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High-Resolution ^{27}Al NMR Shift Calculation for Aluminosilicate Species Structural Units (Q^n)/Q by Gaussian, Deconvolution and Resolution Enhancement Methods

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Abstract: Hartree-Fock self-consistent-field (HF-SCF) theory and the Gauge-including atomic orbital (GIAO) methods are used in calculation of ^{27}Al NMR chemical shifts for units of compounds of various aluminate species of precursors for zeolites. Calculations were performed at geometries optimized at AM_1 semi-empirical method. The GIAO-HF-SCF calculations were carried out using three different basis sets: 6-31G*, 6-31+G** and 6-311+G (2d, p). The intensity of partially overlapping NMR peaks may be separated by deconvolution into individual Gaussian component peaks. The relative concentrations of aluminosilicate species present as q^1, q^2, q^3 and q^4 structural units, have been estimated from integrated intensities of the corresponding signals. It is pertinent to notice that the spectra in and the estimated data showed that the intensity of q^4 (the band at lowest frequency) increased as Si/Al mole ratio (at constant Si=0.875 and TMAOH=1 M) decreased, i.e. with increasing aluminates concentration. However, the bands become broader as the concentration of Al increased, so that the operation of backward linear prediction (BLP) is of variable effect. From this study, one can expect that cage-like species might be dominant due to the stability of the corresponding silicate anions in TMAOH silicate solutions. The formation of three-member rings apparently causes some deshilding compared to the chains or larger rings.

Key words: Gaussian; Deconvolution; ^{27}Al NMR; Aluminosilicate; Chemical shift

INTRODUCTION

The intensities of peaks observed in ^{27}Al NMR spectra are directly related to the number of corresponding aluminium atoms present in the investigated sample. Therefore, from the relative peak intensities the quantitative proportions of various Al sites of the sample can be determined directly. Absolute concentrations of Al may be estimated by comparison with the peak intensities of a standard sample of known composition, which may be mixed in a certain amount with the unknown sample, or may be measured in a separate experiment performed under the same conditions as used for the sample under investigation [1-4]. The work was carefully carried out on the effect of varying Al concentration on ^{27}Al NMR spectra at constant Si and TMAOH concentrations.

The relative concentrations of aluminosilicate species present as q^1, q^2, q^3 and q^4 structural units, which have been estimated from integrated intensities of the corresponding signals, are listed. The spectra in and the estimated data showed that the intensity of q^4 (the band at lowest frequency) increased as the Si/Al mole ratio (at constant Si=0.875 and TMAOH=1 M) decreased, i.e. with increasing aluminates concentration.

Deconvolutions and resolution enhancements were carried out using Lorentz-Gauss transformation. In order to achieve maximum accuracy for the baseline subtraction some ways of compensating for this signal were tried. BLP method was used and Hartree-Fock ^{27}Al chemical shifts using HF/6-31G* method were carried out.

Organic pollution in industrial waste streams is continuously increasing in quantities which cause environmental concern. Adsorption has been applied to

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remove organics from aqueous phase. Commonly novel class of aluminosilicate-based microporous materials with good adsorption capacity and high selectivity are recommended. In order to adsorb selectively the organic molecules from aqueous phase, adsorbents must be hydrophobic [5, 6]. Also, high ratio zeolites are used for such purposes. The important parameters in determination of the selectivity and adsorption capacity of these adsorbents are hydrophobicity of the adsorbent, size of the organic molecules and diameter of the channels which are accessible to adsorbate. Therefore, it is necessary to investigate any further influential factor regarding the aluminosilicate species defined as q^1, q^2, q^3 and q^4 structural units.

MATERIALS AND METHODS

Aqueous sodium aluminate solution was prepared by dissolving $NaAlO_2$ in double distilled water. Aluminosilicate solutions were then obtained by mixing the freshly prepared sodium aluminate and alkali silicate solutions in the correct proportions for our investigations. In this section, the reported results for the solutions with [Si] and [TMAOH] were 0.875 and 1 molar, respectively. The [Si/Al] ratios of 5, 10, 20 and 50 were investigated.

The NMR spectra of ^{27}Al were obtained using Varian VXR 600 spectrometer at 166.3 MHz and ca. 25°C by applying 90° pulses; the time elapsing between pulses being sufficient to allow complete return of the magnetisation to equilibrium. The samples contained 15% D_2O, the D_2O signal served as a field-frequency lock. The probe used for the experiments involved components containing aluminium, so that a broad background signal centred at $\delta \approx 60$ ppm (the same region as the q^4 peak) could be observed [5].

Deconvolutions and resolution enhancements were carried out using the Lorentz-Gauss transformation. In order to give maximum accuracy for the baseline subtraction some ways of compensating for the signal were tried. It was found that the backward linear prediction for the first 12 points of the FID gives spectra of good apparent quality. Therefore, these numbers of points were used in BLP to obtain the spectra of figures, making many aspects of interpretation easier. Hartree-Fock ^{27}Al chemical shifts were calculated using HF/6-31G* method.

RESULTS AND DISCUSSION

Fig. 1 shows ^{27}Al NMR spectra of four samples of aluminosilicate solutions with constant concentrations of

Si and TMAOH equal to 0.875 and 1 M, respectively. But, the Al concentration was changed to obtain solutions with Si/Al ratios of 5, 10, 20 and 50. These spectra were obtained with the same processing parameters (such as BLP number, vertical and horizontal scales and line broadening (lb) and used the absolute intensity (ai) mode. The spectra in Fig. 1 illustrate that we have molecular species which contain aluminium in tetrahedral environments with various structures. The spectra are characterized by at least four distinct bands. The bands appearing at 74-77, 68-73, 63-67 and 52-63 ppm are assigned to q^1, q^2, q^3 and q^4, respectively. These ranges of chemicals shifts for different q^n units were confirmed with Hartree-Fock. ^{27}Al chemical shifts were calculated using the HF/6-31G* method.

It is clear from these spectra that the peak assigned to q^4 showed the highest intensity, which indicates that the solutions were dominated by q^4 environments. This phenomenon can be expected since the corresponding TMAOH silicate solution may react with aluminium ions without breaking Si-O-Si bonds on the formation of cubic octamer aluminosilicates in TMA aluminosilicate solutions. As the mole percent of Al increases, the signal-to-noise ratio improves, but the features of the spectra do not change substantially. However, the spectra significantly changed with different Si concentrations [1, 4].
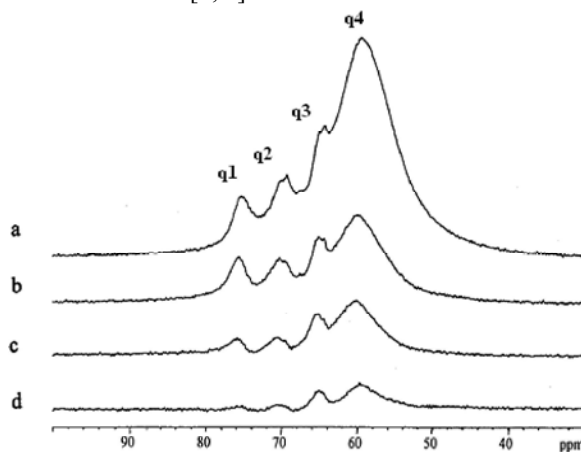

Fig. 1: High-resolution ^{27}Al NMR spectra at 156.3 MHz of TMAOH aluminosilicate solutions of one molar TMAOH, 0.875 molar SiO_2 and Si/Al ratios: a=5, b=10, c=20 and d=50 at 25°C. The spectra were taken in two weeks after mixing. Spectrum conditions: Spectral width 29996 Hz, acquisition time 0.02 s, recycle delay 0.10 s, pulse angle 158.8° (34 μs), number of transients 2048. All spectra were obtained with the same processing. Line broadening was not used. BLP 12
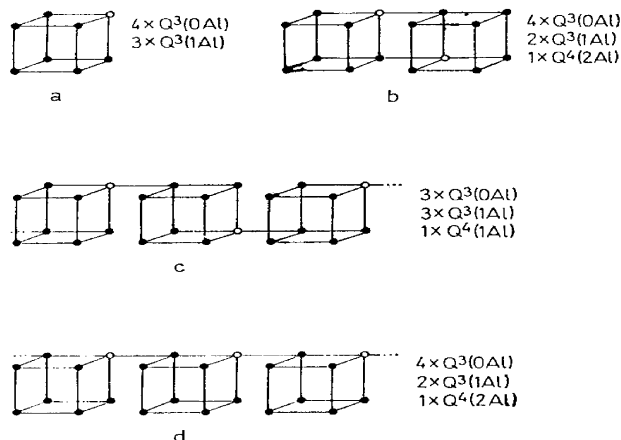
Fig. 2: Schematic representation of the formation of q^4 sites. Open circles represent aluminium atoms and filled circles indicate silicon atoms

Table 1: Data obtained from the deconvolution of Fig. 3

Peak No.	Chemical shift/ppm	Peak Height	Peak Width/kHz	Integral ratio *
1	75.3	27	0.47	1.00
2	69.9	26	0.53	1.10
3	64.8	24	0.29	0.60
4	59.0	114	1.38	12.7

* Relative to peak 1

Table 2: Estimated mole % of aluminosilicate species structural units $(q^n)/q$ for the solutions giving the spectra shown in Fig. 1

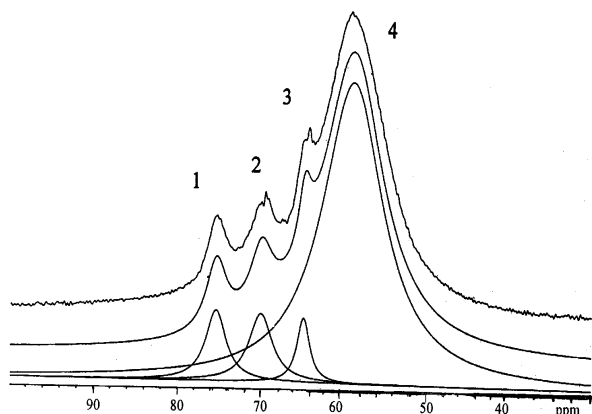| [Si]/[TMAOH]*	[Si]/[Al]	q^1%	q^2%	q^3%	q^4%
0.875	5	6.5	7.0	4	82.0
0.875	10	6.0	2.0	12	72.0
0.875	20	7.5	10.0	12	71.0
0.875	50	4.5	9.5	23	63.5

*Molarity of TMAOH=1

Fig. 3: Deconvolution experiment. Top: actual spectrum of a sample with 1M TMAOH, 0.875 M Si and Si/Al=5; centre: full fitted spectrum and bottom: individual component plots. For the caption of the experimental spectra see the caption of Fig. 1

The peaks intensities observed in the ^{27}Al NMR spectra were directly related to the number of the corresponding aluminium atoms present in the sample being investigated. Therefore, from the relative peak intensities the quantitative proportions of the various Al sites of the sample can be determined directly.

From Fig. 1, one can expect that cage-like species such as Fig. 2 might be dominant due to the stability of the corresponding silicate anions in TMAOH silicate solutions. Fig. 2 shows a schematic representation of the formation of q^4 sites. Aluminosilicate ions can react, without breaking Si-O-Si bonds, in a manner consistent with the observation [5]. They suggested q^4 formation through linkage of Al-O-Si units as presented in Fig. 2.

Absolute concentrations of Al may be estimated by comparison with the peak intensities of a standard sample of known composition, which may be mixed in a certain
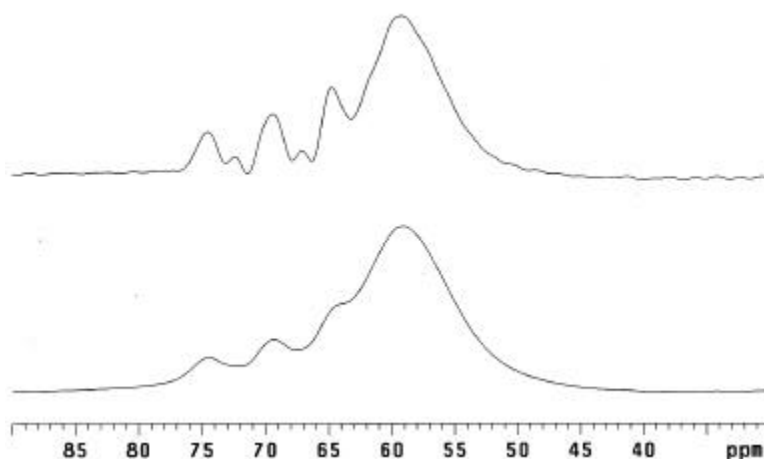
Fig. 4: High-resolution ^{27}Al NMR spectra at 156.3 MHz of TMAOH aluminosilicate solution of the composition of one molar TMAOH, 0.875 molar SiO_2 and Si/Al ratio = 5 at 0°C. The spectra were taken in two weeks after mixing. Spectrum conditions: Spectral width 29996 Hz. Acquisition time 0.02 s. Recycle delay 0.100 s. Pulse angle 158.8° (34 μs). Number of transients is 2048

amount with the unknown sample, or may be measured in a separate experiment performed under the same conditions as used for the sample under investigation.

For structural considerations, the relative numbers of Al atoms present in the distinct sites are mostly sufficient. These can be obtained directly from the normalised intensity ratios of different signals in the spectrum. The intensity of partially overlapping peaks may be separated by deconvolution into individual Gaussian component peaks.

A typical deconvolution experiment for spectrum (a) of Fig. 1 is shown in Fig. 3 and the detailed results are shown in Table 1. For brevity, the other experiments for the spectra b-c are not shown here and just the calculated values of q^1, q^2, q^3 and q^4 are inserted in Table 2.

The relative concentrations of aluminosilicate species present as q^1, q^2, q^3 and q^4 structural units, which have been estimated from the integrated intensities of the corresponding signals of Fig. 1, are listed in Table 2. It is pertinent to notice that the spectra in Fig. 1 and the data in this table show that the intensity of q^4 (the band at lowest frequency), seems to increase as the Si/Al mole ratio (at constant Si=0.875 and TMAOH=1 M) decreases, i.e. with increasing aluminate concentration. However, the bands become broader as the concentration of Al increases, so that operation of BLP is of variable effect.

The spectra in Fig. 4 are of a TMAOH aluminosilicate solution with a Si/Al ratio of 5 at 0°C. The upper trace was obtained using a Lorentz-Gauss transformation and

shows further distinct peaks with respect to the bottom spectrum. The latter shows no peak at shifts of about 67 and 72.5 ppm but these clearly appear in the upper spectrum. Although it is difficult to say exactly which kinds of aluminate species correspond to these signals, on the basis of shielding arguments they are tentatively assigned to Al atoms in anions involving cyclic trimers. For better understanding of the chemical shifts of such trimers were calculated from the Gaussian software after geometry optimization [6], which have a good agreement with the experiment (see Figure 6 in reference [6]). As the same experimental values, five well separated subdivisions have been found which correspond to five possible q^n building units, followed in a regular sequence by q^1 to q^4 units shifted by about 5 ppm to lower frequency (high field) for each newly formed AlOSi bond. The formation of the three-member rings apparently causes some deshilding compared to chains or larger rings. As the same as the experiment, the deshilding effect of this type of species, also could be seen from our calculated values which were not shown here; more details are provided in the literature [7].

However, the apparent resolution of these bands is a direct consequence of using the Lorentz-Gauss transformation, since such peaks have not been observed in aluminosilicate spectra of these compositions, which were not resolution-enhanced [8]. Therefore there are some other facts for resolution of spectra that should also be mentioned as the use of exponential/Gaussian resolution enhancement.

CONCLUSION

From the above discussion and evaluation of the effect of Al concentration on ^{27}Al NMR spectra which discussed elsewhere; one can expect that cage-like species such as Fig. 2 might be dominant due to the stability of the corresponding silicate anions in TMAOH silicate solutions. Resolution of these bands is a direct consequence of using the Lorentz-Gauss transformation, since such peaks have not been observed in aluminosilicate spectra of these compositions, which were not resolution-enhanced. Therefore, the exponential/ Gaussian resolution could be used for the enhancement of the resolution of spectra that should also be mentioned.

However, qualitative or semi-quantitative information on the presence of different AlOH groups may be obtained from comparison of the corresponding intensities observed in the spectra.

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