

## Sorption of Alkanediols by Silicalite-1

STUART G. FEGAN and BARRIE M. LOWE

*Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, U.K.*

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**Abstract.** Isotherms for the sorption of linear alkanediols  $\text{HO}(\text{CH}_2)_n\text{OH}$  ( $n = 2, 4, 6, 8$ ) from aqueous solution by silicalite-1 at  $25^\circ$  are reported.

**Key words.** Sorption, silicalite-1, alkanediols, ethane-1,2-diol, butane-1,4-diol, hexane-1,6-diol, octane-1,8-diol.

### 1. Introduction

The selective sorption of organic compounds from dilute aqueous solutions by the silica molecular sieve silicalite-1 has been the subject of several recent investigations [1–8]. Much work has been concerned with the energy efficient separation of alcohols from fermentation beers [5–8]. The preferential uptake of organic solutes from aqueous solution has also considerable relevance to the crystallisation of silica molecular sieves and high silica zeolites from aluminosilicate gels. Organic void-filling molecules are often required to stabilise silica-rich frameworks during crystallisation [9, 10]. Alkanediols are of particular interest as pore-filling entities as they can be used to stabilise the commercially important high silica zeolite ZSM-5 [11]. In this paper we report post-synthesis alkanediol sorption by silicalite-1, the silica molecular sieve isostructural with ZSM-5 [12, 13].

### 2. Experimental

Silicalite was crystallised at  $95^\circ\text{C}$  from a stirred reaction mixture of composition  $3.5 \text{ Na}_2\text{O} \cdot 2 \text{ TPABr} \cdot 20 \text{ SiO}_2 \cdot 1000 \text{ H}_2\text{O}$  (TPA = tetra-propylammonium). Fully crystalline (Na,TPA)-silicalite-1 was obtained in 5 d. This product was calcined at  $450^\circ\text{C}$  for 48 h, washed with water, twice treated with  $1 \text{ mol dm}^{-3} \text{ NH}_4\text{Cl}$  ( $10 \text{ cm}^3 \text{ g}^{-1}$ ) at  $80^\circ\text{C}$  for 16 h, and then further calcined ( $450^\circ\text{C}$ , 48 h;  $550^\circ\text{C}$ , 12 h). The final product was equilibrated with water vapour ( $a_w = 0.753$ ,  $25^\circ\text{C}$ ). Duplicate thermal gravimetric analyses (TGA) of the equilibrated solid showed it contained 2.85% (w/w) water. Ethane-1,2-diol (SLR) was obtained from Fisons; butane-1,4-diol (99 + %), hexane-1,6-diol (99%) and octane-1,8-diol (96%) were from Aldrich.

Mixtures of silicalite and diol solutions were prepared by weight and were tumbled in closed flasks in a thermostat bath at  $25.0 \pm 0.1^\circ\text{C}$ . Equilibrium was reached within 12 h. The silicalite was then isolated by filtration, washed with small aliquots of cold water to remove adherent solution, dried, equilibrated with water vapour ( $a_w = 0.753$ ,  $25^\circ\text{C}$ ) and analysed by TGA to determine the amount of sorbed organic per unit weight of dry solid.

### 3. Results and Discussion

The TGA curves showed low and high temperature weight losses, due to water and organic material respectively. The losses did not significantly overlap and both the water and the organic content could be determined without difficulty even when the organic loading was low. The equilibrium concentration of the solution was determined from the difference between the initial weight of diol in solution and the total weight of diol sorbed by the silicalite, together with the weight of water in the initial solution. Transfer of water between the silicalite and the solution was considered to be negligible. In some cases equilibrium was achieved by desorption of organic from a prior-loaded sample of silicalite. The results are unlikely to be significantly affected by traces of water which may have been present in the diols, and no evidence of selective sorption of organic impurities was apparent in the TGA curves.

The amount of organic solute sorbed by the molecular sieve showed a marked dependence on the equilibrium concentration of the solution (see Figure 1) and was independent of the way in which the equilibrium was attained. For each sorbate the uptake  $U$  rose over a narrow concentration range from a low value ( $U < 0.02 \text{ g g}^{-1}$ ) to a plateau region corresponding to the maximum sorption capacity. The concentrations at which the plateaux were attained showed a marked decrease as the length of the alkane chain increased and were approximately 3.0,

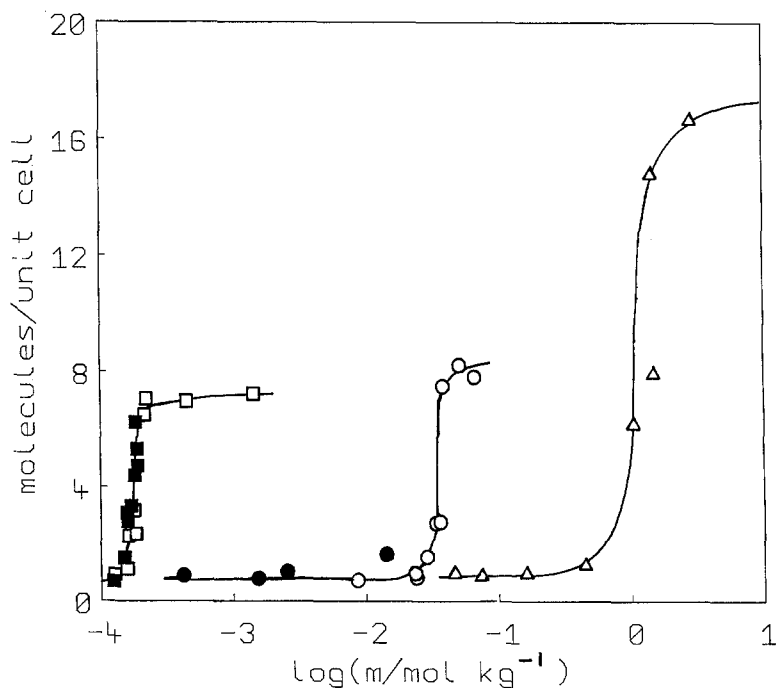


Fig. 1. Uptake (molecules per unit cell of  $96 \text{ SiO}_2$ ) of alkanediols  $\text{HO}(\text{CH}_2)_n\text{OH}$  from aqueous solution by silicalite-I as a function of  $\log_{10}(m)$  where  $m$  = molality of equilibrium solution.  $n = 2$  ( $\Delta$ ),  $n = 4$  ( $\circ$ ),  $n = 6$  ( $\square$ ). Open and filled symbols denote data obtained by absorption and desorption respectively.

$5 \times 10^{-2}$ ,  $2.5 \times 10^{-4}$ , and  $< 2 \times 10^{-6}$  mol kg<sup>-1</sup> for  $n = 2, 4, 6$ , and  $8$  respectively. In the case of octanediol the plateau was reached at such a low concentration that the complete isotherm could not be determined by the employed method; uptakes of  $0.098$ ,  $0.096$  and  $0.096$  g g<sup>-1</sup> were obtained for  $m = 2.1 \times 10^{-6}$ ,  $2.7 \times 10^{-6}$  and  $4.2 \times 10^{-6}$  mol kg<sup>-1</sup> respectively. For the other sorbates significant uptakes [ $1.0$ ,  $0.85$ ,  $0.70$  molecules per unit cell ( $96 \text{ SiO}_2$ ) for  $n = 2, 4, 6$  respectively] were observed at concentrations well below the sharp rises in the isotherms; these uptakes may be caused by preferential sorption at special sites within the sieve, and if so are likely to depend on its preparation and pretreatment. Although this behaviour has not been observed with other sorbates and other samples of silicalite-1 [1, 3, 4, 5], it is unlikely that it is restricted to diols and silicalite-1 samples prepared by the present procedure. The shape of the isotherms (Figure 1), with the sharp rise at threshold concentrations dependent on the chain length, suggests that the sorption is a cooperative process triggered by a particular minimum uptake.

The estimated maximum number of diol molecules per unit cell was  $16.7$  for ethane-1,2-diol, and  $8.1$ ,  $7.6$  and  $4.0$  for the three higher diols ( $n = 4, 6$ , and  $8$ ) respectively. The corresponding volumes occupied by the diols were estimated to be  $0.16$ ,  $0.12$ ,  $0.15$ , and  $0.10$  cm<sup>3</sup> g<sup>-1</sup> compared with the crystallographic void volume of  $0.19$  cm<sup>3</sup> g<sup>-1</sup>. These values can be accounted for by the way in which the diols pack into the silicalite-1 channel system. The hexane-1,6-diol probably lies along the channels with the hydroxyl groups pointing into the channel intersections. This corresponds to a maximum uptake of  $8$  diol molecules per unit cell and leads to the occupation of most of the available void space. The butane-1,4-diol probably occupies the same positions, but being smaller takes up a smaller proportion of the void volume. Two molecules of ethane-1,2-diol take up about the same space as one of hexane-1,6-diol and thus occupy almost the same void volume. The octane-1,8-diol is so long that it extends well into the channel intersections and hence it is difficult for it to occupy more than two of the four intersecting channels. Consequently there are only  $4$  molecules per unit cell and there is a substantial amount of unfilled void space. The water contents of the equilibrated organic-loaded samples were small ( $< 0.03$  cm<sup>3</sup> g<sup>-1</sup>) and showed no systematic variation with organic loading.

In contrast to low silica zeolites which are stabilised during crystallisation by pore filling with water [14], hydrophobic molecular sieves are stabilised by organic molecules. It is clear from the present study that the diol concentrations used in the synthesis of ZSM-5 [9, 11], typically  $0.2$  mol kg<sup>-1</sup>, are well in excess of those required for maximum pore filling by diols with  $n \geq 4$ . In fact the zeolites crystallised from such reaction mixtures are found to be fully loaded with diol [9] so presumably maximising the conferred stability.

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