

Steric effects in the sorption of *n*-butanol and *tert*-butanol by tailored phenyl-modified porous silicas

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Sorption of *n*-butanol and *tert*-butanol on tailored phenyl-modified microporous and mesoporous silicas has been investigated. For the microporous sorbent, the form of the sorption isotherm depends on the stereochemistry of the alcohol. Sorption of straight chain *n*-butanol molecules gives a Type IV isotherm with partial blocking of pores by sorbed molecules. Sorption of the near-spherical *tert*-butanol molecules gives a Type I isotherm, without pore blocking. Sorption isotherms for the isomeric alcohols on the mesoporous sorbent are very similar, reflecting condensation in the same pore structure. In comparison to the weak adsorptive–adsorbent interactions found in earlier studies of water sorption (in which a hydrophobic surface was characterised), the alcohols show strengthened adsorptive–adsorbent interactions, the initial binding to the surface being *via* H-bonds with additional attractive interactions between the alkyl groups and the surface-attached phenyl moieties.

1. Introduction

The synthesis of the ordered mesoporous aluminosilicates (designated M41S materials) in 1992¹ led to great interest in the sorption characteristics of these materials. The high surface area and uniform pore structure of these solids make them ideally suited to applications as model sorbents, catalysts and catalyst supports. Early attempts to incorporate catalytically active guest species in the channels of the material MCM-41 resulted, however, in low guest loadings, probably due to the absence of specific interactions between host and guest. This problem was alleviated by the synthesis of organically-modified porous silicas by the hydrolysis and co-condensation of a siloxane and organosiloxane in the presence of a surfactant *e.g.*² Our initial studies of nitrogen, water vapour and benzene physisorption on a phenyl-modified MCM-41 type material³ indicated that it was microporous (mean pore diameter ≈ 20 Å), showing that the incorporation of phenyl groups resulted in a reduction in pore diameter. One of the most desirable characteristics of unmodified MCM-41 is that its pore diameter can be tailored in the mesoporous range. Mesitylene was subsequently successfully employed by us as a pore-swelling agent during the synthesis of a phenyl-modified porous silica;⁴ characterisation of this material by nitrogen and benzene sorption confirmed its mesoporous character.

In this paper we report the separate sorption at 303 K of *n*-butanol and *tert*-butanol on the tailored phenyl-modified microporous silica above and on the tailored mesoporous analogue. Use of these isomers enables exploration of whether the adsorption process is shape sensitive (*n*-butanol can be thought of as a straight chain, whereas *tert*-butanol approximates to a sphere). Our earlier studies of water sorption and of benzene sorption on the microporous phenyl-modified silica³ pointed to the material being hydrophobic, with some indication of limited steric hindrance in the sorption of benzene. The adsorption isotherms and data reduction presented here are compared with our previously reported nitrogen, water and benzene sorption data for the same samples.^{3,4}

2. Experimental

Synthesis

The microporous and mesoporous phenyl-modified silicas were synthesised *via* the hydrolysis and co-condensation of phenyltriethoxysilane and tetraethoxysilane in the presence of cetyltrimethylammonium chloride using previously reported procedures.^{3,4}

Instrumentation

Studies of the separate adsorption of *n*-butanol and *tert*-butanol at 303 K were performed using a McBain–Bakr gravimetric balance built in-house (Exeter, details reported previously⁴). The samples were outgassed at 373 K under vacuum ($< 10^{-5}$ Torr, monitored by Pirani and Penning gauges) for several hours to remove physisorbed vapour prior to adsorption. Isotherms are presented as plots of amount sorbed (mmol g^{-1}) *vs.* relative pressure, p/p^0 . Adsorptives were exposed to three ‘freeze–pump–thaw’ cycles to remove dissolved gases before sorption studies. For each data point the sample was exposed to the adsorptive and allowed to reach equilibrium, this being defined by the time at which no further decrease in pressure and no further increase in mass of the sample was observed (typically 1–3 h). Sorptive vapour pressure readings of less than 6×10^3 Pa were recorded using a silicone oil manometer containing DC 550 silicone fluid, the density of which was 1.053 g cm^{-3} with a precision of ± 5 Pa. For vapour pressure readings above 6×10^3 Pa, a pressure transducer (Digitron Instruments, model P400) with a precision of ± 7 Pa was used.

3. Results and discussion

Data reduction starting from empirical isotherms employed standard techniques in determining empirical parameters, such as monolayer capacity, BET surface areas and total pore volume, for each sample.^{5,6} The results of data reduction are

summarised in Table 1, which also presents the results similarly obtained from nitrogen, water and benzene sorption isotherms.^{3,4}

As will be outlined below, the sorption characteristics of the isomeric butanols differ significantly in the case of the microporous sorbent, but do not in the case of the larger pore diameter mesoporous sorbent.

Microporous phenyl-modified silica

Empirical isotherms for *n*- and *tert*-butanol sorption are presented in Fig. 1. It is evident that the different isomers result in isotherms of different types⁶ for this material.

***n*-Butanol sorption.** *n*-Butanol adsorption on the microporous phenyl-modified silica yielded an isotherm which appears, upon preliminary examination, to display Type IV physisorption characteristics (Fig. 1). The Gurvitsch total pore volume, $V_p(n\text{-butanol}) = 0.23 \text{ cm}^3 \text{ g}^{-1}$, calculated from this isotherm is considerably lower than those given by other adsorbates for this material (see Table 1), including *tert*-butanol ($V_p(\text{tert-butanol}) = 0.33 \text{ cm}^3 \text{ g}^{-1}$, see below). This suggests that complete surface coverage has not occurred during *n*-butanol adsorption and hence that steric effects may have influenced the structure of the adsorbed layer.

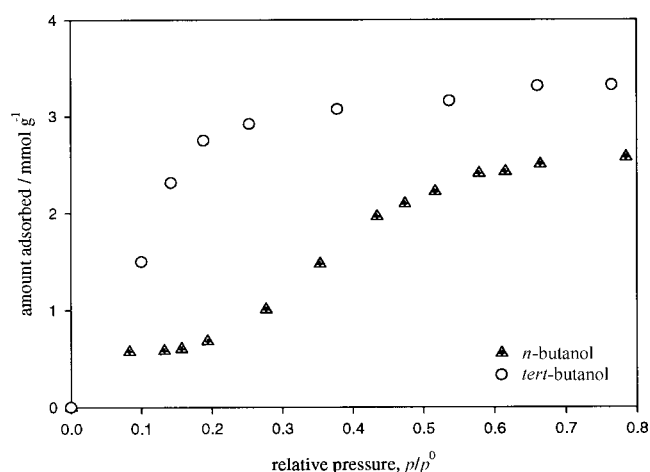


Fig. 1 Comparison of sorption isotherms at 303 K for *n*- and *tert*-butanol on microporous phenyl-modified silica.

A sharp knee evident at $p/p^0 \approx 0.08$ corresponds to a BET monolayer capacity $n_m(n\text{-butanol}) = 0.55 \text{ mmol g}^{-1}$, much lower than those given by other adsorbates (nitrogen, water, benzene) for this sample (Table 1). The specific surface area, $S_{sp}(n\text{-butanol}) = 103 \text{ m}^2 \text{ g}^{-1}$ (calculated from the monolayer capacity value) is much lower than the specific surface areas obtained for this material using other adsorbates (*e.g.* $S_{sp}(\text{N}_2) = 882 \text{ m}^2 \text{ g}^{-1}$). Calculation of this specific surface area was performed using a value for the molecular area $a_m = 31 \text{ \AA}^2$, obtained from the liquid density ($a_m = 1.091(M/\rho_{LL})^{2/3} \times 10^{16}$).⁷ This equation assumes spherical molecules and hexagonal-packing, which is a poor description in the case of *n*-butanol (a straight-chain alcohol), and this value is therefore problematic.

The sorption isotherm resembles the isotherm for water sorption³ where the mechanism of adsorption is dictated by preferential adsorption (*via* H-bonding) at surface hydroxy groups followed by coalescence of sorbed water molecules at these surface sites (rather than monolayer formation). Assuming that *n*-butanol adsorbs on the surface of this material *via* H-bonding interactions with surface hydroxy groups, a notional value for the number of surface hydroxy groups per unit surface area can be calculated assuming one *n*-butanol molecule to adsorb per surface hydroxy. Using the monolayer capacity $n_m(n\text{-butanol})$ and the nitrogen specific surface area ($S_{sp}(\text{N}_2) = 882 \text{ m}^2 \text{ g}^{-1}$), a value of $0.38 \text{ OH groups nm}^{-2}$ is obtained. This is considerably lower than that calculated from water sorption data (0.9 nm^{-2}), and this suggests incomplete utilisation of the surface hydroxy groups *i.e.* *n*-butanol is occupying just over a third of the available surface binding sites. This corresponds either to adsorbed *n*-butanol molecules partially blocking the pores or to their denying access to some adsorption sites by lying across them, inhibiting further adsorption. This would also account for the low value for the Gurvitsch total pore volume for this sorptive.

***tert*-Butanol sorption.** *tert*-Butanol sorption at 303 K on the microporous phenyl-modified sample yielded an isotherm displaying Type I characteristics (Fig. 1). The total pore volume, $V_p(\text{tert-butanol}) = 0.33 \text{ cm}^3 \text{ g}^{-1}$, is within experimental error of that derived from water sorption and within experimental error of that derived from benzene sorption ($0.31 \text{ cm}^3 \text{ g}^{-1}$). It is, however, larger than that obtained from *n*-butanol sorption ($0.23 \text{ cm}^3 \text{ g}^{-1}$), which suggests that *tert*-butanol

Table 1 Summary of butanol, water, benzene and nitrogen sorption data^a

Adsorptive	Physical quantity	Microporous phenyl-modified silica	Mesoporous phenyl-modified silica
<i>n</i> -Butanol $\rho_L = 0.81 \text{ g cm}^{-3}$ $p^0 = 4.24 \text{ kPa}$	$n_m/\text{mmol g}^{-1}$	0.55	1.98
	$S_{sp}/\text{m}^2 \text{ g}^{-1}$	103	461
	$V_p/\text{cm}^3 \text{ g}^{-1}$	0.23	0.62
<i>tert</i> -Butanol $\rho_L = 0.79 \text{ g cm}^{-3}$ $p^0 = 7.73 \text{ kPa}$	$n_m/\text{mmol g}^{-1}$	2.12(3.70) ^b	2.47
	$S_{sp}/\text{m}^2 \text{ g}^{-1}$	644(742)	497
	$V_p/\text{cm}^3 \text{ g}^{-1}$	0.33	0.61
H_2O^3 $\rho_L = 1.00 \text{ g cm}^{-3}$ $p^0 = 1.68 \text{ kPa}$	$n_m/\text{mmol g}^{-1}$	1.32	
	$S_{sp}/\text{m}^2 \text{ g}^{-1}$	83	
	$V_p/\text{cm}^3 \text{ g}^{-1}$	0.33	
$\text{C}_6\text{H}_6^{3,4}$ $\rho_L = 0.88 \text{ g cm}^{-3}$ $p^0 = 10.2 \text{ kPa}$	$n_m/\text{mmol g}^{-1}$	3.00(4.7) ^b	4.20
	$S_{sp}/\text{m}^2 \text{ g}^{-1}$	750(1217)	1051
	$V_p/\text{cm}^3 \text{ g}^{-1}$	0.31	0.76
$\text{N}_2^{3,4}$ $\rho_L = 0.81 \text{ g cm}^{-3}$ $p^0 = 101 \text{ kPa}$	$n_m/\text{mmol g}^{-1}$	9.04 ^b	9.65
	$S_{sp}/\text{m}^2 \text{ g}^{-1}$	882	942
	$V_p/\text{cm}^3 \text{ g}^{-1}$	0.45	0.67

^a ρ_L —density of liquid adsorptive, p^0 —saturated vapour pressure of adsorptive, n_m —monolayer capacity, S_{sp} —derived specific surface area, V_p —total pore volume. Numbers in parentheses are calculated by applying the Langmuir model. ^b These values are calculated from Type I isotherms and are therefore more likely to reflect the micropore volume rather than the monolayer capacity.

(approximately spherical) is packed more efficiently than *n*-butanol (linear) in the pores [in the case of *n*-butanol this is ascribed to the blocking of sorption sites]. $V_p(N_2) = 0.45 \text{ cm}^3 \text{ g}^{-1}$,³ which is therefore greater than calculated for the other sorbents studied; this suggests that *tert*-butanol is packed in a less-dense state than its pure liquid form, as are water and benzene in turn.

At low relative pressures there is a large uptake of adsorbate before the isotherm levels off at $p/p^0 \approx 0.2$. BET analysis yields a monolayer capacity $n_m(\textit{tert-butanol}) = 2.12 \text{ mmol g}^{-1}$, considerably larger than that similarly obtained from *n*-butanol sorption (0.55 mmol g^{-1}) (this analysis should be interpreted with caution in that the knee in the Type I isotherm in microporous solids is likely to reflect micropore filling rather than monolayer formation⁶). The monolayer capacity leads to an estimated $S_{sp}(\textit{tert-butanol}) = 664 \text{ m}^2 \text{ g}^{-1}$, which is lower than would be expected for this material ($S_{sp}(N_2) = 882 \text{ m}^2 \text{ g}^{-1}$). As the isotherm is Type I, Langmuir analysis was also performed and this yielded a monolayer capacity of $n_L(\textit{tert-butanol}) = 3.70 \text{ mmol g}^{-1}$, corresponding to a Langmuir specific surface area $S_L(\textit{tert-butanol}) = 742 \text{ m}^2 \text{ g}^{-1}$, very similar to that obtained from benzene sorption ($750 \text{ m}^2 \text{ g}^{-1}$). Values of the mean area per sorbed molecule, $a_c(\textit{tert-butanol}) = 45 \text{ \AA}^2$ (obtained using the BET monolayer capacity and the N_2 specific surface area) and $a_c(\textit{tert-butanol}) = 38 \text{ \AA}^2$ (using the Langmuir monolayer capacity) are considerably lower than for *n*-butanol on this material ($a_c(\textit{n-butanol}) = 284 \text{ \AA}^2$) suggesting that site blocking is not occurring in the case of *tert*-butanol.

Comparison with water sorption. Our previous study of water sorption on this material³ showed a Type V isotherm with this sorbent, indicating weak adsorptive-adsorbent interactions (a hydrophobic surface). The isotherms for the butanols in this are consistent with considerably stronger adsorptive-adsorbent interactions. This difference is a direct consequence of the organophilic alkyl groups present in the alcohols in this study and able to interact attractively with the surface-attached phenyl moieties.

Mesoporous phenyl-modified silica

In the case of this material, empirical sorption isotherms for the butanol isomers are nearly superimposable (Fig. 2), indicating closely related sorption phenomena in the two cases. In the case of *n*-butanol, low pressure hysteresis was observed in the desorption branch of the isotherm (Fig. 3), which suggests some surface rehydroxylation during the experiment (as in

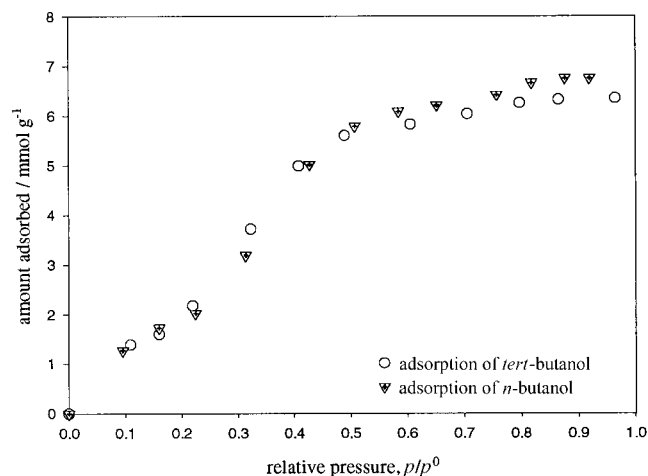


Fig. 2 Sorption isotherms at 303 K for *n*- and *tert*-butanol on mesoporous phenyl-modified silica.

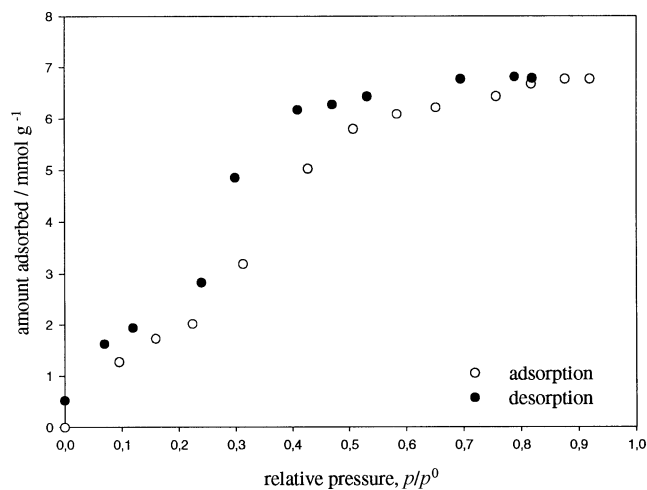


Fig. 3 Sorption-desorption isotherm at 303 K for *n*-butanol on mesoporous phenyl-modified silica.

earlier measurements^{3,4}). The same sample of sorbent was used for the subsequent *tert*-butanol measurements and hysteresis was not observed in that case (rehydroxylation being completed during the first, *n*-butanol, experiment).

***n*-Butanol sorption.** *n*-Butanol sorption at 303 K on the mesoporous phenyl-modified silica yielded a Type IV isotherm exhibiting low pressure hysteresis (Fig. 3), as discussed above. The Gurvitsch pore volume, $V_p(\textit{n-butanol}) = 0.62 \text{ cm}^3 \text{ g}^{-1}$, is close to that derived from the nitrogen isotherm ($0.67 \text{ cm}^3 \text{ g}^{-1}$),⁴ suggesting that *n*-butanol sorption is not sterically hindered in this larger pore sample.

Application of the BET equation yields a monolayer capacity $n_m(\textit{n-butanol}) = 1.98 \text{ mmol g}^{-1}$, leading to a specific surface area, $S_{sp}(\textit{n-butanol}) = 461 \text{ m}^2 \text{ g}^{-1}$. The latter is lower than would be expected for this type of sample ($S_{sp}(N_2) = 942 \text{ m}^2 \text{ g}^{-1}$), which indicates localised adsorption (H-bonding between the alcohol and the surface hydroxy groups), but the value of $a_m(\textit{n-butanol}) = 31 \text{ \AA}^2$ used to calculate the specific surface area is, as discussed above, open to question.

Calculation of a notional surface concentration of surface hydroxy groups present from this isotherm yields a value of 1.26 nm^{-2} , which is higher than in the case of the microporous sorbent (0.9 nm^{-2}). Comparison of the sorption isotherms for the two butanol isomers (Fig. 2) indicates that sorption in each case is very similar in the mesoporous material. The sorption of *n*-butanol is not hindered in the mesoporous sorbent despite the higher surface hydroxy concentration than in the microporous sorbent in the previous section. These considerations indicate that the correct explanation of incomplete surface coverage in *n*-butanol sorption on the microporous material is partial pore blocking by sorbed molecules.

***tert*-Butanol sorption.** The sorption of *tert*-butanol on the mesoporous sample also yielded a Type IV isotherm (Fig. 2). The Gurvitsch pore volume, $V_p(\textit{tert-butanol}) = 0.61 \text{ cm}^3 \text{ g}^{-1}$, is identical within experimental error to that given by the *n*-butanol isotherm ($V_p(\textit{n-butanol}) = 0.62 \text{ cm}^3 \text{ g}^{-1}$). The similarity of the two adsorption isotherms both in shape (Fig. 2) and in total amount adsorbed indicates that in the large pores of this MES-swollen sample adsorption of both of these alcohols is unhindered. The monolayer capacity, $n_m(\textit{tert-butanol}) = 2.47 \text{ mmol g}^{-1}$, and BET surface area $S_{sp}(\textit{tert-butanol}) = 497 \text{ m}^2 \text{ g}^{-1}$ are lower than would be expected for this material ($S_{sp}(N_2) = 942 \text{ m}^2 \text{ g}^{-1}$) suggesting that localised adsorption (due to H-bonding interactions) has also occurred in this case. The mean area per sorbed *tert*-butanol molecule

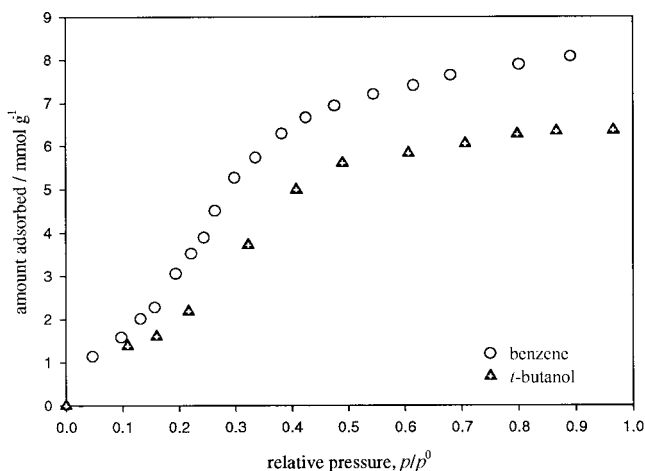


Fig. 4 Comparison of sorption isotherms for benzene and *tert*-butanol on mesoporous phenyl-modified mesoporous silica.

is calculated as $a_s(\textit{tert}\text{-butanol}) = 63 \text{ \AA}^2$.

Calculation of the notional concentration of surface hydroxy groups present, from the *tert*-butanol isotherm, yields a value of 1.58 nm^{-2} . This is greater than that calculated from the *n*-butanol isotherm (1.26 nm^{-2}), which is simply explained in the same manner as the lack of a hysteresis loop in the combined sorption-desorption data for this adsorptive (*i.e.* rehydroxylation of the surface during prior *n*-butanol sorption has increased the number of surface hydroxy groups).

A comparison of the benzene⁴ and *tert*-butanol sorption isotherms for this sample is shown in Fig. 4. The similar shapes of all these isotherms (the isomeric alcohols and benzene) are fully consistent with condensation of the appropriate liquids in the same mesoporous pore structure.

4. Conclusions

A summary of the sorption parameters for *n*- and *tert*-butanol sorption on tailored microporous and mesoporous phenyl-modified silicas samples is presented in Table 1, together with data for nitrogen, water and benzene sorption on the same materials.^{3,4}

In comparison to sorption of water on an essentially hydrophobic modified silica surface, the alcohols show strengthened adsorptive-adsorbent interactions. The interaction with the silica surface is by H-bonding as in the water case, but the alkyl groups in the alcohols interact attractively with surface-attached phenyl moieties. This sorption model constitutes a localised sorption mechanism.

Sorption of *n*-butanol by the microporous material differs from sorption of *tert*-butanol. In the case of the straight chain *n*-butanol molecule, only one third of the available hydroxy groups are involved in H-bonds to sorbed alcohol, sorbed molecules partially blocking access to pores. In the case of the near-spherical *tert*-butanol molecule, pore-blocking does not occur.

In the case of sorption by the mesoporous material, the isomeric butanols result in very similar isotherms, which resemble our earlier results for benzene sorption on this material⁴ and are fully consistent with condensation of the appropriate liquids within the same pore structure.

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