Sorption of Triethyleneglycol and Tetraethyleneglycol by Silicalite at Fixed Water Activities

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Abstract. The sorption of tetraethyleneglycol by silicalite-1 and triethyleneglycol by silicalite-1 and a silicalite-1/silicalite-2 intergrowth has been studied at 25°C and at fixed water activities in the range $0.111 < a_w < 0.902$ by an isopiestic method. All of the glycol uptakes are between 0.95 and 1.2 molecules per unit cell and in all cases they are essentially independent of water activity. The water content of the silicalite-1 was more sensitive to water activity and glycol content than was that of the silicalite-1/2 intergrowth.

1. Introduction

Silica molecular sieves have a low hydrophilicity and are good sorbents for organic molecules. Most studies of their sorption properties have been carried out under anhydrous conditions (water activity, $a_w = 0$) with gaseous sorbates [1] or from very dilute aqueous solution ($a_w = 1$) [2, 3]. Studies of sorption under controlled water activities are difficult to perform by conventional procedures, but it has been recognised [4] that, provided the sorbate is involatile, they should be readily carried out by the isopiestic method [4, 5]. We now report a study of the sorption of triethyleneglycol (trigol) and tetraethyleneglycol (tetragol) by a silica molecular sieve, silicalite [6], carried out at fixed water activities by the isopiestic method.

2. Experimental

2.1. MATERIALS

Triethyleneglycol and tetraethyleneglycol were puriss grade from Fluka, and the inorganic salts were SLR grade from BDH. Silicalite-1 was prepared [7, 8] in a stirred autoclave at 150°C from the reaction mixture 10 Pip·2 TPABr·20 SiO$_2$·1000 H$_2$O (Pip = piperazine, TPABr = tetra-*n*-propylammonium bromide). The organic template (TPA) was removed from the silicalite-1 by calcination for 18 h at 550°C, followed by 1 h at 800°C. The product had uniform crystals of 20 μm × 6 μm × 3 μm, and was free from amorphous material. Several batches of a silicalite-1/silicalite-2 intergrowth [9] were crystallised from the reaction mixture 10 Pip·3TPeABr·20 SiO$_2$·250 H$_2$O (TPeABr = tetra-*n*-pentylammonium bromide) in PTFE-lined, stainless steel bombs at 150°C [7]. The product was calcined as described above; it had 80 μm × 7 μm × 7 μm crystals and was free from amorphous material.

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2.2. APPARATUS

The isopiestic apparatus was a simplified version of that described previously [4]. It consisted of a 5 inch diameter, 1.5 inch deep stainless steel block, drilled with eleven 1.25 inch deep, 1 inch diameter holes, which were just big enough to accommodate Camlab 2 × 1 inch glass sample bottles. The block was supported from the sides of a Jencons 6 inch dry-seal desiccator. A series of smaller holes were also drilled though the block to facilitate the flow of water vapour. The water vapour pressure was controlled by a saturated salt solution contained in a glass Petri dish which rested on the bottom of the desiccator. During the equilibration the desiccator was placed in a thermostated water bath at $25.0 \pm 0.3°C$.

Thermal analysis was carried out with a Stanton Redcroft STA-780 series simultaneous thermal analyser. A Philips semi-automatic diffractometer was used to make X-ray powder diffraction measurements.

2.3. PROCEDURE

The equilibration procedure was similar to that described previously [4, 5]. About 0.5 g of the silicalite was placed in each of the preweighed bottles. After equilibration with water vapour ($a_w = 0.753$) the bottles were reweighed and one sample analysed for occluded water by thermal analysis. This allowed the weights of dry silicalite in each bottle to be determined. An aqueous solution of glycol was then added by weight to each bottle and the system was equilibrated. The use of an aqueous solution facilitated the mixing of the glycol and the molecular sieve; most of the water distilled from the glycol within 3 days. After 3 weeks the bottles were removed, capped and weighed. Equilibrations lasting 1 week were subsequently carried out at successively lower water activities. From this the total weight of water in the equilibrated bottles was determined.

3. Results and Discussion

The weights of dry silicalite, water, and glycol (W_z, W_w and W_s) in each equilibrated bottle are shown as plots of W_w/W_z as a function of W_s/W_z in Figures 1, 3 and 4.

3.1. TETRAETHYLENEGLYCOL + SILICALITE-1

The results for this system are shown in Figure 1. When the ratio of glycol to zeolite is low, all of the glycol enters the zeolite and some of the internal water is displaced, as indicated by the lines of negative gradient. In these bottles the molecular sieve is the only phase present. At high values of W_s/W_z the bottles contain more glycol than can be accommodated by the molecular sieve. The excess glycol is essentially dry at all water activities, as is indicated by the horizontal lines. The intersection of the two lines gives the maximum amount of glycol that can be taken up by the sieve and its water content at this loading. It can be seen that the maximum glycol loading is essentially independent of water activity, as is the amount of water displaced by the glycol. The maximum number of tetragol molecules per unit cell (96 SiO_2) is 1.10 ± 0.1; this corresponds to the occupation of less than a quarter of the total void space. Unit cell compositions for high and low water activities are given in Table I. At all water activities 3.0 ± 0.1 water molecules are
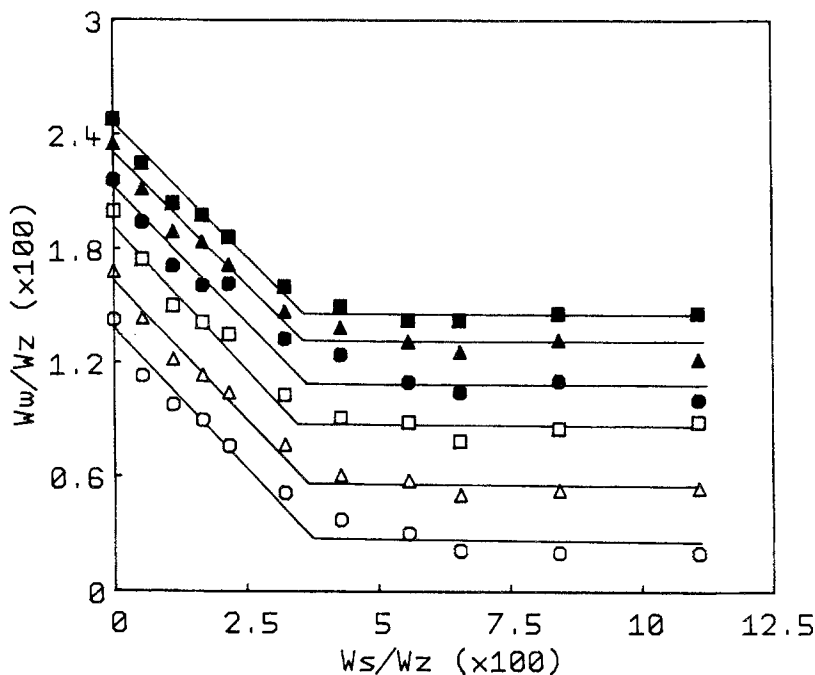
Fig. 1. Sorption results for the tetraethyleneglycol + silicalite-1 system. Water activities and salts used to make the saturated solutions are as follows: (■), 0.902, $BaCl_2$; (▲), 0.843, KCl; (●), 0.753, NaCl; (□), 0.577, NaBr; (△), 0.330, $MgCl_2$; (○), 0.111, LiCl.

displaced by one molecule of tetragol, thus this displacement is independent of the water content of the tetragol free sieve.

After the final equilibration over saturated LiCl ($a_w = 0.111$) the samples were examined by thermal analysis and X-ray powder diffraction. Although the thermal analysis showed the decrease in water content as the sieve became loaded with tetragol, it did not distinguish between internal and external tetragol. The X-ray powder diffraction patterns (Figure 2) show that the occlusion of tetragol leads to a reduction in the heights of the low angle peaks and an increase in those of the high angle ones; this is consistent with

Table I. Unit cell compositions at low and high water activity.

| Sieve	Glycol	a_w	Glycol free	Fully loaded
Silicalite-1	tetragol	0.111	$(H_2O)_{4.4}(SiO_2)_{96}$	$(tetragol)_{1.16}(H_2O)_{0.9}(SiO_2)_{96}$
Silicalite-1	tetragol	0.902	$(H_2O)_{7.8}(SiO_2)_{96}$	$(tetragol)_{1.04}(H_2O)_{4.7}(SiO_2)_{96}$
Silicalite-1	trigol	0.111	$(H_2O)_{5.0}(SiO_2)_{96}$	$(trigol)_{1.04}(H_2O)_{2.3}(SiO_2)_{96}$
Silicalite-1	trigol	0.902	$(H_2O)_{8.2}(SiO_2)_{96}$	$(trigol)_{1.04}(H_2O)_{5.5}(SiO_2)_{96}$
Silicalite-1/2	trigol	0.111	$(H_2O)_{5.2}(SiO_2)_{96}$	$(trigol)_{1.15}(H_2O)_{4.0}(SiO_2)_{96}$
Silicalite-1/2	trigol	0.902	$(H_2O)_{6.3}(SiO_2)_{96}$	$(trigol)_{1.03}(H_2O)_{5.4}(SiO_2)_{96}$
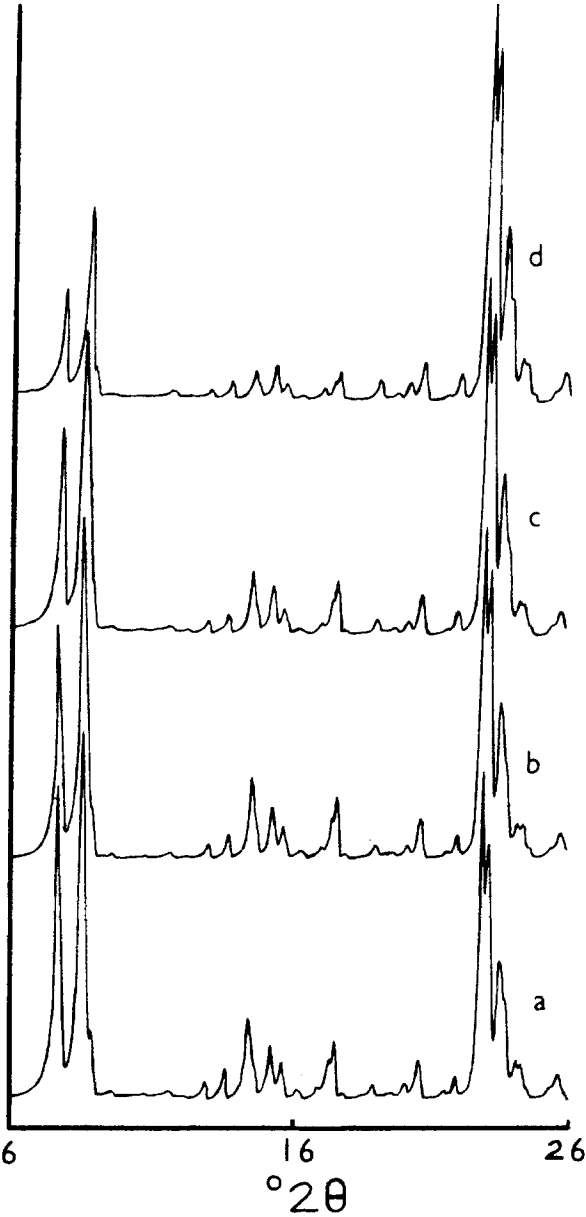
Fig. 2. X-ray powder diffraction patterns for samples of tetraethyleneglycol + silicalite-1 ($a_w = 0.111$). (a) silicalite-1 with no tetragol ($W_s/W_z = 0$); (b) silicalite-1 + sorbed tetragol only ($W_s/W_z = 0.0112$); (c) silicalite-1 fully loaded with tetragol + some external tetragol ($W_s/W_z = 0.0429$); and (d) silicalite-1 fully loaded with tetragol + much external tetragol ($W_s/W_z = 0.1109$).

other work [10, 11] but there appears to be no change in crystal symmetry [12]. A more marked, but similar, effect is observed when excess tetragol is present (Figure 2d). This effect increased with the amount of excess liquid present and could be related to the physical state of the samples which changed from hard solid to soft slurry.

3.2. TRIETHYLENEGLYCOL + SILICALITE-1

Figure 3 shows that this system is very similar to that for tetragol + silicalite-1. For trigol + silicalite-1 the maximum amount of glycol sorbed corresponds to 1.04 ± 0.10 trigol molecules per unit cell and 2.6 water molecules are displaced by one molecule of trigol. The number of displaced water molecules is slightly smaller than that for tetragol (3.0) as is to be expected from its shorter length. It can be seen from Figure 3 that for high glycol contents, and low water activities the excess trigol is essentially dry. However at higher water activities the positive slopes indicate the presence of water. As the lines seem to be essentially parallel it appears that there is a fixed ratio of water to trigol which is independent of the water activity; this suggests the presence of a hydrate of fixed composition. The experimental results indicate that this is $(trigol)_4 \cdot H_2O$.

3.3. TRIETHYLENEGLYCOL + SILICALITE-1/2

The results for this system are shown in Figure 4. Comparison with Figure 3 shows that the water content of this sieve is much less sensitive to both water activity and glycol loading. The exact origin of this difference is unknown; however it is clear that it reflects differences in the sites at which the water is sorbed. The maximum uptake of trigol per unit cell is 1.10 ± 0.1; this is again effectively independent of water activity. While this uptake is very close to that obtained for trigol in silicalite-1 (1.04 ± 0.1), the amount of water displaced per molecule of trigol is much less (0.95 ± 0.1, cf 2.6 ± 0.1). Again, for higher water activities the trigol appears to be present as a hydrate.
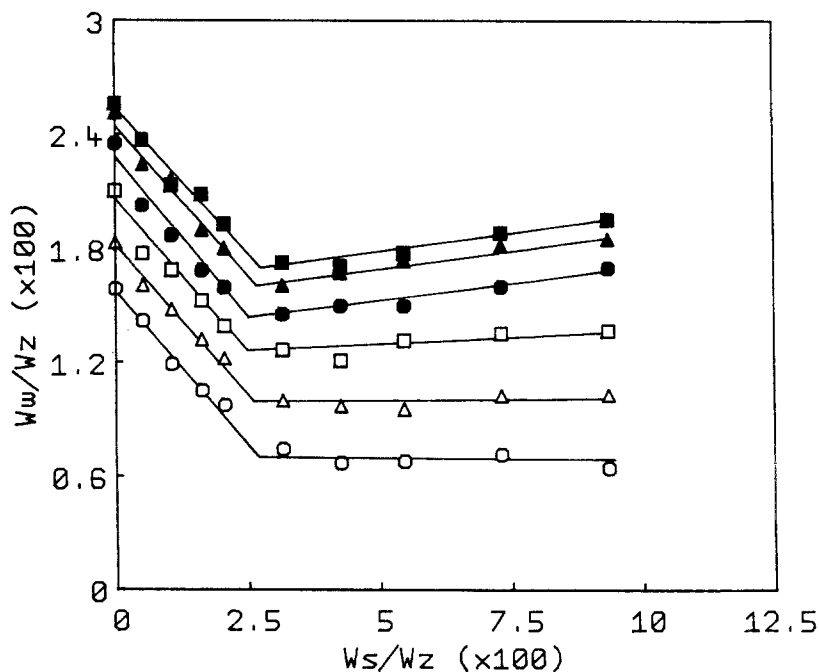

Fig. 3. Sorption results for the triethyleneglycol + silicalite-1 system. See Figure 1 for key.
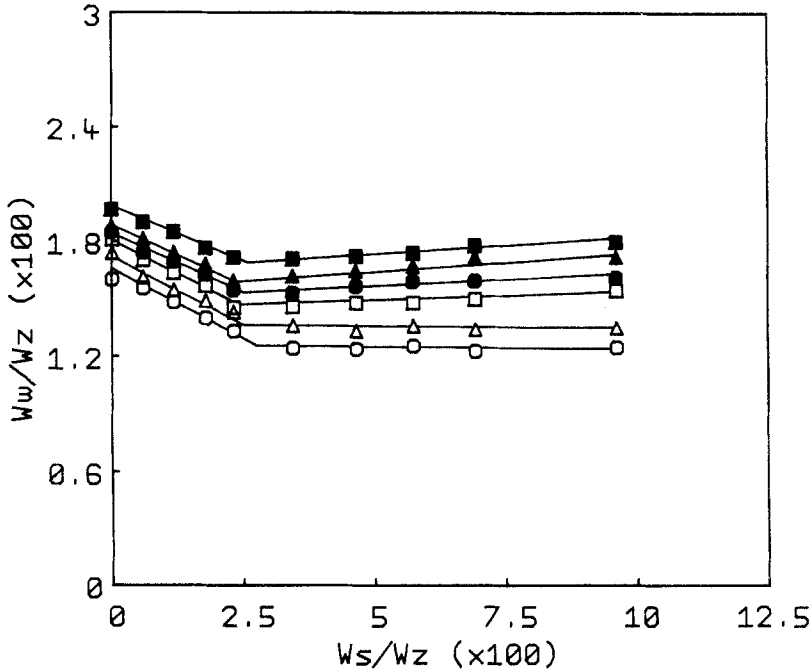
Fig. 4. Sorption results for the triethyleneglycol + silicalite-1/2 system. See Figure 1 for key.

4. Conclusions

The results show that the sorption of involatile liquids by molecular sieves under controlled water activities can be studied by the isopiestic method, and there should be few problems in applying it to other zeolitic sorbents and liquid sorbates. Its chief limitation is that determination of the intersection point, which corresponds to the maximum solute uptake and the water content at that loading, can be difficult unless good straight plots of W_w/W_z against W_s/W_z are obtained. The method could not be applied if the sorbate/water ratio in the sieve was the same as that in the liquid phase with which it is in equilibrium, or if the liquid phase is anhydrous and sorption results in no displacement of water from the sieve. However for the known zeolite and silica molecular sieves this behaviour is unlikely. Unfortunately for sorbates which are sufficiently involatile the equilibration is inevitably slow and about 12 weeks are required to collect results for 6 water activities.

In all of the systems studied the glycols displace water from silicalite in direct proportion to the amount of glycol sorbed and the proportionality factor is independent of water activity for the range $0.111 < a_w < 0.902$. The two silicalites show marked differences in behaviour. The water content of silicalite-1 is much more sensitive to water activity and much more readily displaced by trigol than is that of the silicalite-1/2 intergrowth. This implies that the water sorption sites in the two materials are different, and that water is much more strongly bound in silicalite-1/2. The structure and position of the sites cannot be deduced from these experiments but it seems likely that in both materials they are lattice defects formed by broken siloxane bonds. The differences probably relate to the position of these sites within the frameworks. The maximum

uptake of glycol is in all cases essentially independent of the water activity over the complete range studied, and corresponds to a void space occupancy of less than 25%. Although this low value may be due in part to the difficulty of packing long chain molecules in a system of intersecting channels, its main cause is believed to be the strong molecular attractions in the liquid sorbates. It is to be expected that the lower the volatility of the sorbate the lower will be the uptake by the molecular sieve. One consequence of this is that the water/glycol mole ratio in the sieve is very much larger than that of the liquid phase.

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