Interactions of Silicate Ions with Zinc(II) and Aluminum(III) in Alkaline Aqueous Solution

*Michel R. Anseau, Jennifer P. Leung, Nita Sahai and Thomas W. Swaddle**

Supporting Information

Figure S1. ^{29}Si spectrum of $1.69 \text{ mol L}^{-1} \text{ SiO}_2$ dissolved in $6.4 \text{ mol L}^{-1} \text{ KOH}$ (i.e., $1.69 \text{ mol L}^{-1} \text{ Si(OH)}_2\text{O}_2^{2-}$ and $3.0 \text{ mol L}^{-1} \text{ OH}^-$) at 280 K. Circles in skeleton structures represent Si atoms; filled circles represent positions of ^{29}Si nuclei giving rise to the peak indicated.

Figure S2

Figure S2. ^{27}Al spectra of solutions of Al in 15.0 mol kg^{-1} NaOH at 298 K, relative to $\delta(^{27}\text{Al}) = 0$ for 0.56 mol L^{-1} aqueous AlCl_3 (top spectrum); details are given in Table 2.

Figure S3

Figure S3. ^{29}Si NMR spectra of a solution containing 15.0 mol kg^{-1} NaOH, 0.59 mol kg^{-1} Si^{IV} , 0.61 mol kg^{-1} Zn^{II} , and 0.58 mol kg^{-1} Al^{III} at 280, 298, and 315 K. For the larger peaks F, G and H, $\delta(^{29}\text{Si}) = -72.2$, -72.2 , and -72.1 ppm, with line widths 43, 31 and 13 Hz, respectively. For peaks I, J and K, the corresponding data are $\delta(^{29}\text{Si}) = -77.2$, -77.1 , and -77.0 ppm, with line widths 30, 14, and 8.2 Hz.

Table S1. ^{29}Si Chemical Shifts δ and Line Widths W Relevant to the Calculation of the Rate Constant k for the Exchange of $[(\text{HO})_3\text{ZnOSiO}_2\text{OH}]^{4-}$ (“Zn”) with $[(\text{HO})_3\text{AlOSiO}_2\text{OH}]^{3-}$ (“Al”) at Variable Temperature According to Eq 4.^a

Temp./K	280	298	315
$\delta_{\text{Zn}}/\text{ppm}$	−69.9	−69.7	−69.5
$\delta_{\text{Al}}/\text{ppm}$	−75.3	−75.0	−74.8
$\delta_{\text{AlZn}}/\text{ppm}$	−72.2	−72.2	−72.1
$C_{\text{Si}}/\text{mol kg}^{-1}$	0.515	0.539	0.536
f_{Zn}^b	0.570	0.520	0.505
f_{Al}^b	0.430	0.480	0.495
$\Delta\nu/\text{Hz}$	326	319	313
W_{Zn}/Hz	2.6	3.5	3.6
W_{Al}/Hz	40.4	12.8	5.7
$W_{\text{ZnAl}}/\text{Hz}$	43.3	30.6	12.8
$k/10^4 \text{ kg mol}^{-1} \text{ s}^{-1}$	2.6 ^c	2.6 ^c	7.0
$k/10^4 \text{ kg mol}^{-1} \text{ s}^{-1}$	1.6 ^d	2.3 ^c	7.0

^a $[\text{NaOH}] = 15.0 \text{ mol kg}^{-1}$; $[\text{Si}]_{\text{total}} = 0.591 \text{ mol kg}^{-1}$; $[\text{Zn}]_{\text{total}} = 0.613 \text{ mol kg}^{-1}$; $[\text{Al}]_{\text{total}} = 0.578 \text{ mol kg}^{-1}$. ^bFrom chemical shifts. ^cUsing the tabulated W_{Al} . ^dUsing $W_{\text{Al}} = 5.7 \text{ Hz}$ at all temperatures to show impact of this quantity.

Table S2. ^{29}Si Chemical Shifts δ and Line Widths W Relevant to the Calculation of the Rate Constant k for the Exchange of $[(\text{HO})_3\text{ZnOSiO}_2\text{OH}]^{4-}$ (“Zn”) with $[(\text{HO})_3\text{AlOSiO}_2\text{OH}]^{3-}$ (“Al”) at Variable Composition According to Eq 4.^a

$[\text{Si}]_{\text{total}}/\text{mol kg}^{-1}$	0.559	0.591	0.575	0.567
$C_{\text{Si}}/\text{mol kg}^{-1}$	0.505	0.538	0.519	0.511
$[\text{Zn}]_{\text{total}}/\text{mol kg}^{-1}$	0.306	0.613	0.710	0.865
$[\text{Al}]_{\text{total}}/\text{mol kg}^{-1}$	0.817	0.578	0.417	0.311
f_{Zn}^b	0.333	0.520	0.611	0.685
f_{Al}^b	0.667	0.480	0.389	0.315
$\delta_{\text{AlZn}}/\text{ppm}$	-73.2	-72.2	-71.7	-71.3
$W_{\text{AlZn}}/\text{Hz}$	32.8	30.6	22.9	18.7
$k/10^4 \text{ kg mol}^{-1} \text{ s}^{-1 c}$	2.4	2.6	3.7	4.4
$k/10^4 \text{ kg mol}^{-1} \text{ s}^{-1 d}$	2.0	2.3	3.2	3.7

^a At 298 K; $[\text{NaOH}] = 15 \text{ mol kg}^{-1}$; $\delta_{\text{Zn}} = -69.65 \text{ ppm}$; $\delta_{\text{Al}} = 75.0 \text{ ppm}$; $\Delta\nu = 319 \text{ Hz}$; $W_{\text{Zn}} = 3.5 \text{ Hz}$.
^b From chemical shifts. ^c $W_{\text{Al}} = 12.8 \text{ Hz}$ (measured, 298 K). ^d $W_{\text{Zn}} = 5.7 \text{ Hz}$ (as for 315 K).

Complete reference (32): Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A.D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Gaussian Inc.: Pittsburgh, PA, 1998.