Exchange reactions in aluminosilicate solutions

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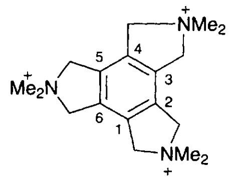
Aluminium-27 NMR spectra at 156.3 MHz for alkaline aqueous aluminosilicate solutions show that full equilibria between species is approached slowly at room temperature but that some exchange processes are rapid.

Alkaline aqueous solutions of silicates contain a variety of anionic species in dynamic equilibrium. Silicon-29 NMR has proved to be the most valuable tool for obtaining information about the molecular structures (see, for example, ref. 1): Aluminosilicate solutions are even more complex, and although both ^{29}Si and ^{27}Al NMR[2–6] have been used to considerable effect, uncertainties about the nature of the species present and their equilibria remain. Both silicate and aluminosilicate solutions are of immense industrial significance, the latter being involved in the synthesis of zeolites. We have undertaken new



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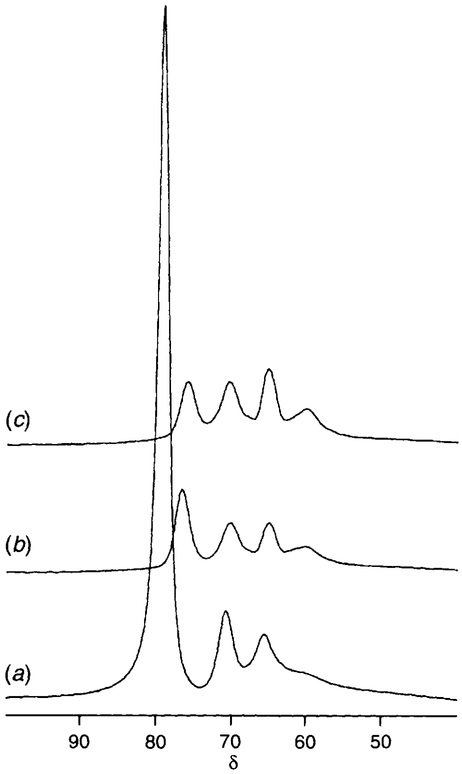

Fig. 1 156.3 MHz ^{27}Al NMR spectra at *ca.* 25 °C for a HMBTP solution (see text): (*a*) within 2 min of mixing the components; (*b*) 3 h after mixing; (*c*) 16 h after mixing. A 90° flip angle of 45 μs was used, with a recycle delay of 0.1 s and 960 transients for each spectrum. Chemical shifts are referenced to the signal for aqueous aluminium trichloride, *i.e.* to the $Al(H_2O)_6^{3+}$ cation.

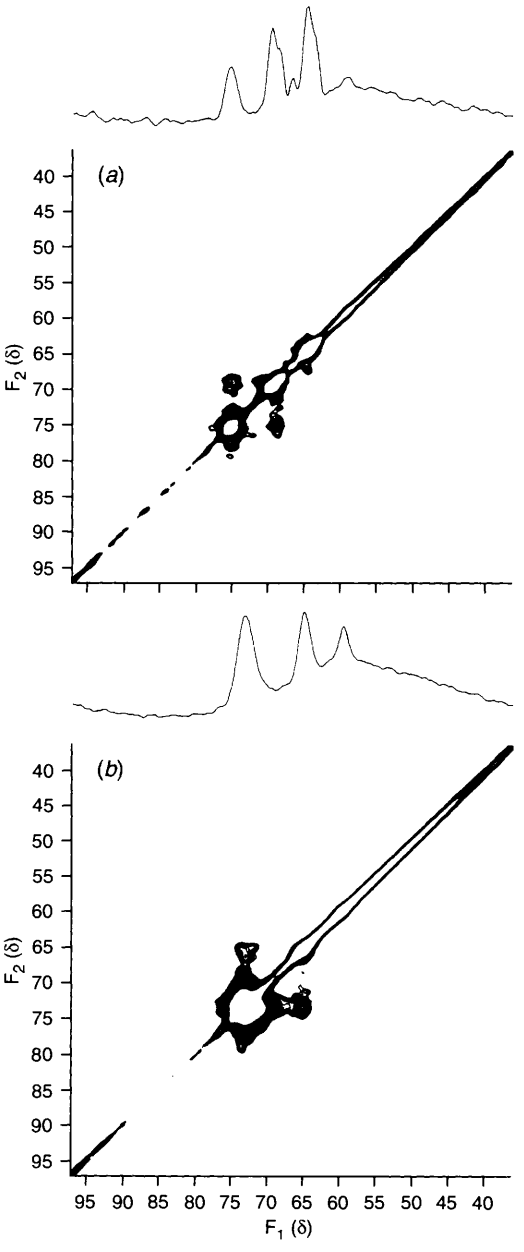

Fig. 2 156.3 MHz ^{27}Al NMR exchange spectra of the solution described in the text, approximately two weeks after preparation, at (*a*) 10 °C and (*b*) 75 °C. The recycle delay was 0.05 s and 128 transients were accumulated for each of 64 increments in t_1, with zero-filling before Fourier transformation.

^{27}Al NMR experiments at the highest magnetic field available to us (14.1 T, with aluminium resonance at 156.3 MHz) in order to understand the dynamics of aluminosilicate solutions. Specifically we have (*a*) studied for the first time the evolution of the ^{27}Al NMR spectra with time, and (*b*) examined two-dimensional EXSY spectra as a function of temperature. The novel triply-charged species **I**, referred to here as HMBTP, has been used as the organic counter-ion. We have synthesized HMBTP hydroxide using a procedure slightly modified from that in ref. 7. It is of interest as a template because of its triple charge, and it leads[8] to the synthesis of a unique zeolite, ZSM-18.

Fig. 1 shows ^{27}Al NMR spectra at ambient probe temperature (*ca.* 25 °C) of an aqueous solution prepared, with rapid mixing, by addition of an equal volume of fresh sodium aluminate ($NaAlO_2$) solution to an aged HMBTP silicate solution, with final composition: 0.875 mol dm^{-3} SiO_2, Si:HMBTP = 2:1 and Si:Al = 5:1. There is clearly rapid appearance of peaks arising from species other than monomeric aluminate anions, but there are also slow changes in the spectra. Ultimately four peaks are observed, the lower frequency ones developing with time at the expense of the one at highest frequency. A crucial observation is that the latter (and only the latter) significantly changes in chemical shift with time. Bell and coworkers[6] have made a similar observation for tetraalkylammonium aluminosilicate solutions as a function of Si:Al ratio. They decided it resulted from an exchange reaction, but their conclusions appear clouded by a problem over peak assignments. Apparently contrary to earlier workers,[3,5] they assign the analogous peaks to the four in Fig. 1(*c*) to q^0, q^1, q^2 and q^3, where q stands for the tetrahedral AlO_4 environment and the superscript gives the number of siloxane bridges.

The previous reports[3,5] suggested the lowest-frequency band is q^4. Moreover, the assignment of Bell and coworkers[6] takes no obvious account of the exchange phenomenon.[4] It is our belief that the earlier workers are correct and that the highest frequency peak arises from averaging of q^0 and q^1 environments, the shift with time (and with Si:Al ratio) being a measure of changes in the $q^0:q^1$ ratio, as suggested in ref. 4 for shift variations with Si:Al ratio. Any q^4 peak presumably relates to a potential Brönsted acid site.

Our two-dimensional experiments support such a conclusion by proving the occurrence of a variety of exchange processes as the temperature varies. Figs. 2(*a*) and (*b*) show EXSY spectra of a fully equilibrated solution for a mixing time of 1 ms taken at (*a*) 10 °C and (*b*) 75 °C, one-dimensional projections being shown above them. In (*a*) the peak at δ ca. 75 can be assigned primarily to q^1 (with perhaps a little q^0 in rapid exchange). The small off-diagonal peaks show exchange beginning with q^2 (but not q^3 or q^4). At 75 °C the q^1/q^2 peaks have merged at δ *ca.* 73, and off-diagonal peaks indicate some exchange with q^3. Naturally, the peaks not involved in exchange do not vary in chemical shift. These experiments show, as is to be expected, that exchange of Al sites bonded to silicate units is increasingly inhibited as the number of siloxane bridges increases. Thus cage structures involving aluminium have relatively long lifetimes, a fact we believe to be of significance for zeolite synthesis. Also particularly relevant is the occurrence of q^4 sites under conditions where analogous silicate solutions contain no detectable Q^4 environments. The relatively slow approach to full equilibrium at room temperature is clearly related to the variation in exchange rates for different species, but is yet to be explained in detail.

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