarrow AlOOH + 3H^+ + 4H_2O$. To investigate formation mechanisms of solids and characterize intermediate polycondensates, one needs to follow pH variations while hydrothermal synthesis proceeds. Potentiometric studies are usually undertaken at room temperature[10,11] to determine the pH of solutions containing polycondensates. But, to the best of our knowledge, such potentiometric pH measurements were never reported under hydrothermal conditions in these inorganic aqueous systems.

To obtain the desired data, NMR looks attractive. First, it provides an opportunity to obtain measurements under hydrothermal conditions. Second, a development of NMR tubes and probes suitable for NMR experiments at high temperature or high pressure or in corrosive media has recently occurred.[12−21] Several designs have been published for solution NMR at high pressures and temperatures. Merbach et al. distinguished two groups of designs: on one hand, specific strong NMR tubes located in conventional probes[13−19] and, on the other hand, high-pressure NMR probes where the radio frequency coil, NMR sample, and pressurizing fluid are contained in a strong vessel.[22−28] Temperatures and pressures involved in the synthesis of inorganic materials do not usually require the use of high-pressure probes but just the availability of strong vessels withstanding autogenous pressures for samples heated to 200 °C, using commercial probes. Because of harsh chemical conditions encountered in the experiments (extreme pH values, fluoride ions), the vessels we use are protected by sealed inert Teflon (Dupont de Nemours) inserts.[29] Furthermore, NMR experiments allow repetitive and noninvasive measurements. In addition, hydrothermal synthesis of inorganic materials very often involves biphasic solid−liquid media like gels or colloidal suspensions, and in such conditions, NMR appears as a very convenient way to analyze the liquid part.

There was an earlier use of NMR for the determination of aqueous pH values or acidity functions at room temperature. The method is based on the fact that the averaged chemical shift of nuclei in the protonated and the nonprotonated forms of a molecule, undergoing fast chemical exchange, can be used to calculate the degree of protonation. Earlier studies employed ^1H[30−33] and ^{19}F[34] NMR, but also ^{13}C,[35−37] ^{31}P,[38] and ^{17}O[38] NMR, to determine the extent of protonation of weak bases. ^1H and ^{13}C NMR were used to investigate acid−base equilibria of weak organic bases in strongly acidic media. For example, protonation equilibria of ketones were studied by ^{13}C NMR in sulfuric acid,[39] and the basicity of ethers was also evaluated by a ^{13}C NMR technique.[40] ^{13}C NMR was extensively used to determine Hammet acidity functions and acid strengths.[41] The determination of acidity constants was also done by an NMR method;[42] for example, ^{31}P NMR pH titration was used to calculate apparent pK_a values of phosphate groups in biological compounds.[43]

NMR pH measurement is a method which is also widely developed in current biological research using the ^{31}P chemical shift of naturally occurring P-containing molecules as a pH indicator, as well as using external probes.[44−46] The pH value in microenvironments such as cells or micelles is one of the most important factors that determine their properties. Measurements of intracellular pH are also performed by means of high-resolution ^{19}F NMR spectroscopy.[47−50] α-(difluoromethyl)alanine was reported as being an accurate probe of pH gradients under physiological conditions. This is due to slow exchange conditions between ^{19}F resonance lines of the indicators from the extracellular medium and from each intracellular compartment.[51] Imidazoles bearing a 1-fluorinated substituent were also identified as potentially useful probes for intracellular pH determination the basis of ^{19}F NMR.[52] Some interest also developed in the synthesis of probes that possess dual spectroscopic responses to pH. Some materials displayed pH sensitivity in both ^{19}F NMR and

(10) Brosset, C. *Acta Chem. Scand.* **1952**, *6*, 910.
(11) Brosset, C. *Acta Chem. Scand.* **1954**, *8*, 1917.
(12) Vanni, H.; Earl, W. L.; Merbach, A. E. *J. Magn. Reson.* **1978**, *29*, 11.
(13) Roe, D. C. *J. Magn. Reson.* **1985**, *63*, 388.
(14) Horvath, I. T.; Ponce, E. C. *Rev. Sci. Instrum.* **1991**, *62*, 1104.
(15) Bai, S.; Taylor, C. M.; Mayne, C. L.; Pugmire, R. J.; Grant, D. M. *Rev. Sci. Instrum.* **1996**, *67*, 240.
(16) Yamada, H. *Rev. Sci. Instrum.* **1974**, *45*, 640.
(17) Yamada, H.; Nakatsuka, M.; Yamochi, H.; Sawamura, M.; Sera, A. *Rev. Sci. Instrum.* **1991**, *62*, 700.
(18) Tison, K.; Hunt, E. R. *J. Chem. Phys.* **1971**, *54*, 1526.
(19) von Jouanne, J.; Heidberg, H. *J. Magn. Reson.* **1972**, *7*, 1.
(20) Kinrade, S. D.; Swaddle, T. W. *J. Magn. Reson.* **1988**, *77*, 669.
(21) Gerardin-In, C.; In, M.; Taulelle, F. *J. Chim. Phys. Phys.-Chim. Biol.* **1995**, *92*, 1877.
(22) Jonas, J. *Rev. Sci. Instrum.* **1972**, *43*, 643.
(23) Earl, W. L.; Vanni, H.; Merbach, E. *J. Magn. Reson.* **1978**, *30*, 571.
(24) Shimokawa, S.; Yamada, E. *J. Magn. Reson.* **1978**, *30*, 571.
(25) Rathke, J. W. *J. Magn. Reson.* **1989**, *5*, 150.
(26) Frey, U.; Helm, L.; Merbach, E. *High-Pressure Res.* **1990**, *2*, 237.
(27) Jonas, J. *Science* **1982**, *216*, 1179.
(28) DeFries, T. H.; Jonas, J. *J. Magn. Reson.* **1979**, *35*, 111.
(29) Gerardin, C.; Haouas, M.; Taulelle, F. Manuscript in preparation.
(30) Grunwald, E.; Loewenstein, A.; Meiboom, S. *J. Chem. Phys.* **1957**, *27*, 641.
(31) Levi, A.; Modena, G.; Scorrano, G. *J. Am. Chem. Soc.* **1974**, *96*, 6585.
(32) Metzger, P.; Casadevall, A.; Casadevall, E. *Tetrahedron* **1975**, *31*, 733.
(33) Fastrez, J.; Daffe, V. *J. Chem. Soc., Dalton Trans.* **1981**, *317*.
(34) Taft, R. W.; Levins, P. *Anal. Chem.* **1962**, *34*, 436.
(35) Siigur, J.; Pehk, T.; Haldna, U.; Lippmaa, E. *Reakts. Sposobn. Org. Soedin.* **1971**, *8*, 267.
(36) Butler, R. *J. Chem. Soc., Perkin Trans.* **1976**, *2*, 959.
(37) Scorrano, G.; Lucchini, V. *J. Org. Chem.* **1979**, *44*, 1726.
(38) Hibbert, R. C.; Logan, N. *J. Chem. Soc., Dalton Trans.* **1985**, 865.
(39) Farcasiu, D.; Ghenciu, A. *J. Am. Chem. Soc.* **1993**, *115*, 10901.
(40) Bonvicini, P.; Levi, A.; Lucchini, V.; Modena, G.; Scorrano, G. *J. Am. Chem. Soc.* **1973**, *95*, 5960.
(41) Farcasiu, D.; Ghenciu, A. *J. Prog. NMR Spectrosc.* **1996**, *29*, 129.
(42) Cookson, R. F. *Chem. Rev.* **1974**, *74*, 5.
(43) Swanson, M. G.; Robert, J. M.; Keller, R. K.; Bangalore, P. *Magn. Reson. Chem.* **1997**, *35*, 447.
(44) Moon, R. B.; Richards, J. H. *J. Biol. Chem.* **1973**, *248*, 7276.
(45) Roberts, J. K. M.; Wade-Jardetzky, N.; Jardetzky, O. *Biochemistry* **1981**, *20*, 5389.
(46) De Fronzo, M.; Gillies, R. J. *J. Biol. Chem.* **1987**, *262*, 11032.
(47) Deutsch, C. J.; Taylor, J. S. *Ann. N. Y. Acad. Sci.* **1987**, *508*, 33.
(48) Taylor, J. S.; Deutsch, C. *Biophys. J.* **1983**, *43*, 261.
(49) Taylor, J. S.; Deutsch, C. *Biophys. J.* **1989**, *55*, 799.
(50) Rhee, C. K.; Levy, L. A.; London, R. E. *Bioconjugate Chem.* **1995**, *6*, 77.
(51) Deutsch, C.; Taylor, J. S.; Wilson, D. F. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 7944.
(52) Harper, J. L.; Smith, R. A. J.; Bedford, J. J.; Leader, J. P. *Tetrahedron* **1997**, *53*, 8211.

visible spectroscopy[53] or also in both ^{19}F NMR and fluorescence spectroscopy.[54]

In inorganic materials science, a solid-state NMR approach is often used to characterize the surface acidity of solid catalysts at room temperature and at low temperature. Surfaces' acidity for strong solid acids is an issue which is still not well understood in comparison to liquids' acidity. There are several literature reports that cover the use of NMR for determining the number and strength of acidic protons in zeolites.[55−57,67] ^1H MAS NMR spectroscopy is often used to estimate the relative strengths of Lewis- and Brønsted-type acid sites in zeolite frameworks by examining the ^1H chemical shifts of OH acidic groups. Another method involves induced ^1H NMR chemical shift changes of surface Brønsted hydroxyl groups interacting with adsorbed molecules, which are weak bases.[58] The ^{15}N CPMAS NMR technique has emerged as a useful technique that yields concentration values for both Brønsted and Lewis acid sites using ^{15}N-enriched pyridine.[59−61] ^{15}N NMR was shown to be a more promising probe for adsorbing amines than ^{13}C NMR[62] because of the greater chemical shift range and because of a more direct influence of binding on nitrogen chemical shifts relative to the shifts of the more remote carbons.[60,61]

To our knowledge, NMR measurement of pH and its evolution has never been reported in hydrothermal inorganic chemistry. Potentiometric measurements were usually performed at room temperature to study for instance the acid dissociation of $M(H_2O)_n^{z+}$ aquo ions and the formation of the corresponding metal hydroxide phases. One of the advantages of using NMR for in situ pH determinations while syntheses proceed is the possibility of simultaneously monitoring NMR spectra that directly characterize the metal condensation rate.

To measure the pH of a medium by NMR, a pH probe compound must either be naturally present in the system or be introduced into the system of interest. The pH indicator must exhibit some properties concerning its chemical activity and its NMR characteristics. Many NMR pH indicators exist, but because of the peculiar conditions of hydrothermal synthesis, the indicators that are needed must fulfill some specific requirements. First, the probe compound must present optimal acid−base chemical sensitivity over a pH range which is of interest for the study. This means that it must have a

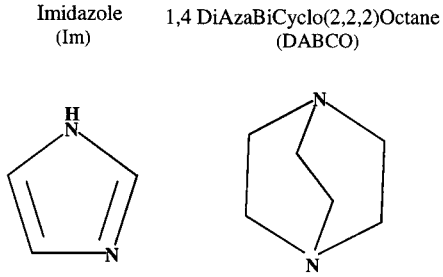

Figure 1. Amines used as pH probes.

pK_a value in the pH range under study since maximum chemical shift sensitivity to pH is found in the region of pK_a. When the probe molecule is not a component of the system under study, it needs to be added into the medium in very small quantities in order not to disturb the system. The pH probe must then contain an NMR active nucleus with a good NMR sensitivity. To obtain a time-resolved analysis, rapid acquisitions of NMR spectra with sufficient signal-to-noise ratios are needed. A significant difference in the chemical shifts of the different protonation states of the nucleus in the molecule is also necessary. The indicator must be water soluble and stable toward temperature and pressure changes since it will be used in hydrothermal media up to 200 °C. The simplest case is when the indicator is not involved in any chemical reaction other than protonation changes and does not form complexes with the metal cations. The chosen nucleus must have a chemical shift solely a function of the pH, i.e., as little sensitivity as possible to medium effects at a given temperature. A very careful analysis of the data is required when the probe molecule plays roles other than just pH indicator in the system in order to investigate the validity of the pH measurement method. During the study of formation of a metal oxide or metallophosphate framework, the ^{31}P NMR chemical shift of the H_3PO_4 system cannot usually be used as a pH indicator because phosphate species often behave as strong complexing ligands of metals in aqueous solutions. In such cases, at high temperature, the ^{31}P NMR signals observed are the result of a rapid exchange between free phosphate species and bound phosphate species in complexes.

Some amines and polyamines were found to meet all those requirements, and ^{14}N NMR chemical shifts of the amine nitrogens were used as pH indicators. Considering the large nuclear shielding range that ^{14}N NMR presents, use of this nucleus becomes an attractive possibility in this study. Because of the low sensitivity of natural abundance ^{15}N NMR and the small quantities of the probe material usually involved, the ^{14}N isotope was chosen. A selection process examining the NMR response to pH changes and the chemical stability in hydrothermal media lead to the identification of two amines, imidazole (Im) and 1,4-diazabicyclo[2.2.2]octane (DABCO), as useful pH probes (Figure 1). They possess attractive complementary pK_a values, which are 3 and 8.9 for DABCO and 7 for imidazole at room temperature. The combined use of both amines permits a wide pH range to be covered, from 1.5 to 10.5 at room temperature.

The present work describes a method to measure the pH of hydrothermal solutions using ^{14}N NMR of amines. $\delta(^{14}N)$ versus pH calibration relations are established

(53) Hamada, K.; Hirano, T.; Mitsuishi, M.; Ohira, M.; Mesuda, K. *Chem. Commun.* **1994**, 693.
(54) Kirshenlohr, H. L.; Metcalfe, J. C.; Morris, P. G.; Rodrigo, G. C.; Smith, G. A. *Proc. Natl. Acad. Sci. U.S.A.* **1988**, *85*, 9017.
(55) Pfeifer, H.; Freude, D.; Hunger, M. *Zeolites* **1985**, *5*, 274.
(56) Pfeifer, H.; Freude, D.; Karger, J. In *Catalysis and Adsorption by Zeolites*; Ohlmann, G., et al., Eds.; Elsevier: Amsterdam, 1991.
(57) Farneth, W. E.; Gorte, R. J. *Chem. Rev.* **1995**, *95*, 615.
(58) Brunner, E.; Pfeifer, H. *Z. Phys. Chem.* **1996**, *192* (Part 1), 77.
(59) Haw, J. F.; Chuang, I.-S.; Hawkins, B. L.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 7206.
(60) Ripmeester, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 2925.
(61) Maciel, G. E.; Haw, J. F.; Chuang, I.-S.; Hawkins, B. L.; Early, T. A.; MacKay, D. R.; Petrakis, L. *J. Am. Chem. Soc.* **1983**, *105*, 5529.
(62) Dawson, W. H.; Kaiser, S. W.; Ellis, P. D.; Inners, R. R. *J. Phys. Chem.* **1982**, *86*, 867.
(63) Yu, L.; Pang, W.; Li, L. *J. Solid State Chem.* **1990**, *87*, 241.
(64) Férey, G.; Loiseau, T.; Lacorre, P.; Taulelle, F. *J. Solid State Chem.* **1993**, *105*, 179.
(65) Van Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227.
(66) Haouas, M.; Gérardin, C.; Taulelle, F.; Estournes, C.; Loiseau, T.; Férey, G. *J. Chim. Phys. Phys.-Chim. Biol.* **1998**, *95*, 302.
(67) Simon, A.; Delmotte, L.; Chezeau, J. M.; Huve, L. *Chem. Commun.* **1997**, 263.

for these two amines. The sensitivity and the precision of the method are evaluated and tested in different media. The interaction of those probes with our systems is studied. The applicability of the method is illustrated by two examples of pH measurements during hydrothermal syntheses of inorganic materials. The first one shows a forced hydrolysis of Al^{3+} ions by TMAOH, leading to the formation of $Al(OH)_3$ at 127 °C. The second one presents the pH variation during hydrothermal preparation at 150 °C of $AlPO_4$−CJ2.

Principle of the Method

The objective is to establish calibration equations, which relate amine ^{14}N NMR chemical shifts with pH values. The dependence of the δ versus pH relations upon the chemical composition of the medium and upon a temperature and pressure increase must then be evaluated.

First, solutions of imidazole and DABCO titrated with HNO_3 are prepared. Let us call m the molar ratio between the added acid and the Im or DABCO base, $m = [NO_3^-]/[B]_t$, where $[B]_t$ represents the total base concentration. For Im, m is varied from 0 to 1.6, and for DABCO, which is a dibase, m is varied from 0 to 2.6. The ^{14}N NMR spectra were collected from room temperature to 177 °C. For both amine titrations, the spectra present a signal due to NO_3^- ions and a signal due to the rapid exchange between the different protonation states of the amine.

The method is based on the observation that the chemical shifts of nuclei in molecules undergoing protonation changes are usually sensitive to the degree of protonation. Most of the time, exchange reactions between protonated and nonprotonated molecules are fast compared to the NMR time scale, so a single signal corresponding to the average degree of protonation of the molecule is observed. The averaged chemical shift for corresponding nuclei in the two molecules undergoing fast chemical exchange can be used to calculate the ratio of the two forms, protonated and nonprotonated, by chemical shift interpolation. The calibration method is detailed below for the general case of a dibase. The resulting ^{14}N NMR chemical shift of the signal of the amine is expressed as a population-weighted sum of chemical shifts of individual nonexchanging forms:

$$\delta = \sum x_i \delta_i$$

where

$$x_i = [BH_i^{i+}]/[B]_t$$

and

$$\delta_i = \delta(BH_i^{i+})$$

The x_i molar ratios are easily expressed as functions of proton concentration $h = [H_3O^+]$ and the acid dissociation constants K_{a_i}.

In the case of a dibase, the observed chemical shift can then be expressed as

$$\delta_{obs} = \frac{1}{1 + \frac{h}{K_{a_1}} + \frac{h^2}{K_{a_1}K_{a_2}}}\left(\delta_0 + \delta_1\frac{h}{K_{a_1}} + \delta_2\frac{h^2}{K_{a_1}K_{a_2}}\right) \quad (1)$$

When K_{a_1} is much larger than K_{a_2}, the following simple formula can be directly used:

$$pH = pK_i + \log\frac{(\delta_{obsd} - \delta_i)}{(\delta_{i-1} - \delta_{obsd})}$$

Chemical shifts of the "pure" protonation states, δ_i, are unknown and have to be determined. K_{a_i} values of amines also have to be determined in the temperature range of interest. They are determined by potentiometric measurements at several temperatures from room temperature to 50 °C. The determinations are done by fitting $m = f(h)$ with the following relation:

$$m = \frac{[NO_3^-]}{[B]_t} = \frac{h}{[B]_t} - \frac{K_w}{[B]_t h} + \left(\frac{h}{K_{a_1}} + \frac{2h^2}{K_{a_1}a_2}\right)/\left(1 + \frac{h}{K_{a_1}} + \frac{h^2}{K_{a_1}K_{a_2}}\right) \quad (2)$$

This relation considers the hydrolysis effects for conditions far from the pK_a. Determinations are also carried out using just several points near the points of inflection. Both methods gave similar results. Then, K_{a_i} values of molecules at temperatures higher than 50 °C are obtained by extrapolation of K_{a_i} at the working temperature.

Knowing h and K_{a_i} values at room temperature, the δ_i values are obtained by fitting δ_{obsd} as a function of h with eq 1. To evaluate the variation of calibration relations with temperature, δ_i values have to be measured at various temperatures. So, spectra of titrated solutions of amines with different m ratios are registered from room temperature to 150 °C.

Once δ_i and K_{a_i} parameters are determined at different temperatures, it is possible to fit δ_{obsd} versus pH data for the different amines and at different temperatures, and obtain equations which can be used to determine pH from the measurement of δ_{obsd}.

Experimental Section

Solutions for the Calibration Procedure, Potentiometric Titrations, and NMR Measurements. Solutions of imidazole of concentration 1 M (Aldrich) and DABCO (0.5 M) (Aldrich) are prepared and titrated with a 1 M aqueous solution of HNO_3 (Aldrich). Different amounts of water are added to keep the amine concentration constant in solutions with different m (molar ratio $[NO_3^-]$/amine) values. Initial concentrations C(Im) and C(DABCO) are, respectively, 0.1 and 0.3 M. During titration m(Im) and m(DABCO) vary, respectively, from 0 to 1.6 and from 0 to 2.6. The pH values of solutions are measured by potentiometric measurements from 20 to 50 °C using a glass electrode. An ORION-420A pH meter is used with a pH ORION triode electrode with an Ag/AgCl internal reference. ^{14}N NMR spectra of titration solutions are recorded from room temperature to 177 °C on a Bruker AM400 NMR spectrometer at a resonance frequency of 28.91 MHz. ^{14}N chemical shifts are referenced to pure nitromethane using an aqueous solution of HNO_3 (1 M) at −5.93 ppm as an external secondary reference. Acquisitions are done with a 90° excitation pulse (20 μs at room temperature, 24.5 μs at 127 °C), and a recycle delay of 0.5 s is used. D_2O is used as a lock

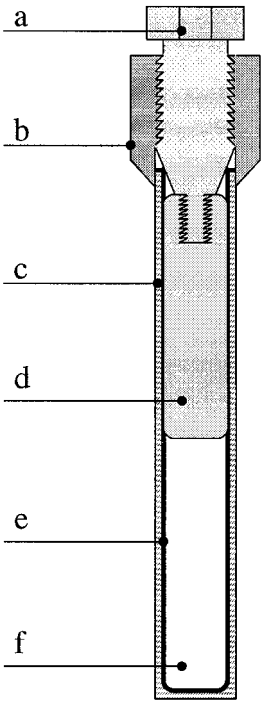

Figure 2. High-pressure NMR tube: (a) Teflon stopper; (b) titanium head; (c) polyimide (Vespel or Torlon) tube; (d) volume reducer (Teflon stopper); (e) Teflon sleeve; (f) sample volume.

solvent. At room temperature, the usual glass NMR tubes are used. At higher temperature, the experiments are performed in a suitable high-pressure Torlon (Amoco) or Vespel (Dupont de Nemours) NMR tube that was specially designed for our measurements under hydrothermal conditions and in corrosive media (in the presence of fluoride ions).[29] The tube is described in Figure 2. It is protected with a Teflon insert to ensure chemical inertness. Heating is achieved using a flow of hot air controlled by a Eurotherm variable temperature unit from Bruker. The temperature is calibrated using the ^{1}H chemical shift of ethylene glycol.[65]

Hydrolysis and Condensation of Al^{3+} at 127 °C. Forced hydrolysis of $Al(NO_3)_3$ is carried out at 27 °C as follows. The Al source is an aqueous solution of $Al(NO_3)_3$ (0.5 M) (Prolabo). The basic solution is a mixture of tetramethylammonium hydroxide (Aldrich) and imidazole so that the TMAOH concentration is 1 M and the Im/(Im + TMAOH) ratio is 3.5%. The total hydrolysis ratio (TMAOH + Im)/Al equals 2.8. Addition of base to the aluminum nitrate solution is performed under fast magnetic stirring at 27 °C. A white precipitate forms as the first drop of base is added. After addition of all the basic solution, the resulting mixture is a very viscous white solution. The mixture is then transferred into a Pyrex 10 mm NMR tube and tightly closed with a Teflon screw cap (Wilmad). The pH is monitored by ^{14}N NMR, during a thermal treatment at 127 °C, for 12 h using imidazole resonance.

Hydrothermal Synthesis of $AlPO_4$−CJ2 at 150 °C. The AlPO4−CJ2 phase,[63,64] whose formula is $AlPO_4(OH)_{0.33}F_{0.67}$-$(NH_4)_{0.88}(H_3O)_{0.12}$, is obtained by hydrothermal synthesis at 150 °C. $Al(^iOpr)_3$ (Aldrich) is mixed with an aqueous solution containing H_3PO_4 (Janssen), NH_4F (Prolabo), and amine with the following molar ratio: $1Al_2O_3/1P_2O_5/2NH_4F/1DABCO/80H_2O$. The ammonium ions but not the amine are occluded in the pores of the microporous phase. The DABCO is a necessary compound in the synthesis mixture: it adjusts the pH of synthesis, and it is also used as a pH probe. The synthesis is carried out in the high-pressure Torlon NMR tube (Figure 2) at 150 °C for 24 h, during which ^{14}N NMR spectra are recorded. The final solid product is filtered, washed with distilled water, and dried at ambient temperature. Powder X-ray diffraction patterns show that crystalline $AlPO_4$−CJ2 is obtained. ^{14}N NMR spectra are obtained at 36.14 MHz using a DSX 500 Bruker spectrometer at 150 °C while hydrothermal synthesis proceeds. Each spectrum is recorded as an accumulation of 320 scans with a 60° pulse angle excitation and a recycle delay of 1 s.

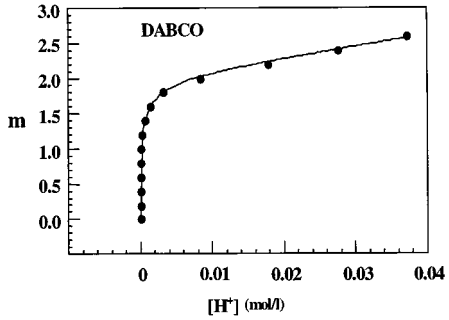

Figure 3. $m = [NO_3^-]/[B]_t$ as a function of pH for DABCO.

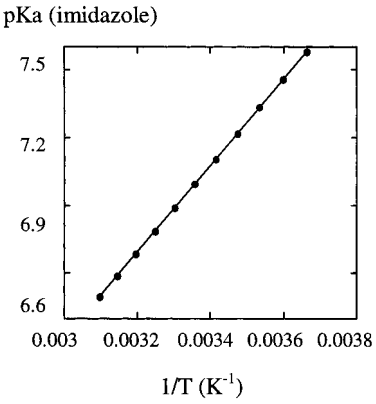

Figure 4. pK_a of imidazole versus 1/T.

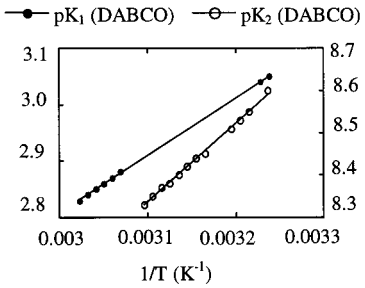

Figure 5. pK_1 and pK_2 of DABCO versus 1/T.

Calibration Results

Determination of pK_{a_i} Values of Im and DABCO as a Function of Temperature. pH measurements were carried out from room temperature to 50 °C. Figure 3 shows the graph m versus h in the case of DABCO, at room temperature. Fitting these data using eq 2 gave the following acidity constants: $pK_{a_1} = 3 \pm 0.1$ and $pK_{a_2} = 8.9 \pm 0.1$. An identical procedure is used in the case of imidazole (graph not shown here), and the fitted data lead to $pK_a = 7.0 \pm 0.1$.

The method using several pH measurements around the inflection points gave the same results. pK_a determinations are done up to 50 °C. Figures 4 and 5 show the variations of pK_{a_i} as a function of 1/T. Linear interpolations can be carried out and give

$$\text{DABCO:}\quad pK_{a_1} = \frac{1017.5}{T} - 0.24 \quad \text{and}$$

$$pK_{a_2} = \frac{1866.2}{T} + 2.55$$

$$\text{imidazole:}\quad pK_a = \frac{1917.7}{T} + 0.57 \quad \text{with } T \text{ in Kelvin}$$

Figure 6 shows extrapolations of acid dissociation constants of both amines as a function of T assuming that these relations hold up to 177 °C. Imidazole and DABCO exhibit a decrease in acidity constants with increasing temperature. Figure 6 also presents the similar variation known for pK_w of water in the same temperature range. These graphs reveal the ranges of pH that can be studied using two amines, as a function of temperature, knowing that they are best pH indicators around their pK_a values.

Determination of δ_i Values Characteristic of Amine Protonation States as a Function of Temperature. Fitting of δ_{obsd} versus h using eq 1 leads to determination of the δ_i chemical shifts of both amines. K_{a_i} values are determined at room temperature, h is known from potentiometric measurements at room temperature, and δ_{obsd} is measured at room temperature. The fits are shown in Figure 7 in the case of DABCO. They lead to the following values for the two amines:

$$\delta_0(\text{Im}) = -178.6 \pm 0.2 \text{ ppm}$$

$$\delta_1(\text{ImH}^+) = -209.3 \pm 0.2 \text{ ppm}$$

$$\delta_0(\text{DABCO}) = -369.9 \pm 0.2 \text{ ppm}$$

$$\delta_1(\text{DABCOH}^+) = -363.3 \pm 0.2 \text{ ppm}$$

$$\delta_2(\text{DABCOH}_2^{2+}) = -353.4 \pm 0.2 \text{ ppm}$$

The signal moves upfield by about 31 ppm when the imidazole is protonated, while it moves downfield by about 7 ppm for the first protonation of DABCO and by 10 ppm for the second protonation. The widths of the entire shielding ranges that are covered upon protonation of the amines are an important factor in estimating the precision of the pH probe. As will be emphasized later, chemical shifts obtained here permit precise pH measurements.

Variation of δ versus m with temperature is found to be negligible in the temperature range studied (up to 150 °C) in the case of DABCO, showing that DABCO δ_i variations with temperature are negligible. In the case of imidazole, there is a slight linear variation of δ_i with temperature. The following relations are obtained (T in Kelvin):

$$\delta_0(\text{Im}) = (9.12 \times 10^{-3})T - 180.0 \pm 0.2 \text{ ppm}$$

$$\delta_1(\text{ImH}^+) = (-3.40 \times 10^{-3})T - 207.5 \pm 0.2 \text{ ppm}$$

Calibration Curves and Sensitivities. Since δ_i and K_{a_i} parameters have been determined as a function of temperature, calibration relations can be established at different temperatures. Figure 8 shows for both amines the sigmoid curves δ_{obsd} versus pH obtained from potentiometric pH measurements and from ^{14}N chemical shift measurements at room temperature. Calibration functions can be calculated at any temperature using eq 1, and their derivatives $d(\delta_{obs})/d(pH)$ versus pH can be deduced. Figures 9 and 10 present results obtained at a temperature of 127 °C. The derivative function leads to an estimation of the sensitivity of each amine as a pH indicator, and it gives the pH ranges in which the amine can be used. The sensitivity is maximal at the pK_a values. It is better for imidazole, which presents a maximum $d\delta/d(pH)$ of about 18, compared to $d\delta/d(pH)$ sensitivities of less than 6 for DABCO. It is noticeable that the combined use of both amines permits pH variations to be followed from about 1.5 to 10.5 at room temperature and from 1 to 9 at 127 °C. The maximum slopes $d\delta/d(pH)$ obtained here are quite large, which will allow precise pH measurements. Table 1 reports characteristics of NMR probes (from our data and from the literature) comparing pK_a values, chemical

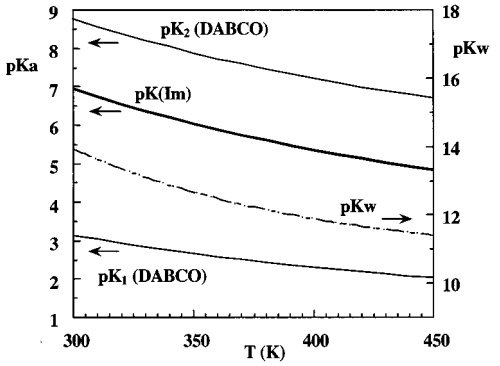

Figure 6. pK_w and extrapolations of pK_a values of the two amines as a function of temperature.

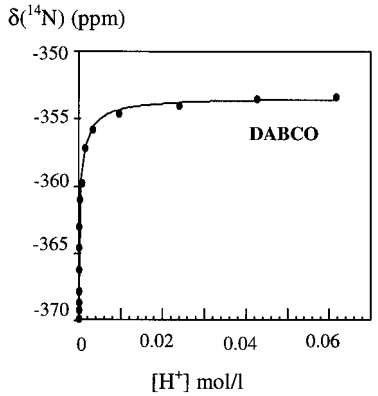

Figure 7. $\delta(^{14}N)$ of DABCO versus h at room temperature.

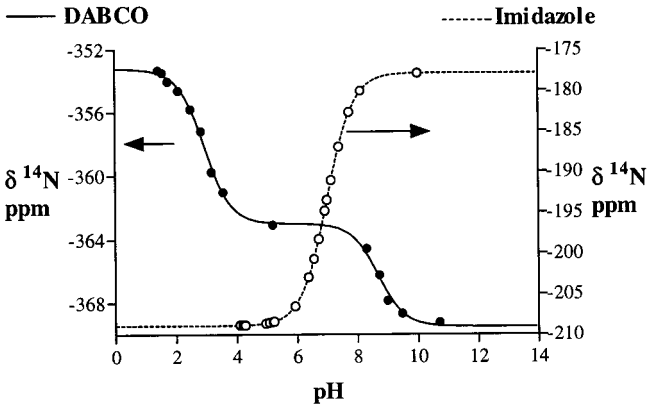

Figure 8. Calibration curves: ^{14}N chemical shifts of Im and DABCO versus pH at room temperature.

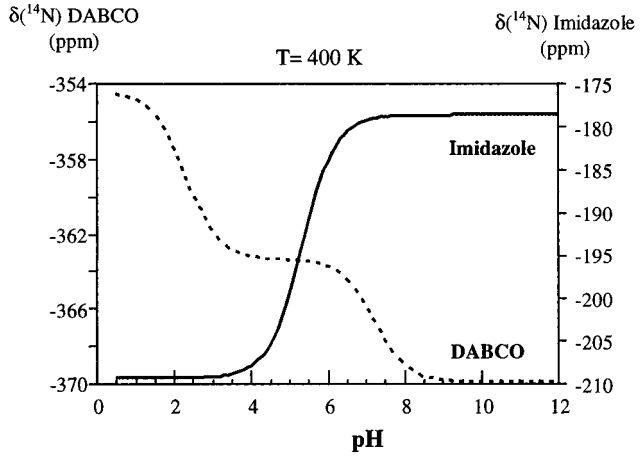

Figure 9. Calibration curves at 127 °C.

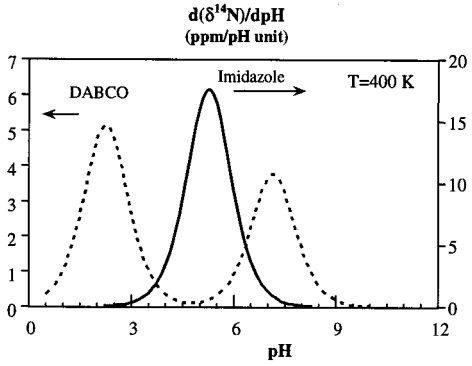

Figure 10. Sensitivities, $d\delta(^{14}N)/d(pH)$, of the two amines versus pH at 127 °C.

Table 1. Characteristics of NMR pH Probes from Our Data and from the Literature

NMR indicator	NMR nucleus	pK_a	$\Delta\delta$	$d\delta$/d(pH)
imidazole	^{14}N	7.0	31	18
DABCO	^{14}N	3.0	10	5.1
		8.9	6.6	3.8
H_3PO_4[a]	^{31}P	2	0.2	0.12
		6.6	2.4	1.4
		11.4	4.1	2.3
Im-(4-FC_6H_4)[52]	^{19}F	5.78	3.94	1.49
Im-CH_2-(4-FC_6H_4)[52]	^{19}F	6.58	1.78	0.66

[a] Data not shown here, from our laboratory.

shifts $\Delta\delta$ due to protonation of the base under study, and the sensitivity $d\delta$/d(pH) for each pK_a value. Sensitivities obtained with ^{14}N NMR pH probes are shown to be greater than what is usually reported in the literature using other NMR indicators. The average sensitivities encountered with fluorinated imidazoles or fluorinated compounds looking at $d\delta(^{19}F)/d(pH)$ are typically around 1 ppm/pH unit.

The relative error in the measurement of the pH by NMR can be estimated considering $\Delta pH = \Delta pK_{a_i} + (1/\ln 10)[(\Delta\delta_{obsd} + \Delta\delta_{i+1})/(|\delta_{obsd} - \delta_{i+1}|) + (\Delta\delta_{obsd} + \Delta\delta_i)/(|\delta_{obsd} - \delta_i|)]$. This expression shows the different sources of errors. A first type of error may be due to estimation of pK_a in the systems of interest at high temperature. Error in pK_a values arises from the extrapolation value of pK_a values at high temperature. In real systems chemical compositions and heating treatments in materials synthesis conditions influence their values. A second type of error may be due to chemical shift δ_{obsd} measurement. This error is larger in the case of the DABCO indicator than in the case of imidazole. DABCO lines are broader (from 450 Hz for $m = 0$ to 70 Hz for $m = 2$) than those of imidazole (from 140 Hz at $m = 0$ to 45 Hz at $m = 1$). It is also noticeable that the error increases with $\delta_{obsd}(\delta_i + \delta_{i+1})/2$, i.e., when pH is further apart from pK_a (Figure 10).

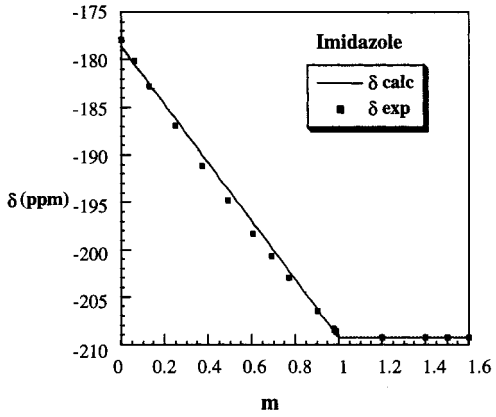

Figure 11. Experimental and calculated curves for $\delta(^{14}N)$ of imidazole as a function of m.

The stability of the δ versus pH calibration curve is evaluated as a function of the medium chemical composition at room temperature. As we are interested in our laboratory in understanding formation of alumina- and aluminophosphate-based materials, the δ−pH relation was tested in the presence of various quantities of phosphoric acid, aluminum nitrate, DABCO, and solid aluminum hydroxide. In that evaluation, DABCO is used as the pH probe and its ^{14}N chemical shift monitors the pH. The calculated pH values are compared to pH obtained from potentiometric measurements. The results reveal an accuracy of the DABCO probe of ±0.1 pH unit, around pK_a values. These experiments permit the sensitivity of the calibration curves to medium effects to be tested. The sensitivity to medium effects is also illustrated by comparing the simulated curve δ_{obsd} versus m to the experimental data. This comparison is shown in Figure 11 in the case of imidazole. The calculated curve presents a linear variation between $m = 0$ and $m = 1$, and a constant value out of the region of protonation changes (i.e., for m greater than 1). The small discrepancy between the calculated and the experimental curves, between $m = 0$ and $m = 1$, corresponds to a relative maximum error in the pH measurement of ±0.05 pH unit. This discrepancy arises from the small medium effects on ^{14}N NMR chemical shifts.

Applications

Hydrolysis and Condensation of Al^{3+} at 127 °C. Hydrolysis of aluminum cations followed by hydrothermal treatment leads to formation of aluminum hydroxide or aluminum oxyhydroxide depending on the temperature. The nature of the intermediate aluminum condensed species produced by forced hydrolysis is still a subject of controversy. To investigate the hydrolysis and condensation processes, ^{27}Al NMR is measured in situ under hydrothermal conditions to identify the species in solution.[21] The ^{14}N NMR measurements presented here were undertaken to follow pH variations while condensation reactions take place (total hydrolysis ratio (TMAOH + Im)/Al = 2.8).

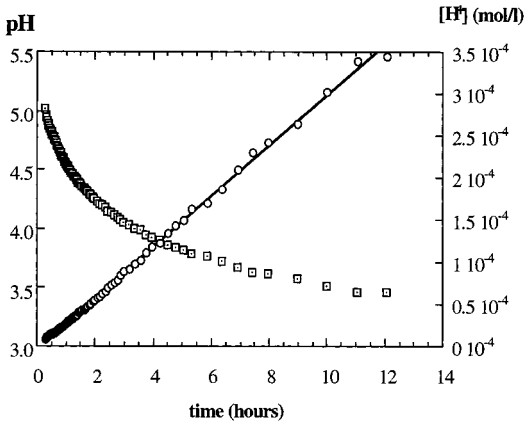

Figure 12. In situ H^+ concentration and pH evolutions at 127 °C during the hydrolysis of $Al(NO_3)_3$ with a hydrolysis ratio of 2.8.

Variation of the ^{14}N NMR chemical shift of imidazole is monitored as a function of time, and the pH is calculated. Figure 12 shows the pH variation and the *h* variation as a function of time. pH decreases from 5 to 3.4, and the H^+ concentration presents a linear increase with time, which suggests a zero-order kinetic reaction with respect to proton.

These data can be interpreted by the following processes.

First, hydrolysis reactions take place which lead to the rapid formation of OH ligands:

$$Al(H_2O)_6^{3+} + nOH^- \rightarrow Al(OH)_n(H_2O)_{6-n}^{(3-n)+}$$

Al−OH bonds then react quickly with each other to form di-μ^2-hydroxo bridges; this condensation reaction does not involve any acid−base reaction. These first steps lead to the formation of the observed white gel.

Condensation reactions between the remaining terminal OH groups and H_2O ligands can lead to formation of more di-μ^2-hydroxo bridges.

$$Al{-}OH + Al{-}OH_2 \rightarrow Al(OH)_2Al + H^+$$

This reactions takes place within the gel that quickly formed. It is a slow reaction which is controlled by diffusion within the gel phase. It involves an olation process with H^+ elimination. The NMR kinetics results show that the reaction rate is independent of time. The rate-limiting step is the time required for the remaining terminal OH groups and H_2O ligands to diffuse and react together.

After the rapid hydrolysis and condensation processes, changing H_2O ligands into OH groups that rearrange into di-μ^2 hydroxo bridges, condensation seems to go on within the gel in order to react with all the remaining terminal OH groups. This may lead to a higher overall hydrolysis ratio than 2.8 within the gel, leading to a more acidic solution.

Hydrothermal Synthesis of $AlPO_4$−CJ2 at 150 °C. The $AlPO_4$−CJ2 compound is synthesized hydrothermally in high-pressure NMR tubes, and its structure is checked by XRD.[66] Figure 13 shows pH variations obtained from monitoring DABCO ^{14}N NMR chemical shifts as a function of time during hydrothermal synthesis. Results indicate a rapid pH increase from about 3.5 to 6 at the beginning of the synthesis (during the first hour) and then a fairly constant pH value of about 6. This result indicates the protonation state of the DABCO molecules in the synthesis conditions: they are predominantly monoprotonated. The result also shows the presence of a first period of about 1 h during which the pH increases considerably. This occurs simultaneously to rapid dissolution of an initially formed amorphous phase. The final pH value of about 6 reveals pH conditions close to neutral since $pK_w = 11.5$ at 150 °C. This result is crucial when the formation mechanisms of the microporous structure are investigated, and especially the aluminum speciation in hydrothermal solution during synthesis. A neutral pH is consistent with the presence of pentacoordinated aluminum species, which were actually evidenced in the synthesis mixture at 150 °C.[66]

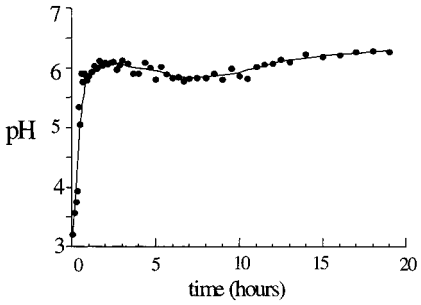

Figure 13. In situ pH evolution with time during the hydrothermal synthesis of $AlPO_4$−CJ2 at 150 °C.

Conclusions

^{14}N NMR chemical shifts of carefully selected amine compounds were shown to be useful and precise pH indicators in aqueous solutions, from room temperature to 200 °C. pH calibration relations, $\delta_{obsd}(^{14}N)$ versus pH, were established for two amines, imidazole and DABCO, possessing complementary pK_a values. Use of both amines permitted a wide range of about 9 pH units to be covered. Sensitivities expressed as $d\delta(^{14}N)/d(pH)$ are large and attained a maximum of 18 ppm per pH unit for imidazole. The applicability of the method was successfully demonstrated by following the pH during hydrothermal syntheses of inorganic materials. Kinetic data could be extracted from the pH results due to rapid acquisition of time-resolved spectra with a good signal-to-noise ratio. This NMR method for probing pH presents two major advantages. First, it allows pH measurements in heterogeneous environments, which is of particular importance when the formation of inorganic materials from gels is investigated, for example. Second, it permits the simultaneous characterization of pH evolution and metal condensation reactions by allowing alternating NMR experiments of different nuclei. Such experiments with simultaneous monitoring of the condensation rate and pH are now in progress.

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