Dianin's Compound as a Zeolitic Sorbent

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Summary Dianin's compound, suitably agitated, has been shown to sorb freely Ar, Kr, Xe, CO_2, CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, iso-C_4H_{10}, and neo-C_5H_{12}, and behaves in some respects like an organic zeolite; the numbers of molecules filling each cavity in the host lattice varied from 6 for Ar (−196 °C) and CH_4 (−183 °C) to 2 for iso-C_4H_{10} and neo-C_5H_{12} (0 °C), and saturation numbers depended upon the size and shape of the guest molecules, in the same way as for zeolites.

Dianin's compound[1] (4-*p*-hydroxyphenyl-2,3,4-trimethylchroman) has been shown to crystallise from pure liquids or liquid mixtures, forming inclusion complexes with many of the molecules in these liquids,[2] often in a very selective way.[3] The crystal structure[4] is based upon a unit of six host molecules hydrogen bonded through their hydroxy-groups to give a 6-membered ring, with three of the molecules projecting above and three below the plane of this ring. The units so produced are stacked in columns so that six host molecules form a cavity, three belonging to one unit and three to the unit immediately above or below. The cavity is *ca.* 11 Å in length (the height of the unit cell) and has a waist of *ca.* 4·2 Å free diameter at half the cell height, with free diameters of *ca.* 6·4 Å at 0·3 and 0·7 of the cell height.[5] These hour-glass-shaped cavities limit the size and shape of the guest molecules which can be included and hence introduce notable selectivity into the clathration process.[4]

Dianin's compound, and its thiachroman analogue,[6] are noteworthy in that the crystal topology is the same whether or not guest molecules occupy the cavities. In this respect they differ from host lattices of water, quinol, or phenol which collapse in absence of guest molecules. Instead they recall porous zeolite structures which are permanent in absence or presence of guest molecules, and so should behave as sorbents in rather similar ways. Since this possibility has not been investigated it was of interest to explore the behaviour of Dianin's compound towards gases and vapours.

Table

Apparent saturation capacities of Dianin's compound towards guest species.

Guest	T/°C	Capacity (cm³ at s.t.p. g⁻¹)	Composition
Ar	−196	83·8	6D, $5{\cdot}9_7$Ar
Kr	− 78	17·8	6D, $1{\cdot}2_8$Kr
Xe	− 78	45·8	6D, $3{\cdot}2_9$Xe
CO_2	− 78	46·6	6D, $3{\cdot}3_4CO_2$
CH_4	−183	83·0	6D, $5{\cdot}9_5CH_4$
C_2H_6	− 78	52·7	6D, $3{\cdot}7_9C_2H_6$
C_3H_8	− 78	41·4	6D, $2{\cdot}9_7C_3H_8$
n-C_4H_{10}	0	39·5	6D, $2{\cdot}8_4$ n-C_4H_{10}
iso-C_4H_{10}	0	27·3	6D, $1{\cdot}9_5$ iso-C_4H_{10}
neo-C_5H_{12}	0	27·3	6D, $1{\cdot}9_5$ neo-C_5H_{12}

Sorption was examined for Ar, Kr, Xe, CO_2, CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, iso-C_4H_{10}, and neo-C_5H_{12} using an apparatus like that of Barrer and Edge.[7] In the apparatus 0·1 g of Dianin's compound was shaken in the reaction bulb with 250 1/8 in steel ball bearings. The crystals were similarly shaken during outgassing to ensure removal of all residual guest species. The reaction bulb was immersed in appropriate thermostatic fluids from liquid nitrogen to liquid water. Dianin's compound sorbed Ar at −196 °C and Xe at −78 °C without any shaking, but sorption slowed down after a while, only to be dramatically increased in rate when shaking was commenced (Figure 1). Kinetic runs made with shaking at different pressures all had the same form (Figure 2), and no threshold pressure was required before clathration would occur, in contrast with gas hydrates[8,9] or phenol and quinol clathrates,[10] and also no induction periods were observed such as were sometimes found with the above clathrates. The behaviour of Dianin's compound was in these respects the same as that of a zeolite. The framework of the host structure is however less rigid than that of a zeolite and guest molecules can penetrate into the cavities, even though wide windows giving access to these cavities do not exist. When the host crystals were agitated with the ball-bearings n-butane, isobutane, and neo-pentane were freely sorbed at 0 °C, with times for half the final uptakes of about 8, 15, and 38 min, respectively. These times show some influence of the cross-

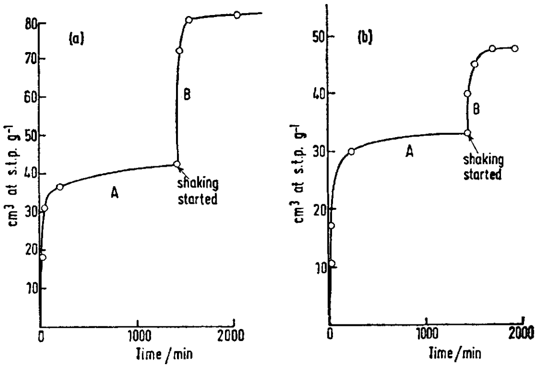

Figure 1. (a) Sorption of Ar by Dianin's compound at −196 °C and 7·15 cmHg pressure. Section A: without agitating the host crystals; section B, with agitation. (b) Sorption of Xe at −78 °C and 27·29 cmHg pressure. Section A: without agitation; section B with agitation.

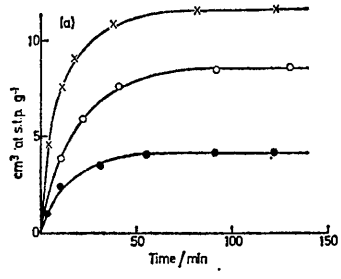

Figure 2. Sorption kinetics with agitation of host crystals; Kr at −78 °C. ×, pressure 17·30 cmHg; ○, pressure 8·47 cmHg; ●, pressure 2·43 cmHg.

sectional diameters upon the sorption kinetics. Rate curves were measured at one or more pressures at the following temperatures: Ar (−196 and −183 °C); Kr (−78 °C); Xe (−78 °C); CO_2 (−78 °C); CH_4 (−183 °C); C_2H_6 (−78 °C); C_3H_8 (−78 °C); n-C_4H_{10}, iso-C_4H_{10}, and neo-C_5H_{12} (all at 0 °C).

Isotherms were next determined for Ar at −196, −183, −78, and 0 °C; Kr at −78 °C; Xe at −78, 0, and 23·1 °C; CO_2 at −78 and 0 °C; CH_4 at −183 and −78 °C; C_2H_6 at −78 and 0 °C; C_3H_8 at −78 °C; n-C_4H_{10} and iso-C_4H_{10} at 0 °C; and neo-C_5H_{12} at 0 and 24·9 °C. All were of Type I in Brunauer's classification, just as with zeolite sorbents, as illustrated in Figure 3. Plots of p/v against p were used to estimate apparent saturation capacities, where v (cm^3 at s.t.p. g^{-1} of Dianin's compound) denotes the uptake at pressure p. The apparent saturation capacities appeared to depend upon the temperature. Because of this only the capacities at the lowest experimental temperatures are given in the Table, when the value obtained comes nearest to true saturation. Even so the figure for Kr is much too low because −78 °C was not sufficiently cold. The final column of the Table gives the apparent saturation numbers of guest molecules per cavity, and hence per six molecules of Dianin's compound denoted in the Table by D. Since each cavity is closed in Dianin's compound it is not possible for two cavities to share a guest molecule as is the case when the guest straddles the window joining two cages. Thus the true saturation capacities in Dianin's compound would require an integral number of guest molecules per cavity. On this basis from the experimental figures in the last column of the Table we expect the true saturation capacities in molecules per cavity to be: Ar and CH_4, 6; Xe, C_2H_6, and CO_2, 4; C_3H_8 and n-C_4H_{10}, 3; iso-C_4H_{10} and neo-C_5H_{12}, 2. The clusters of six molecules of Ar and CH_4 (van der Waals diameters 3·83 and *ca.* 4·0 Å respectively) seem compatible with the cavity dimensions already given. As the dimensions of the guest increase the number of guest molecules per cavity falls. n-C_4H_{10} and propane can each straddle the 4·2 Å waist of the cavity, but for globular molecules like iso-C_4H_{10} and neo-C_5H_{12} this is not possible. Thus only two molecules of the two latter hydrocarbons can be accommodated one in each of the wide 6·4 Å parts of the cavity, as compared with three n-C_4H_{10} or C_3H_8 molecules.

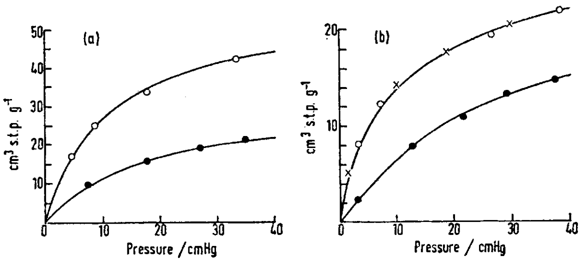

FIGURE 3. Sorption isotherms for (a) C_2H_6 at −78 (○) and 0 °C (●), (b) neo-C_5H_{12} at 0 (○ = sorption points; × = desorption points) and at 24·9 °C (●).

It can be concluded that Dianin's compound possesses the kind of sorptive properties shown by the zeolite molecular sieves and that these properties arise from the permanent character of the porous lost lattice. It can be expected that the corresponding thiachroman will behave in an analogous way. Zeolite-like properties have also been demonstrated[11] in β-M(4-methylpyridine)$_4$(CNS)$_2$ where M is Ni^{II} or Co^{II}, and may be discovered in other clathrate-forming crystals.

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