

The Gelation Behaviour of Aluminosilicate Solutions containing Na⁺, K⁺, Cs⁺, and Me₄N⁺

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The rate of gelation of aluminosilicate solutions depends on the cation present; solutions containing Na⁺, K⁺, Cs⁺, and Me₄N⁺ have been investigated, and some n.m.r. evidence is presented.

The gelation of potassium aluminosilicate solutions (contour plot, Figure 1, darker shading = longer gel times) has been found to depend on alkali and silica concentration in an unexpected way.¹ At low silica concentrations the time taken for the solutions to gel increased as more alkali was present. At high silica concentrations the opposite was true; the

solutions with the lowest amounts of alkali had the longest gel times. A region of minimum gel times separates the two types of behaviour.

Similar solutions containing cations other than potassium have now been studied. The test solutions were prepared in the same way as the potassium aluminosilicate solutions,

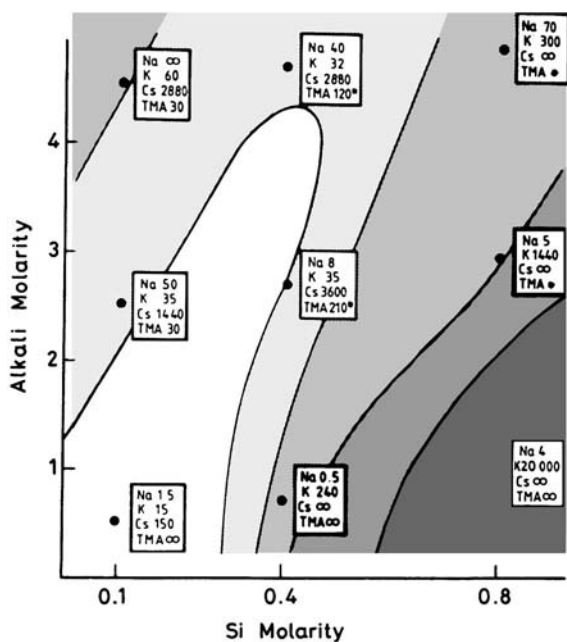


Figure 1. Gel times (min) for selected Na, K, Cs, and TMA aluminosilicate solutions, superimposed on a contour plot showing the behaviour of potassium aluminosilicate solutions (adapted from ref. 1). Unshaded region, gel time <30 min. Successively darker shadings indicate gel times of (1) 30 min to 1 h, (2) 1 h to 1 day, (3) 1 day to 1 week, and (4) more than 1 week, for the potassium system. * Indicates the presence of aluminosilicate crystals.

substituting sodium, caesium, or tetramethylammonium (TMA) for potassium. The solubilities in the lithium system are too low to permit analogous studies. As before the time from mixing to gel formation (or other behaviour) was noted (Figure 1).

Changing the cation has a profound effect on the behaviour of the solutions. In terms of the topography displayed by the potassium system (contours, Figure 1) the pattern of behaviour in the sodium system seems to be displaced towards the top left hand corner of the diagram, in that reaction times increase with increasing alkali regardless of how much silica is present. The highly alkaline solutions put down a white amorphous precipitate rather than gelling; reaction times are in most cases faster than for the equivalent potassium solutions.

The behaviour of the caesium system, on the other hand, seems to be shifted towards the bottom right of the potassium diagram. Gelation times are generally much longer than for the corresponding potassium solutions, and are particularly retarded in the solutions of highest silica content.

The pattern for the TMA solutions is complicated by the formation of crystalline aluminosilicate compounds² from the high silica, high alkali solutions. In contrast to the pattern for caesium, it is the low alkali solutions that are particularly inert. There is not, therefore, a smooth trend in behaviour with cation size.

It is still not clear why behaviour should depend on cation in this particular way. Studies by n.m.r. spectroscopy on alkaline silicate³ and aluminate⁴⁻⁶ solutions, show no significant variation with cation, except for TMA silicate solutions.⁷ So there seems to be little difference in the anionic species present before mixing. ²⁹Si N.m.r. spectra of the mixed solutions show only subtle differences from those of the

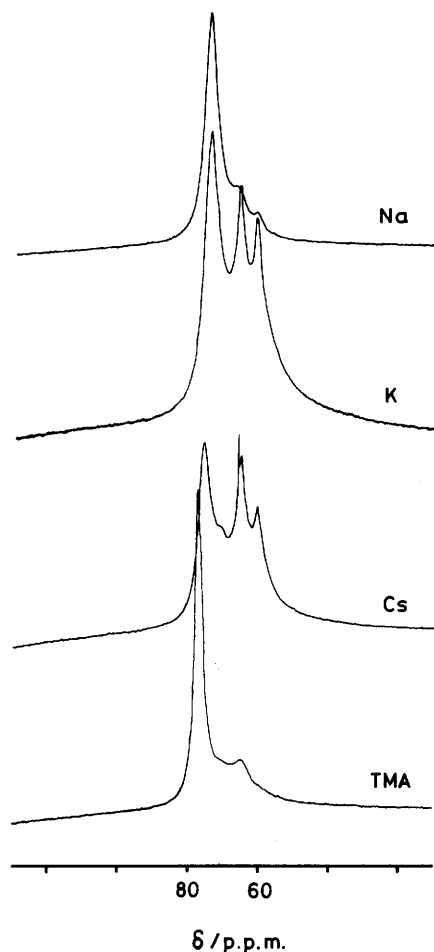


Figure 2. ²⁷Al N.m.r. spectra of aluminosilicate solutions corresponding to the composition at the top right of Figure 1 (0.1 M Al, 0.8 M Si, and 4.98 M alkali). The spectra were obtained at 93.841 MHz on a Bruker WH-360 spectrometer. The acquisition time was 0.067 s for the potassium spectrum and 0.0338 s for the others. The number of pulses obtained was Na = 12 913, K = 12 252, Cs = 33 125, and TMA = 5 145. The data were collected in 2 K and transformed in 32 K and the observed peaks are plotted relative to an external standard of Al(H₂O)₆³⁺.

original silicate solutions. In contrast, ²⁷Al n.m.r. spectra are often profoundly changed. In general, the 'inert' solutions that have high alkali contents seem to have the aluminate present largely in the uncomplexed form, Al(OH)₄⁻. 'Inert' solutions with low alkali, on the other hand, show little or no uncomplexed aluminate. For a given alkali-silicate-aluminate composition, the distribution of aluminium between uncomplexed aluminate and aluminosilicate complexes may vary with the cation present (Figure 2). The effect of the cation on gelation is thus structural, and not merely a reflection of simple electrostatic association with the colloid species.

The behaviour of caesium is particularly interesting as it may explain why caesium zeolites are formed only with great difficulty.^{8,9} It is also of significance in relation to the attempted immobilisation of ¹³⁷Cs-containing radioactive wastes in aluminosilicate systems such as cements and concretes.

We wish to thank the S.E.R.C. and Unilever Research for a C.A.S.E. studentship for G. H., and also Drs. Sadler and

Reed at the University of Edinburgh for help in obtaining the n.m.r. spectra.

Received, 4th June 1984; Com. 773

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