Sorption of Benzene on Chromosorb Porous Polymers, and Evolution of BET Surface Areas from their Adsorption Isotherms

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Summary: Sorption of benzene on chromosorb (101-105) has been studied from gas chromatography retention data. The effect of sample size and thus surface coverage on the heats of sorption was also assessed, BET surface area measurement has also been made using benzene sorptive.

Introduction

The chromosorb polymers are produced by copolymerizing monofunctional and difunctional monomers. Functional groups, such as acrylonitrile and acrylic ester, when incorporated into the polymer matrix, provide a moderately polar to polar surface of the copolymer [1]. These polymers differ in the degree of cross- linking, and thus differ in pore size and surface areas even though their chemical structure may be the same. The gas chromatographic behaviour of porapak and chromosorb porous polymers was investigated by analysing mixture of hydrogen, carbon dioxide, methane, acetylene, ethylene and ethane at different temperatures on columns packed with various types of beads of porapak and chromosorbs [2,3]. The relative retention with respect to ethylene was used for the rapid identification of the type of porapak and chromosorb and also to compare the gas chromatographic behaviour of these porous polymers.

The surface area, micropore volume, pore diameter and average particle diameter were considered to be the most important features of the porous polymers [4].

Results and Discussion

Gas chromatography

0.2 μl of benzene was injected over appropriate temperature ranges. This was 140°C to 190°C for chromosorb 101 and 102, 110° to 170 °C for chromosorb 103 and 104 and 160°C to 200°C for chromosorb 105. Their retention time (tR) were measured, and the adjusted retention volume (V,R) were calculated long V,R versus 1/T was plotted. All the plots were linear with correlation coefficient between 0.999. From these slopes, the heats of sorption were calculated and these are shown in Table 1.

Table 1: Heats of sorption (KJ moel^{-1}) of benzene on chromosorb.

Chromosorbs				
101	102	103	104	105
35.75	42.40	49.00	47.80	39.65

All the chromosorbs are polyaromatic, but there is a wide variation in pore size ranges. The polarity of the chromosorbs changes with the chemical composition. Chromosorb 104 being the most polar [1]. Looking at Table 1 the heats of sorption of chromosorb 103 seem to be the highest, suggesting that in the retention mechanism partition makes an important contribution. Its average pore diameter is larger than chromosorb 102, 104 and 105 (300-400 nm), and these larger pores are more readily available to larger molecules. The chromosorb 103 shows the greatest partition effect, so the high value ΔH_a (heat of interaction) may be due to high degree of partitioning. This effect is less marked in chromosorb 101.

Sorption of benzene sorbate

The data obtained by the adsorption of benzene on chromosorb porous polymers are given in Table 2-6 and BET plots for the sorption of ben-

Table 2: Adsorption data for benzene on chromosorb 101

Points	(Recorder range on 2) ε Δ	P/mV (mg.)	ε Mass (mg.)	ε Mass adsor-bed	Mass adsor bed/g (Sample)	P/Po	P/Po/ W_a (1-/Po)
0	0	0	24.30	0	0	0	0
1	2.6	0.21	24.82	0.52	0.021	0.027	1.321
2	3.2	0.32	24.94	0.64	0.026	0.041	1.644
3	5.0	0.80	25.30	1.00	0.041	0.101	2.740
4	6.0	1.10	25.50	1.2	0.049	0.139	3.294
5	7.0	1.43	25.70	1.4	0.057	0.190	4.115
6	8.5	1.80	26.00	1.7	0.069	0.24	4.576
7	9.5	2.11	26.20	1.9	0.078	0.29	5.236
8	12.8	2.86	26.86	2.56	0.105	0.41	6.618
9	14.8	3.41	27.26	2.96	0.121	0.48	7.628
10	16.8	3.92	27.66	3.36	0.138	0.54	8.500

Sample weight (weighted) = 24.9 mg
Sample weight on Cahn by deflection (1 x 10 = 10) = 24.8 mg.
Saturation pressure = 100 mm
Thermostat bath at 27°C

Table 3: Adsorption data for benzene on chromosorb 102

Points	(Recorder range on 2) ε Δ	P/mV (mg.)	ε Mass (mg.)	ε Mass adsor-bed	Mass adsor bed/g (Sample)	P/Po	P/Po/ W_a (1-/Po)
0	0	0	26.40	0	0	0	0
1	2.2	0.20	26.84	0.44	0.016	0.026	1.668
2	3.0	0.32	27.00	0.60	0.022	0.041	1.943
3	5.0	0.80	27.40	1.00	0.037	0.101	0.036
4	7.0	1.09	27.80	1.40	0.053	0.138	3.020
5	8.6	1.39	28.12	0.065	0.190	3.608	
6	10.8	1.80	28.56	2.16	0.081	0.240	3.898
7	12.2	2.10	28.84	2.44	0.092	0.287	4.375
8	15.4	2.84	29.48	3.08	0.116	0.387	5.442
9	18.0	3.47	30.00	3.60	0.136	0.478	6.733
10	21.0	4.07	30.60	4.20	0.159	0.561	8.037
11	24.0	4.88	31.28	4.80	0.181	0.674	11.422

Sample weight (weight) = 27.1 mg
Sample weight on Cahn by deflection (1x10 = 10) = 26.4 mg
Saturation pressure = 100 mm.
Thermostat bath at 27°C.

Table 4: Adsorption data for benzene on chromosorb 103

Points	(Recorder range on 2) ε Δ	P/mV (mg.)	ε Mass (mg.)	ε Mass adsor-bed	Mass adsor bed/g (Sample)	P/Po	P/Po/ W_a (1-/Po)
0	0	0	28.30	0	0	0	0
1	2.6	0.20	28.82	0.52	0.018	0.026	1.483
2	3.0	0.30	28.90	0.60	0.021	0.038	1.881
3	5.0	0.79	29.30	1.00	0.035	0.100	3.174
4	6.0	1.09	29.50	1.20	0.042	0.138	3.811
5	6.8	1.39	29.66	1.36	0.048	0.190	4.886
6	8.0	1.78	29.90	1.60	0.056	0.240	5.639
7	9.0	2.07	30.10	1.80	0.063	0.287	6.389
8	11.5	2.84	30.60	2.30	0.081	0.387	7.794
9	13.0	3.45	30.90	2.60	0.091	0.475	9.942
10	15.8	4.00	31.46	3.16	0.111	0.551	11.055
11	19.4	4.99	32.18	3.88	0.137	0.689	16.171
12	23.8	6.05	33.06	4.76	0.168	0.836	30.342

Sample weight (weight) = 29.7 mg
Sample weight on Cahn by deflection (1x10 = 10) = 28.50 mg.
Saturation pressure
Thermostat bath at 27°C.

Table 5: Adsorption data for benzene on chromosorb 104

Points	(Recorder range on 2) ε Δ	P/mV (mg.)	ε Mass (mg.)	ε Mass adsor-bed	Mass adsor bed/g (Sample)	P/Po	P/Po/ W_a (1-/Po)
0	0	0	23.70	0	0	0	0
1	2.0	0.20	24.10	0.40	0.016	0.026	1.668
2	3.0	0.31	24.30	0.60	0.025	0.039	1.623
3	4.4	0.80	24.58	0.88	0.037	0.101	3.036
4	5.2	1.10	24.74	1.04	0.043	0.139	3.754
5	6.0	1.39	24.90	1.20	0.050	0.190	4.691
6	7.0	1.80	25.10	1.40	0.059	0.240	5.352
7	7.6	2.10	25.22	1.52	0.064	0.287	6.289
8	9.0	2.87	25.50	1.80	0.075	0.394	8.668
9	11.0	3.44	25.90	2.20	0.092	0.473	9.755
10	12.0	3.95	26.10	2.41	0.101	0.544	11.833

Sample weight (weighed) = 23.7 mg.
Sample weight on Cahn by deflection (1x10 = 10) = 23.8 mg
Saturation pressure = 100 mm.
Thermostat bath at 27°C.

zene are shown in Fig. 1. Surface areas measured by the adsorption of benzene are given in Table 8.

The area occupied by a molecule of benzene on the surface of a solid can be very different according to whether the molecule is lying flat or standing end on. The value of the area of a benzene molecule was taken to be $[43.0A^{\circ}]^2$ [6,7]. This assumed that the molecule is lying flat on the surface. It is also assumes that there is the possibility of partition involving uptake of the molecule into the body of the sorbent with resultant swelling of the structure. This is not adsorption, but would lead to a higher value of the apparent surface area.

In general, a sorbate with a chemical structure and nature similar to that of the sorbent will exhibit most partition. These porous polymers are generally based on styrene and thus there is a relatively large affinity for aromatic compounds and other hydrocarbons.

However, before partition can occur, the sorbate must come into contact with the sorbeat,

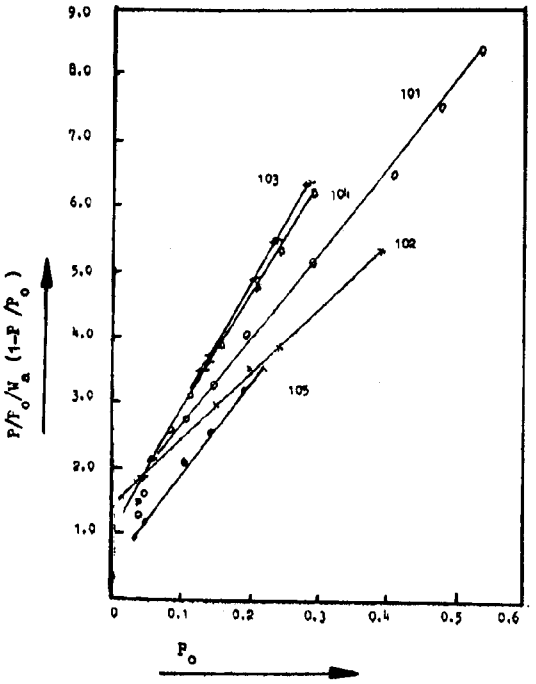

Fig.1: BET plots for the sorption of benzene on various sorbents

101 = Chromosorb 101
102 = Chromosorb 102
103 = Chromosorb 103
104 = Chromosorb 104
105 = Chromosorb 105

Table 6: Adsorption data for benzene on chromosorb 105

Points	(Recorder range on 2) $\varepsilon\Delta$	P/mV (mg.)	ε Mass (mg.)	ε Mass adsorbed	Mass adsor bed/g (Sample)	P/Po	P/Po/ W_a (1-/Po)
0	0	0	22.10	0	0	0	0
1	3.0	0.20	22.70	0.60	0.027	0.026	0.988
2	3.6	0.30	22.82	0.72	0.032	0.038	1.234
3	5.8	0.80	23.26	1.16	0.052	0.101	2.160
4	7.0	1.10	23.50	1.40	0.063	0.139	2.562
5	8.0	1.40	23.70	1.60	0.072	0.192	3.300
6	10.0	1.78	24.10	2.00	0.090	0.240	3.508
7	11.2	2.08	24.34	2.24	0.101	0.267	3.606
8	14.4	2.87	24.98	2.88	0.130	0.394	5.000
9	17.6	3.46	25.62	3.52	0.159	0.476	5.713
10	20.4	3.95	26.18	4.08	0.184	0.544	6.483

Sample weight (weighed) = 22.6 mg
Sample weight on Cahn by deflection (1x10 = 10) = 22.0 mg.
Saturation pressure = 100 mm
Thermostat bath at 27°C.

hence both the surface area and pore size characteristics of the sorbents are important. These features determine the amount of surface contact between sorbate and sorbent and this in part determines the amount of partition which can occur since the first step of the partition mechanism involves migration of the sorbate to the sorbent surface. A high surface area is preferred in general, but the pore diameter is equally important. If the high surface area is a result of a great number of small pores, this will little benefit since the large molecules being considered are unlikely to be able to move into small pore structure. Thus large pores are at least as vital as large surface area. In many ways these two factors are incompatible, since a sorbent with large diameter pores is unlikely to have a very large surface area and the ideal sorbent is likely to be a compromise between these two factors.

Table 7: Values of BET surface areas with benzene as sorbate

Sorbent	BEt surfafcee area $m^2 g^{-1}$
Chromosorb 101	231
Chromosorb 102	290
Chromosorb 103	170
Chromosorb 104	177
Chromosorb 105	226

Experimental

1. Gas chromatographic measurements

All the gas chromatographic measurements were made using a Perkin-Elmer model F. 30 gas chromatograph, equiped with a flame ionization detector. Stainless column (2-6 meter long and 1/8" o.d) were packed separately with chromosorb 101, 102, 103, 104 and 105 under pressure and vibration. The columns were conditioned for about three hours at 220°C in a flow of nitrogen, which was used as a carrier gas 0.2 μl of reagent grade benzene was injected by means of 1 μl Hamilton syringe for every column at four or five temperatures in the range of 120-200°C. Isothermal conditions were used for each analysis.

2. Sorption of benzene using the Cahn electrobalance

The adsorption of benzene vapours was studied on chromosorbs using Cahn RG electrobalance. The balance was developed by Cahn [5] to measure weight changes in high vacuum, controlled atmosphere and room air. It has

a maximum capacity of 2.5 gm and an ultimate sensitivity of 0.1 μg. Twenty-forty mg of the sample was accurately weighed into the bucket suspended from a loop. All the samples were out gassed overnight at 150°C. The organic compound (benzene) was then placed in an adosprtive reservoir at ambient temperature. The vapours of benzene were passed by opening the valve very slowly. The adsorptive pressure generated was read from the digital voltameter and was converted to mm Hg. through appropriate table. The uptake of the adsorbate by the sorbent was recorded on a flat-bed recorder, linseis LS4 series. About 10-15 readings were recorded at 30 minutes intervals covering the range p/po 0.02-0.8. A straight line was obtained by plotting p/po/Wa(1-p/po). Vm was calculated from the slope and intercept using the expression,

$$Vm = 1/\text{slope} + \text{intercept}$$

The BET surface area was then calculated from the expression

$$S(BET) = \frac{Vm.\ No.\ Am}{M}$$

Vm = The monolayer capacity ($cm^3\ g^{-1}$)
No = Avogadro's constant
Am = Crossectional area of benzene
M = Molecular weight of the adsorbate
Wa = wt adsorbed per gm of adsorbent
p/po = Relative pressure
p/po/Wa(1-p/po) = BET relationship

p/po was also plotted against Wa to determine the type of isotherms produced.

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