

Sorption of Galactose by Zeolite Y

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Abstract. The sorption of galactose by Na-Y, K-Y and Ba-Y zeolites has been investigated by isopiestic equilibration at 25°C. The equilibrium galactose and water contents of the zeolites were determined for water activities a_w in the range $0.111 < a_w < 0.98$. It was found that the maximum uptake of galactose U_G^0 (observed for $a_w \rightarrow 0$) was highest for Na-Y and least for Ba-Y. In contrast at high water activities the galactose uptake was highest for Ba-Y and least for Na-Y.

Key words. Sorption, isopiestic equilibration, galactose, zeolite Y.

1. Introduction

The use of zeolites to separate low molecular weight sugars by selective sorption from aqueous solution has been the subject of extensive investigation and it is now possible to perform several commercially important separations [1–3]. It has been shown [2] that the extent to which zeolites sorb sugars from aqueous solutions depends on the strength of the complex formed between the sugar and the zeolitic cations and on the geometric constraints imposed by the number, type and position of the cations within the zeolitic cavities. Hence for a given zeolite the separation behaviour depends on the Si/Al ratio of the framework and the nature of the cations. As it is essential for the sugar to enter the zeolite channel system separations are restricted to wide pore zeolites, such as zeolites X and Y.

Most investigators have used liquid phase chromatography to study the separations, and this method has also been used to obtain equilibrium constants and diffusivities [1]. In contrast we now report the use of isopiestic equilibration to determine the sugar and water content of the zeolite and the concentration of the solution phase with which it is in equilibrium. In previous studies [4–6] isopiestic equilibration has been used to study salt imbibition by zeolites and although it has been recognised that it can be used with other involatile solutes few studies have been made [7] and none with sugars have been published. Although the method was devised to study sorption from solution it can also be used to measure the uptake of solutes at water activities below those of the saturated solution; under these conditions solid solute is in direct contact with the zeolite. The measurements now reported were made with galactose and Na, K and Ba exchanged zeolite Y.

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2. Experimental

2.1. MATERIALS

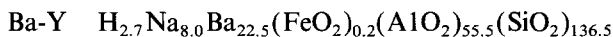
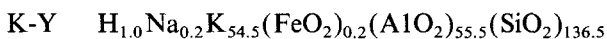
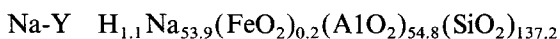
Na-Y zeolite was supplied by Strem Chemicals Inc and D(+)galactose (puriss grade) was obtained from Fluka Ltd. All salts were Analar grade from BDH Ltd.

2.2. PRETREATMENT OF ZEOLITE Y

To ensure that the zeolite was in the homoionic sodium form it was contacted three times with 1 mol dm^{-3} aqueous NaNO_3 (40 g/500 mL) at room temperature. The zeolite was then washed with water, dried at 110°C and finally equilibrated with water vapour in a desiccator over saturated aqueous NaCl.

The potassium and barium forms were prepared by contacting 40 g of Na-Y with 500 mL of either 1 mol dm^{-3} KNO_3 or 0.5 mol dm^{-3} BaCl_2 solution at 65°C . This process was repeated ~ 35 times. The final ion exchanged products were washed with water, dried at 110°C , and equilibrated with water vapour over saturated aqueous NaCl.

The water contents of the water vapour equilibrated zeolites were determined by thermal gravimetric analysis. X-ray fluorescence analysis was used to obtain the Si, Al, Fe, Na and K contents of the zeolites. The Ba and Na contents of the Ba-Y zeolite were obtained by atomic absorption spectroscopy. The unit cell compositions were found to be:



2.3. APPARATUS AND PROCEDURE

The apparatus and the procedure used to determine the weights of zeolite W_z , water W_w and solute W_s in equilibrium at a fixed water activity a_w have been described elsewhere [4, 7]. About 0.4 g zeolite (dry weight) was used for each equilibration. Galactose was added as an aqueous solution to give W_s/W_z in the range 0 to 0.5 g g^{-1} . The equilibration temperature was $25.0 \pm 0.3^\circ\text{C}$.

3. Results

Plots of W_w/W_z as a function of W_s/W_z at various water activities (a_w) are shown for zeolite Na-Y in Figure 1. In this the lines of negative slope correspond to the situation in which all of the galactose has entered the zeolite and there is no solution phase. The lines of positive slope obtained for the higher water activities indicate the presence of a solution phase, and the horizontal lines obtained for high galactose contents and low water activities are for zeolite in contact with solid galactose. For each water activity the coordinates of the intersection point of the straight lines give the maximum loading of galactose U_G and the water content U_w of the zeolite at this loading. The results for the other ion exchanged forms can be

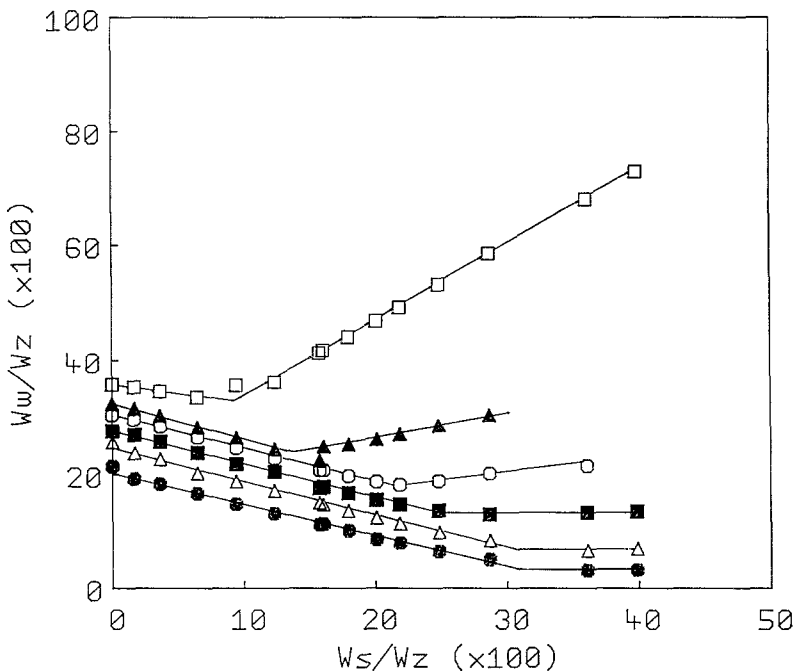


Fig. 1. Isopiestic plots for the galactose + Na-Y system. For clarity the curves have been displaced on the W_w/W_z axis. The water activities and displacements are as follows: (\square), 0.925, 0.00; (\blacktriangle), 0.843, -0.02; (\circ), 0.753, -0.04; (\blacksquare), 0.577, -0.06; (\triangle), 0.330, -0.08; (\bullet), 0.111, -1.00.

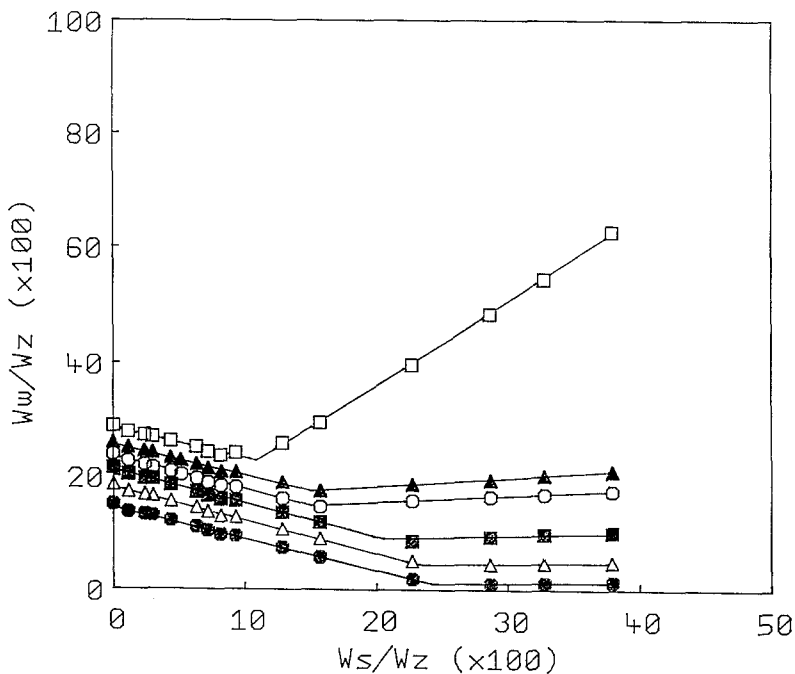


Fig. 2. Isopiestic plots for the galactose + K-Y system. For clarity the curves have been displaced on the W_w/W_z axis. The water activities and displacements are as follows: (\square), 0.925, 0.00; (\blacktriangle), 0.843, -0.02; (\circ), 0.753, -0.04; (\blacksquare), 0.577, -0.06; (\triangle), 0.330, -0.08; (\bullet), 0.111, -1.00.

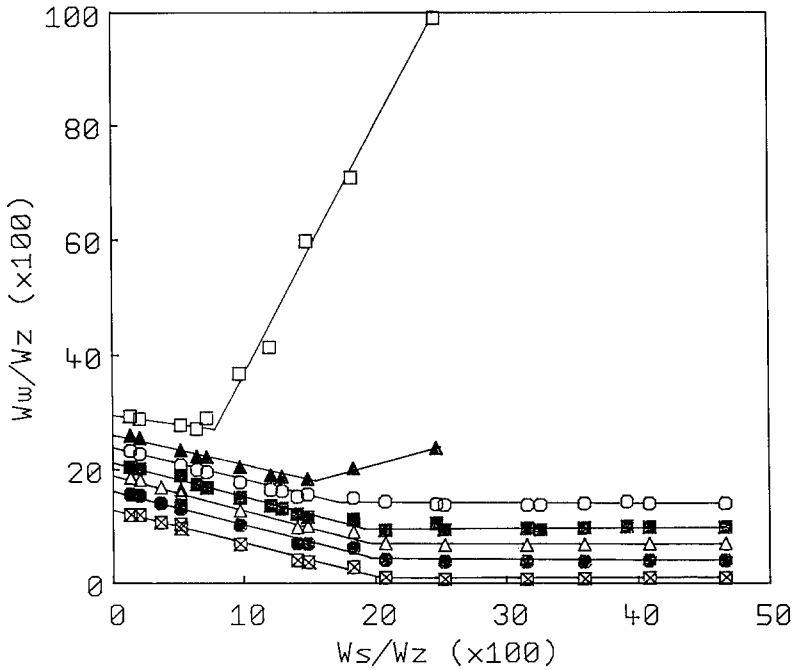


Fig. 3. Isoopiestic plots for the galactose + Ba-Y system. For clarity the curves have been displaced on the W_w/W_z axis. The water activities and displacements are as follows: (\square), 0.980, 0.00; (\blacktriangle), 0.925, -0.02; (\circ), 0.871, -0.04; (\blacksquare), 0.753, -0.06; (\triangle), 0.577, -0.08; (\bullet), 0.330, -0.10; (\times), 0.111, -0.12.

Table I. Water contents of equilibrated zeolites^a

a_w	Zeolite Na-Y			Zeolite K-Y			Zeolite Ba-Y		
	M_w	M_w^0	D	M_w	M_w^0	D	M_w	M_w^0	D
0.980	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	219	252	5.2
0.925	219	252	5.2	171	219	5.9	164	239	6.2
0.871	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	144	232	6.7
0.843	179	241	6.4	144	211	6.1	n.a.	n.a.	n.a.
0.753	151	241	5.9	140	210	5.8	125	228	6.3
0.577	135	238	5.8	109	207	5.8	120	224	6.5
0.330	105	238	5.8	93	200	6.2	111	220	6.5
0.111	92	212	5.5	80	189	6.1	103	207	6.4

^a M_w = water content (mole per unit cell) calculated from the uptake U_w ($g\ g^{-1}$). M_w^0 = water content in the absence of galactose. D = displaced water (mole per mole galactose) = $(M_w^0 - M_w)/M_G$ where M_G is the galactose content (mole per unit cell) calculated from U_G . n.a. = not available.

described similarly; they are presented for K-Y in Figure 2, and for Ba-Y in Figure 3. The water contents of the equilibrated zeolites calculated from U_w are given in Table I.

4. Discussion

The negative slopes in Figures 1–3 show that the galactose displaces the zeolitic water. The displacement shows little variation with water activity (Table I) and over the range $0.111 < a_w < 0.925$ the average values in moles of water per mole of galactose are 5.8 ± 0.6 for Na-Y, 6.0 ± 0.2 for K-Y and 6.4 ± 0.3 for Ba-Y. That these values are almost independent of the zeolite cation suggests that they are determined primarily by spatial requirements and that the galactose molecule occupies the space of ~ 6 water molecules.

Figure 4 shows the galactose uptakes U_G as a function of water activity. Although the curves for Na-Y and K-Y appear to differ from that for Ba-Y all three can be represented by the empirical equation,

$$P = [U_G / (U_G^0 - U_G)] [a_w / (1 - a_w)] \quad (1)$$

in which P is a constant and U_G^0 is the uptake for $a_w = 0$. The best fit values of P and U_G^0 are given in Table II. The curves calculated with these constants are shown in Figure 4 and can be seen to be a good fit to the experimental data. The limiting slopes (dU_G/da_w) for $a_w \rightarrow 1$ are given by $-U_G^0 P$ and are $1.55 \pm 0.51 \text{ g g}^{-1}$ for Na-Y, $1.97 \pm 0.74 \text{ g g}^{-1}$ for K-Y, and $6.23 \pm 2.10 \text{ g g}^{-1}$ for Ba-Y. Thus for dilute solutions the order of selectivity is Ba-Y > K-Y > Na-Y.

The marked difference between the limiting uptakes U_G^0 is probably related to the way in which the galactose is held in the zeolite. With Ba-Y the galactose is relatively tightly bound to the cations and the limiting uptake U_G^0 which corresponds to 0.72 molecules per barium ion is achieved at quite high water activities. Although there is sufficient void space to accommodate additional galactose molecules, it seems likely that access is restricted because of the constraints placed on the positions of the sorbed molecules by the strong interaction with the barium ions. With Na-Y the cation-sugar interactions are much weaker, the positions of the galactose molecules are less constrained and a much higher limiting uptake U_G^0 is attained. With K-Y the strength of the cation-sugar interaction lies between those for Na-Y and Ba-Y, as does the limiting uptake U_G^0 .

The difference between the behaviour of the Ba-Y and the alkali metal exchanged zeolites is even more marked in Figure 5 which shows the internal galactose molality

Table II. Constants for Equations 1 and 2

Zeolite	P	U_G^0 g g^{-1}	Q	m_i^0 mol kg^{-1}
Na-Y	4.76 ± 1.18	0.325 ± 0.021	1.63 ± 0.36	14.27 ± 0.98
K-Y	8.25 ± 2.43	0.239 ± 0.015	2.22 ± 0.65	12.90 ± 1.13
Ba-Y	30.41 ± 8.54	0.205 ± 0.009	10.61 ± 2.53	8.76 ± 0.45

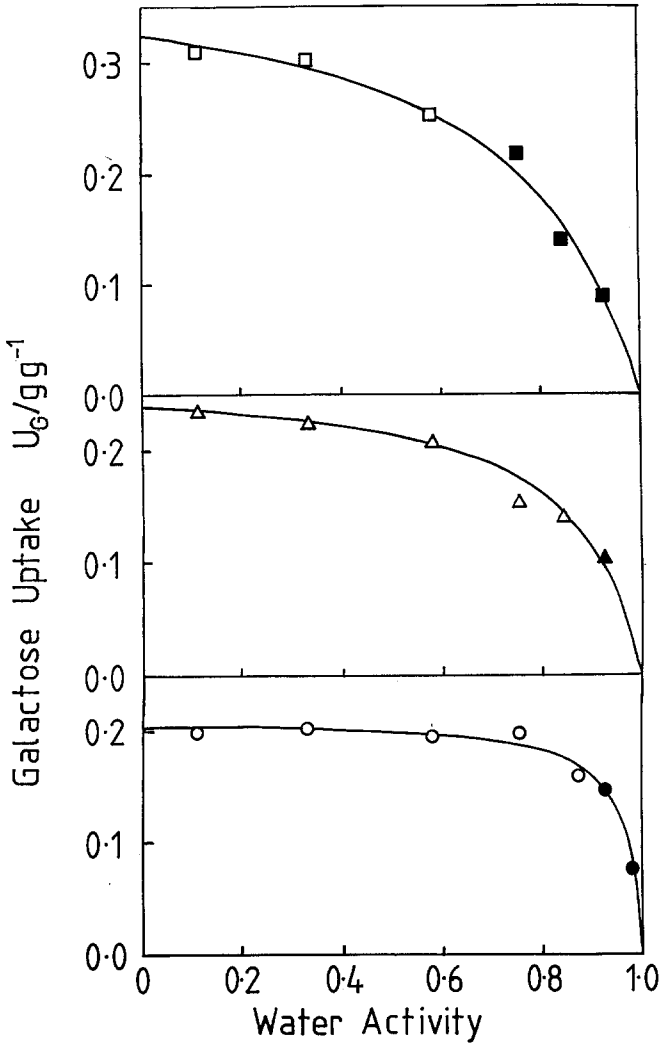


Fig. 4. Galactose uptake, U_G , as a function of water activity. (\square), Na-Y; (Δ), K-Y; (\circ), Ba-Y. Filled symbols indicate that a solution phase was present at equilibrium. Curves calculated with Equation 1 using the best fit values of P and U_G^0 given in Table II.

m_i (calculated from U_G and U_w) as a function of the water activity. It can be seen from this Figure that the equation,

$$Q = [m_i / (m_i^0 - m_i)] [a_w / (1 - a_w)] \quad (2)$$

in which Q is a constant and m_i^0 is the value of m_i for $a_w = 0$, provides a good fit to the experimental results. Least squares best fit values of Q and m_i^0 are given in Table II.

The horizontal lines in Figures 1–3 show that for most of the water activities the excess galactose did not form a solution phase, but the sugar in contact with the

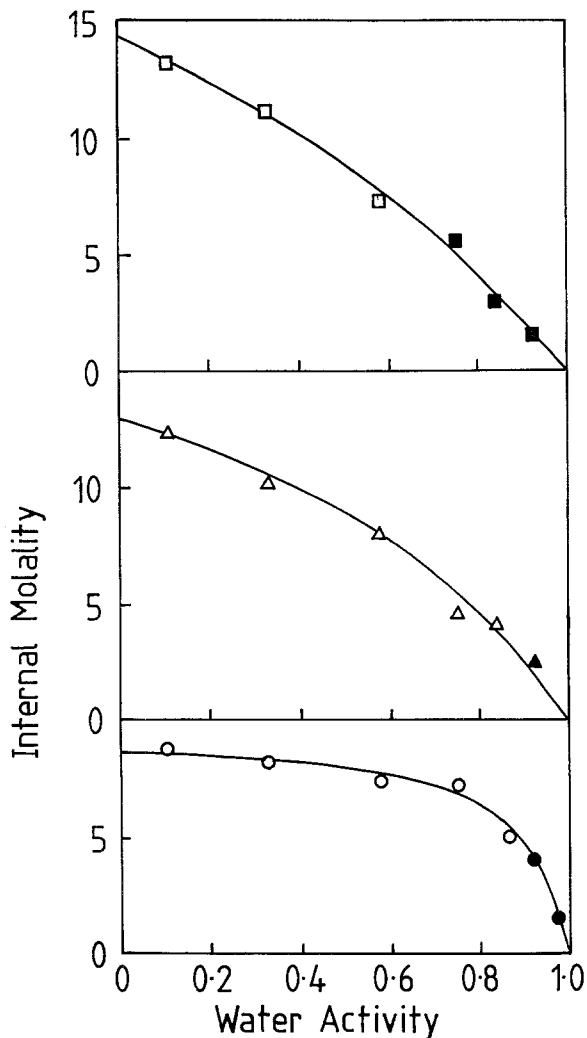


Fig. 5. Internal galactose molalities, m_i , as a function of water activity. (\square), Na-Y; (Δ), K-Y; (\circ), Ba-Y. Filled symbols indicate that a solution phase was present at equilibrium. Curves calculated with Equation 2 using the best fit values of Q and m_i^0 given in Table II.

zeolite at equilibrium, was present as an essentially dry solid. However at high water activities solution phases were observed and their concentrations could be calculated from the reciprocals of the positive slopes. As is to be expected when comparison is possible ($a_w = 0.925$) concentrations observed at identical water activities are in good agreement (Na-Y, 4.2 molal; K-Y, 4.0 molal). In the case of Na-Y external solutions were also observed for $a_w = 0.843$ (11.5 molal) and $a_w = 0.753$ (18.5 molal); it seems likely that these were metastable supersaturated solutions as they were not observed for K-Y or Ba-Y. However for these water activities the plots for K-Y were parallel and had a very slight positive slope which suggests the presence of a crystalline hydrate. For a given water activity the same external phase should be observed irrespective of the nature of the zeolite. That this

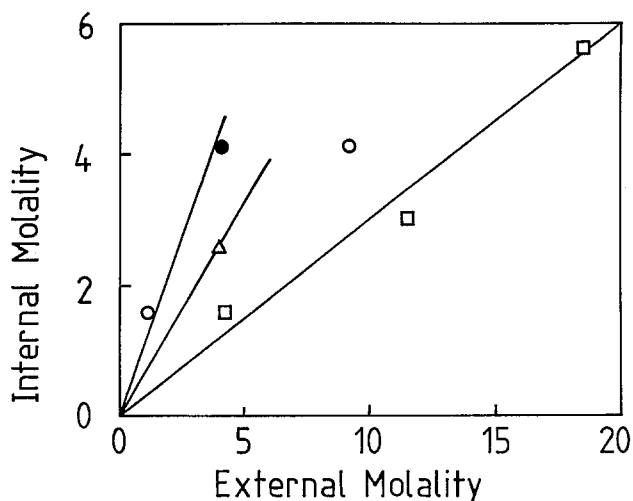


Fig. 6. Internal galactose molalities, m_i , as a function of the external molality m . (\square), Na-Y; (\triangle), K-Y; (\circ), Ba-Y. (\bullet) assumes m has the value observed for Na-Y and K-Y at the same water activity.

did not occur for two of the water activities, is however not unexpected given the well-known difficulties encountered in the crystallisation of sugars. It seems likely that processes such as hydronium ion exchange which would lead to a slight release of alkali metal cations from the zeolite could influence the nature of the external phase. It should be noted that the plots of U_G and m_i as a function of a_w (Figures 4 and 5) do not show a discontinuity consequent on a change in the nature of the external phase.

Figure 6 shows a plot of internal molality against external molality. The slopes m_i/m are 0.30 for Na-Y, 0.65 for K-Y, and 1.09 for Ba-Y; these support the selectivity order Ba-Y > K-Y > Na-Y.

5. Conclusions

These investigations provide further evidence that isopiestic equilibration is an effective means by which the sorption of nonvolatile sorbates by zeolites may be observed. As demonstrated the method can be used to measure sorbate uptakes and zeolitic water contents at water activities below those of saturated aqueous sorbate solutions and thus provides information not readily obtained by other methods. It is particularly suitable for investigation of the sorption of sugars and should find widespread use in this area of research.

Direct comparison of the present results with those of previous investigations [1–3] is not possible, but the larger uptake from dilute solution found for Ba-Y is consistent with the general observation that sugars complex more strongly with alkaline earth cations than with those of the alkali metals [8]. Although we would expect that other sugar + zeolite combinations will behave in a similar manner to that observed for galactose + zeolite-Y, the exact details will be very dependent on the cation content and framework structure of the zeolite and on the chemical

structure of the sugar. It seems likely that the highest maximum sugar uptakes ($\equiv U_G^0$) will be observed with cations that bind weakly to the sugar and allow freedom in the way in which its molecules pack in the zeolitic cavities. On the other hand when the cation + sugar interaction is strong high sugar uptakes will be observed at low water activities, but the maximum sugar uptakes will be lower than when the interaction is weak. In either case it is to be expected that to obtain maximum sugar uptakes it will be necessary to use solid phase equilibration and water activities well below those of saturated sugar solutions.

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