

Imbibition of Sodium Nitrate and Tetrapropylammonium Bromide by the Molecular Sieve $\text{AlPO}_4\text{-5}$

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Sodium nitrate and tetrapropylammonium bromide are imbibed from aqueous solution by the aluminophosphate molecular sieve $\text{AlPO}_4\text{-5}$.

The aluminophosphate molecular sieves,¹ like the porasils, have no net charge on their frameworks, nor do they have exchangeable cations, but the alternating Al and P atoms in the structures result in a somewhat polar surface. Their properties as sorbents therefore lie between those of zeolites and those of porasils.²⁻⁴ The interaction of aluminophosphate sieves with salts is particularly interesting. As there is no framework charge, ion exchange and Donnan exclusion effects should be absent, but salt uptake must certainly be influenced by ion solvent and ion framework interactions. Quaternary ammonium ions are often used as templating agents in AlPO_4 sieve synthesis, and the organic material is retained in the crystalline products; this suggests that imbibition of their salts may be substantial.

We now report measurements of the uptake of sodium

nitrate and tetrapropylammonium bromide by $\text{AlPO}_4\text{-5}$. Sodium nitrate was chosen as a typical salt, and because the cation-anion closest approach distance was fairly similar to the Al-P spacing in the $\text{AlPO}_4\text{-5}$.^{5,6} Tetrapropylammonium bromide is of interest as the cation is a preferred templating agent in the synthesis.

$\text{AlPO}_4\text{-5}$ was crystallised under static conditions from the reaction mixture $\text{Pr}_4\text{NBr}/\text{Pr}_3\text{N}/\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3/40\text{H}_2\text{O}$ in a poly-(tetrafluoroethylene)-lined steel bomb at 150 °C. The sample had hexagonal rod-shaped crystals, 25 μm in length and 15 μm in width, and was calcined at 550 °C for 18 h in air before use. Salt uptake measurements were made by the isopiestic method of Fegan and Lowe^{7,8} at 25 °C. The experimental curves are shown in Figures 1 and 2.

The results with sodium nitrate at water activity $a_w > 0.87$

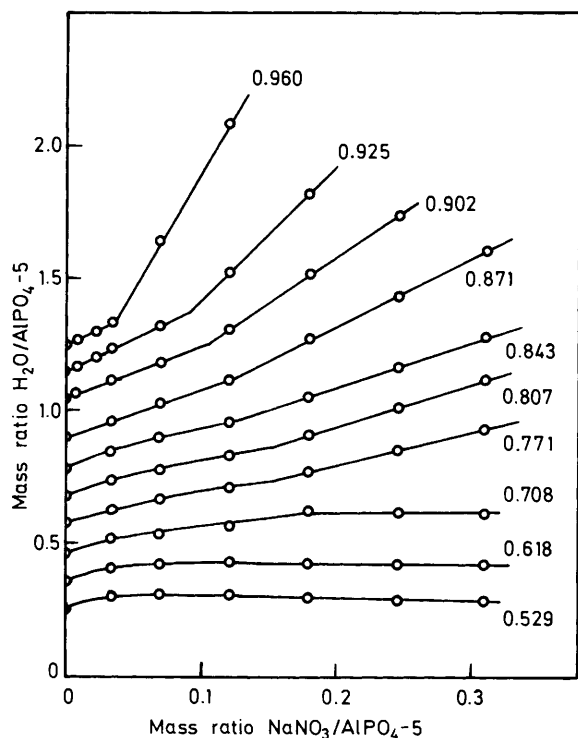


Figure 1. Isopiestic curves for sodium nitrate imbibition in $\text{AlPO}_4\text{-5}$. Water activities are marked on the curves. For clarity the curves are displaced on the ordinate by 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9.

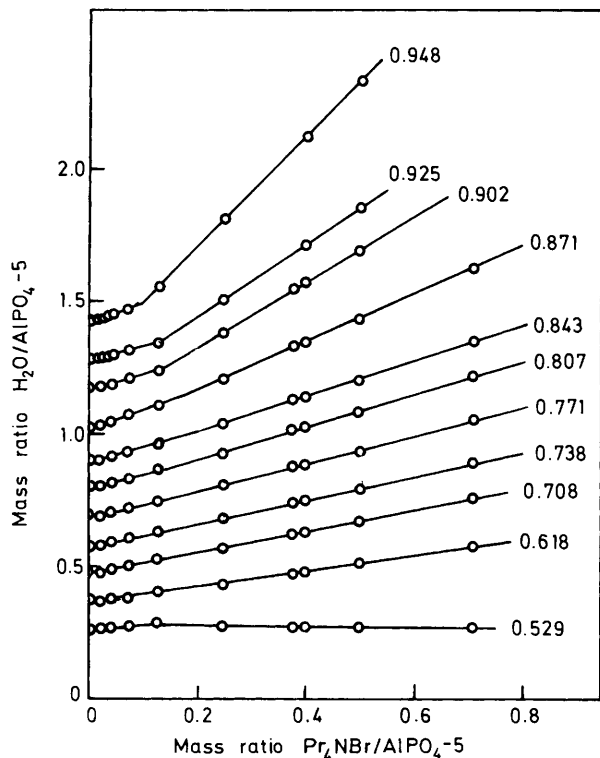


Figure 2. Isopiestic curves for tetrapropylammonium bromide imbibition in $\text{AlPO}_4\text{-5}$. Water activities are marked on the curves. For clarity the curves are displaced on the ordinate by 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0.

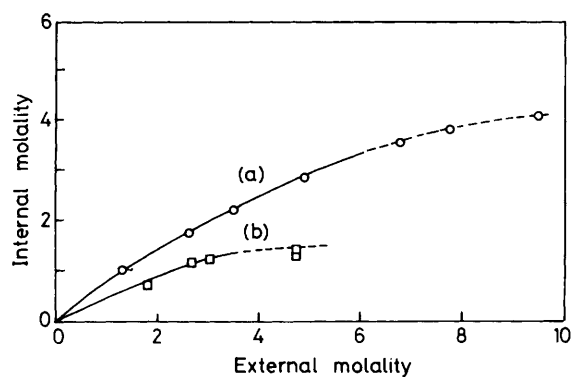


Figure 3. Imbibition of (a) sodium nitrate and (b) tetrapropylammonium bromide at 25°C .

are very like those which have been reported for zeolites,^{7,8} except for the positive slope of the lines at low salt loading. This indicates that salt entering the $\text{AlPO}_4\text{-5}$ pores takes in water molecules with it. The intersection points between the lines for the mixtures in which all the salt is imbibed by the $\text{AlPO}_4\text{-5}$, and those at higher salt loadings where NaNO_3 solution is in equilibrium with the salt loaded molecular sieve, are readily determined. At lower water activities, the plots at low salt content became progressively more curved, and it becomes increasingly difficult to determine an intersection point. The curvature probably results from the pore space gradually becoming more crowded, so that eventually more salt can be accommodated only if water is expelled.

The experiments with tetrapropylammonium bromide give similar results, except that the curvature of the isopiestic curves is much less marked. Analysis of the shapes of the curves at low salt content shows that 8–12 water molecules on average accompany each NaNO_3 entering the $\text{AlPO}_4\text{-5}$. The corresponding result with tetrapropylammonium bromide is 8–10 molecules.

Figure 3 shows the relation between the salt concentrations inside and outside the crystal. Sodium nitrate is slightly less concentrated inside than out, and the effect becomes slightly larger at high concentrations. This is probably due to restrictions on ion hydration imposed by the limited space inside the pores, and the stronger pore surface–water interaction. As would be expected Donnan exclusion is absent. Tetrapropylammonium bromide behaves rather similarly, but surprisingly imbibition is lower with this salt. No slow, continued uptake was observed, so this does not appear to be a kinetic effect. Templating ability is thus not related in this case to an especially large affinity between the salt and the channel system.

The water uptake by salt-free $\text{AlPO}_4\text{-5}$ is shown in Figure 4. The values are in excess of that ($0.19\text{ cm}^3\text{ g}^{-1}$) calculated from the crystallographic void volume^{5,6,9} and that obtained for oxygen sorption ($0.18\text{ cm}^3\text{ g}^{-1}$),³ and increase sharply with water activity. Simple calculations show that the effect is too large to be accounted for by capillary condensation, and its absence in similar experiments¹⁰ with Na-Y zeolite crystals smaller than those of the $\text{AlPO}_4\text{-5}$ (Figure 4) supports this conclusion (see also ref. 4). A possible alternative explanation is that the crystals react with water to release hydrophilic species which dissolve to give a surface film of solution. This requires that at high water activities the total water uptake U should be given by the limiting equation (1), where U_0 is the water uptake not due to the surface film and n is the number of moles of soluble species per g of $\text{AlPO}_4\text{-5}$. $U = U_0 + 18n/(1 - a_w)$. This provides a good fit to the results with $U_0 = 0.24 \pm$

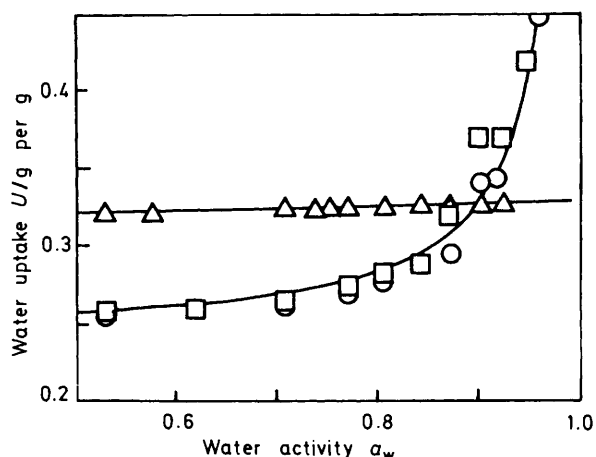


Figure 4. Water uptakes by $\text{AlPO}_4\text{-5}$ in absence of added salt: (○) sodium nitrate experiments; (□) tetrapropylammonium bromide experiments. Curve: equation (1) with $U_0 = 0.24$ g per g and $n = 5 \times 10^{-4}$ mol g^{-1} . Water uptakes for zeolite Na-Y (△).

0.02 g per g and $n = 5 \pm 1 \times 10^{-4}$ mol g^{-1} . Other workers have also observed high water uptakes (for $0.6 < a_w < 0.9$, 0.24–0.28 g per g)³ [saturation capacity 0.31 g per g (ref. 1); 0.275 g per g (ref. 11)] and similarly shaped curves,³ but experimental data for $a_w > 0.9$ are not available. Although equation (1) represents the results to within their experimental error, further experiments are required to confirm the model on which it is based and to identify the hydrophilic species. The molecular sieve was examined by X-ray powder diffraction before and after the experiments: and pattern was substantially unchanged, although with both salts a slight decrease in the peak heights, possibly corresponding to dissolution of the crystals and subsequent precipitation of amorphous material, was observed.

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