

## Sorption isotherms of organic vapours on Tenax

K. SCHOENE\*, J. STEINHANSES and A. KÖNIG

*Fraunhofer-Institut für Umweltchemie und Ökotoxikologie, D-5948 Schmallenberg (F.R.G.)*

(First received December 18th, 1989; revised manuscript received April 13th, 1990)

---

### ABSTRACT

Sorption isotherms of *o*-xylene, *n*-octane and tetrachloroethene on Tenax were determined at different temperatures, applying vapour concentrations in the range 10–10 000 ppm. In the range up to 120 ppm the isotherms were derived from the results of breakthrough experiments; for the higher concentrations a headspace gas chromatographic method was applied. At lower gas concentrations, corresponding to bed loads of *ca.* 100  $\mu\text{mol/g}$  Tenax, the sorption follows the Freundlich equation, whereas in the higher ppm range the isotherms become linear. For the Freundlich part of the isotherms, the isosteric heats of sorption were calculated to be in the range 40–> 100 kJ/mol.

---

### INTRODUCTION

The porous polymer Tenax [poly(*p*-2,6-diphenylphenylene oxide)], originally developed for gas chromatographic purposes<sup>1</sup>, has proved to be an efficient trapping material for organic vapours. Additionally, it allows most of the substances collected to be desorbed thermally, which facilitates the analytical procedure appreciably<sup>2</sup>. As a consequence, Tenax became one of the most promising sorbents for sampling gaseous pollutants.

On account of its growing practical importance, it seemed of interest to obtain more information about the sorption characteristics of Tenax. In the lower ppm range, the sorption isotherms have been described by both the Freundlich<sup>3</sup> and the Langmuir<sup>4</sup> equations. At higher concentrations, the Tenax isotherms were found to become linear<sup>5</sup>.

The investigations described here were undertaken to re-examine these earlier findings and the sorption isotherms of *o*-xylene, *n*-octane and tetrachloroethene on Tenax TA were determined at different temperatures in the concentration range 10–10 000 ppm. The results confirmed the biphasic shape of the Tenax isotherms with a Freundlich-type section at lower and a linear course at higher vapour concentrations.

## EXPERIMENTAL

Tenax TA (20–35 mesh) was purchased from Alltech (Unterhaching, F.R.G.); the characteristic data were (according to the supplier) specific surface area 35 m<sup>2</sup>/g, pore volume 2.4 cm<sup>3</sup>/g and average pore radius 200 nm. *o*-Xylene (“99+ %”), *n*-octane (“99+ %”) and tetrachloroethene (“99.9%”) were purchased from Aldrich (Steinheim/Buch, F.R.G.).

For determining the sorption isotherms in the concentration range 10–120 ppm, a continuous flow of the sample vapour was conducted through a bed of 220 mg of Tenax (bed length 5 cm) in a stainless-steel tube (8.9 cm × 0.49 cm I.D.) housed in a thermostated cabinet (Heraeus-Vötsch, ±0.5°C). At the downstream side, the breakthrough concentrations were measured at time intervals of 3 min by use of a process gas chromatograph. Plotting the measured concentrations against time yielded the breakthrough curve, from which the equilibrium load  $\alpha$ , *i.e.*, the capacity of the bed, was calculated. Varying the exposure concentration  $c$  led to correspondingly different equilibrium loads  $\alpha$ . By plotting  $\alpha$  vs.  $c$ , the sorption isotherm was obtained. Measurements were carried out at 5, 20 and 40.5°C. The procedural details concerning vapour generation, calibrations, controls and evaluation were given in a previous paper<sup>6</sup>.

The sorption isotherms at higher vapour concentrations (200–10 000 ppm) were determined by headspace gas chromatography (HSGC). Known amounts of Tenax and the liquid test substance were introduced into an HSGC vial in such a way that the liquid did not touch the sorbent. After closure with a septum, the vessel was stored at the test temperature until the sorption equilibrium (via the gas phase) was established. The equilibrium gas concentration  $c$  was then measured by HSGC as usual. The equilibrium load  $\alpha$  on the sorbent was calculated as the difference between the amount originally introduced and the amount found in the gas phase. When applying different amounts of test substance (and keeping that of the sorbent constant), correspondingly different results for  $c$  and  $\alpha$  were obtained. Plotting  $\alpha$  against  $c$  yielded the sorption isotherm. The details of the experimental and evaluation procedure have been described previously<sup>5</sup>. With the HSGC system used (Perkin-Elmer HS 100), the lowest applicable test temperature is about 40°C. Therefore, sorption measurements were performed at 40.5, 50.1 and 60.5°C.

## RESULTS

The complete sorption isotherms obtained at 40.5°C are given in Fig. 1. The curved sections up to 113 ppm represent the results derived from the breakthrough curves and those for the upper range from the HSGC measurements. The shape as shown in Fig. 1 is representative also of the isotherms obtained at the other temperatures; in the range measured, at the higher concentrations no deviation from linearity was observed in any instance.

On account of the biphasic character, in the following the two parts of the isotherm are treated separately and denoted as the “linear section” and the “curved section”.

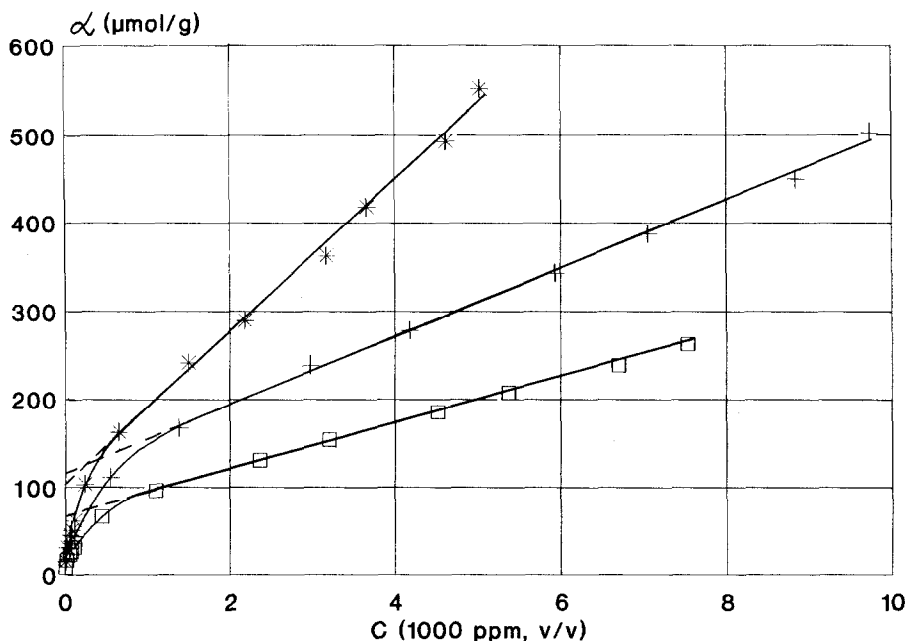


Fig. 1. Sorption isotherms of *o*-xylene (\*), *n*-octane (□) and tetrachloroethene (+) on Tenax at 40.5°C. The straight lines are the result of linear regression according to eqn. 1.

#### Linear section

Except for the one or two lowest values, the sorption data were subjected to linear regression according to

$$\alpha = Sc + \alpha_0 \quad (1)$$

with  $c$  in ppm,  $\alpha$  in mol/g Tenax and  $\alpha_0$  (mol/g) as the intercept with the ordinate, as shown in Fig. 1. The regression parameters are given in Table I. The temperature functions of  $S$  and  $\alpha_0$  follow the equations

$$\log S = A(1/T) + B \quad (2)$$

$$\log \alpha_0 = A'(1/T) + B' \quad (3)$$

The respective data are summarized in Table II. By means of eqns. 2 and 3, the parameters  $S$  and  $\alpha_0$  at 20°C, as given in Table I, were calculated.

#### Curved section

The sorption isotherms obtained with the lower vapour concentrations up to 113 ppm are shown in Fig. 2. The straight lines were drawn on the basis of linear regression according to the Freundlich equation:

$$\log \alpha = p \log c + q \quad (4)$$

TABLE I

LINEAR SECTION: RANGE AND REGRESSION PARAMETERS ACCORDING TO EQN. 1

Compound	<i>T</i> (K)	Range of $\alpha$ (mol/g $\times 10^6$ )	<i>S</i> [mol/(g · ppm)]	$a_0$ (mol/g $\times 10^6$ )	<i>r</i>	<i>n</i>
<i>o</i> -Xylene	313.65	160–550	8.596	104.5	0.997	7
	323.25	150–480	5.559	87.0	0.9998	7
	333.65	90–320	3.943	62.1	0.9994	6
	293.15 <sup>a</sup>		20.98	197		
<i>n</i> -Octane	313.65	100–260	2.550	69.7	0.9997	7
	323.25	80–210	1.880	52.1	0.9997	7
	333.65	50–170	1.826	37.7	0.9992	7
	293.15 <sup>a</sup>		3.59	143		
Tetrachloroethene	313.65	170–500	3.872	116.3	0.9990	7
	323.25	140–430	2.875	90.8	0.998	7
	333.65	90–340	1.796	71.9	0.9990	8
	293.15 <sup>a</sup>		9.76	203		

<sup>a</sup> Extrapolated using eqn. 2 (*S*) and eqn. 3 ( $\alpha_0$ ).

with *c* in ppm and  $\alpha$  in mol/g Tenax. The results are summarized in Table III. Evaluation according to the Langmuir equation led to unsatisfactory results, similar to those reported recently<sup>4</sup>.

#### Heats of sorption

For calculating the heats of sorption (the differential molar enthalpy of sorption<sup>7</sup>), the sorption isotherms in eqn. 4 were converted into the respective sorption isosteres:

$$\log c = (1/p) \log \alpha - q/p \quad (5)$$

For four arbitrarily chosen  $\alpha$  values (10, 30, 50 and 70  $\mu$ mol/g), the corresponding *c* values were calculated at each of the three test temperatures. From these sets of data, the temperature functions of *c* were evaluated according to

$$\log c = f(1/T) + g \quad (6)$$

TABLE II

LINEAR SECTION: TEMPERATURE FUNCTIONS OF *S* AND  $\alpha_0$  ACCORDING TO EQNS. 2 AND 3

Parameter	<i>o</i> -Xylene	<i>n</i> -Octane	Tetrachloroethene
<i>A</i>	1770	757	1747
<i>B</i>	-12.72	-10.03	-12.97
<i>r</i> ( <i>n</i> = 3)	0.997	0.90	0.9998
<i>A'</i>	1184	1397	1093
<i>B'</i>	-7.74	-8.61	-7.42
<i>r</i> ( <i>n</i> = 3)	0.990	0.9997	0.9998

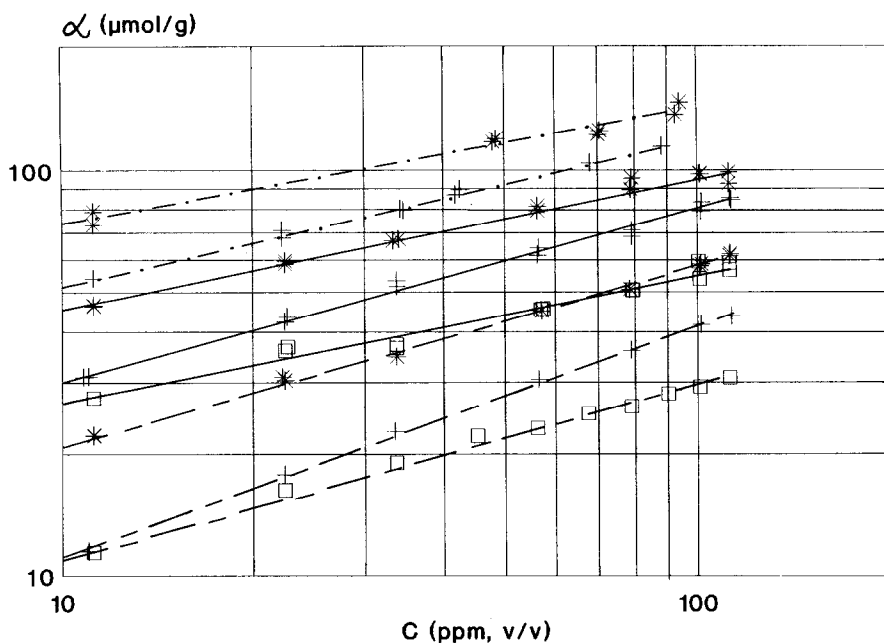


Fig. 2. Sorption isotherms of *o*-xylene (\*), *n*-octane (□) and tetrachloroethene (+) on Tenax according to the Freundlich equation (eqn. 4) at 5°C (···), 20°C (—) and 40.5°C (---).

The correlation coefficients  $r$  resulting for *o*-xylene and tetrachloroethene were  $\geq 0.996$ . For technical reasons, the measurements with *n*-octane could be done at two temperatures only, so that the respective values are based tentatively on two point-calculations.

The heats of sorption,  $Q_s$ , were calculated from the slopes  $f$  by use of the equation

$$Q_s \text{ (kJ/mol)} = 19.147 [T_1 T_2 / (T_1 - T_2)] \log (c_1 / c_2) \quad (7)$$

TABLE III

CURVED SECTION: REGRESSION PARAMETERS OF THE FREUNDLICH EQUATION (EQN. 4)

Compound	$T$ (K)	$p$	$q$	$r$	$n$
<i>o</i> -Xylene	278.15	0.2854	-4.417	0.990	8
	293.15	0.3357	-4.684	0.997	14
	313.65	0.4497	-5.134	0.999	12
<i>n</i> -Octane	293.15	0.3181	-4.895	0.990	14
	313.65	0.4390	-5.404	0.997	11
Tetrachloroethene	278.15	0.3656	-4.652	0.998	9
	293.15	0.4218	-4.940	0.997	14
	313.65	0.5721	-5.526	0.9994	7

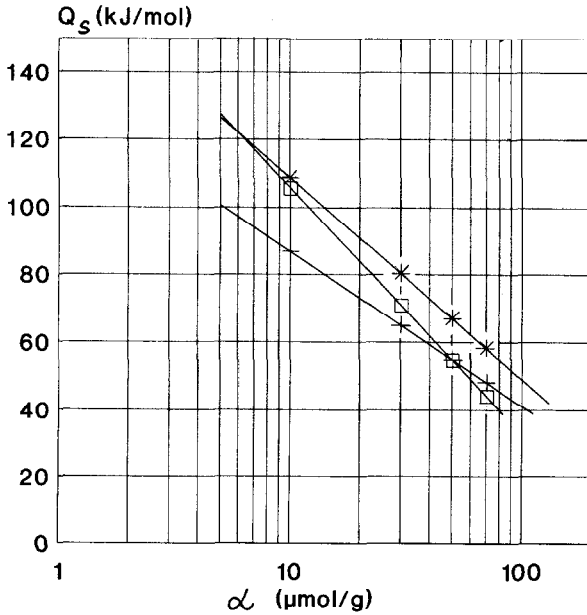


Fig. 3. Heats of sorption,  $Q_s$ , on Tenax in the range of the Freundlich isotherm for *o*-xylene (\*), *n*-octane (□) and tetrachloroethene (+) as a function of the bed load  $\alpha$ .

The resulting  $Q_s$  was found to be related to the bed load  $\alpha$  according to

$$Q_s = -F \log \alpha - G \quad (8)$$

as shown in Fig. 3. The regression parameters are given in Table IV.

#### DISCUSSION

The previously reported biphasic character of the sorption isotherm of tetrachloroethene on Tenax<sup>5</sup> was verified by breakthrough measurements in the lower concentration range. Biphasic isotherms were also found with *o*-xylene and *n*-octane, which suggests that this shape is typical of the sorption behaviour of Tenax.

With regard to the analytical application of Tenax, the relevant part of the isotherm is that following the Freundlich equation (eqn. 4)<sup>6</sup>. The range of validity of

TABLE IV  
CURVED SECTION: REGRESSION PARAMETERS OF EQN. 8 ( $r = 1.00$ )

Compound	$F$	$G$
<i>o</i> -Xylene	59.5	189
<i>n</i> -Octane	72.7	258
Tetrachloroethene	45.7	142

TABLE V

UPPER LIMITS OF THE FREUNDLICH-TYPE SORPTION AND LINEAR REGRESSION DATA OF THE EQUATION  $\log c_0 = v(1/T) + w$ 

Compound	$T$ (K)	$\alpha_0$ ( $\mu\text{mol/g}$ )	$c_0$ (ppm)	$v$	$w$	$r$
<i>o</i> -Xylene	278.15	329 <sup>a</sup>	1876	1730	-2.963	0.998
	293.15	197	822			
	313.65	105	367			
<i>n</i> -Octane	293.15	143	2004	2066	-3.744	
	313.65	70	694			
Tetrachloroethene	278.15	323 <sup>a</sup>	1500	963	-3.000	0.993
	293.15	203	907			
	313.65	116	605			

<sup>a</sup> Extrapolated by means of eqn. 3.

this equation is smaller than the curved part of the isotherm (this becomes obvious from a  $\log \alpha$  vs.  $\log c$  plot up to the regression line). Hence, it seems reasonable to conclude that the  $\alpha_0$  values (Table I) indicate the upper end-points of the Freundlich-type sorption. Introducing the  $\alpha_0$  values into eqn. 5 yields the corresponding concentration limits  $c_0$ . The results in Table V show that, as for  $\alpha_0$ , the  $c_0$  values decrease with increasing temperature; the plots of  $\log c_0$  vs.  $1/T$  appear to be linear.

Interestingly, there is a clear correlation ( $r \geq 0.998$ ) between the  $\alpha_0$  values and the respective molar volumes,  $V_M$  ( $\text{cm}^3/\text{mol}$ ), according to

$$\log \alpha_0 = n \log (1/V_M) + m \quad (9)$$

The  $V_M$  values were calculated using the temperature functions of the specific densities<sup>8</sup>.

Multiplying  $\alpha_0$  by  $V_M$  yields the volume occupied by the quantity  $\alpha_0$  per gram of Tenax. At 20°C these "specific volumes",  $V_s$  ( $\text{cm}^3/\text{g}$ ), are 0.024 (*o*-xylene), 0.023 (*n*-octane) and 0.021 (tetrachloroethene), *i.e.*, 1% of the total pore volume.

Calculation of the specific surface areas,  $A_s$  ( $\text{m}^2/\text{g}$ ), according to  $A_s = \alpha_0 N (V_M/N)^{2/3}$  ( $N$  = Avogadro's number) at 20°C gave 40.5 (*o*-xylene), 35.6 (*n*-octane) and 37.1 (tetrachloroethene), which are in satisfactory agreement with the values of 35  $\text{m}^2/\text{g}$  given by the supplier. It should be noted, however, that with increasing temperature the  $A_s$  values decrease, *e.g.*, down to 9–13  $\text{m}^2/\text{g}$  at 60.5°C.

The heats of sorption,  $Q_s$ , decrease with increasing load,  $\alpha$ . The regression lines (according to eqn. 8) in Fig. 3 were extrapolated to the respective heats of condensation,  $Q_c$  ( $\text{kJ/mol}$ )<sup>9</sup> of 41.9 (*o*-xylene), 38.6 (*n*-octane) and 38.7 (tetrachloroethene). Hence, the differential heat evolved in the Freundlich-type sorption exceeds the heat of condensation up to loads of *ca.* 100  $\mu\text{mol/g}$  Tenax.

In the literature, Tenax is generally referred to as an adsorbent. Following this view, and taking into account the structural characteristics and the curve shape, the isotherms should be considered as type IV isotherms in the Brunauer classification<sup>7</sup>,

the Freundlich-type part indicating adsorption at the pore walls in the form of monomolecular layers and the linear part representing the formation of multilayers.

There are, however, several findings, which do not satisfactorily fit into this concept. The pronounced temperature dependence of the heats of sorption on the load  $\alpha$  is not consistent with that theory<sup>7</sup>. After sampling vapours of hydrolysable compounds on Tenax from a humid atmosphere (50% relative humidity), the sampling tubes could be stored (up to at least 2 months) and subsequently thermally desorbed without loss of analyte, despite the relatively high water content in the tubes<sup>10</sup>. Obviously the state of sorption of the organic compounds prevented the access of (and/or the reaction with) water molecules, which seems hardly to be compatible with the concept of wall adsorption in open pores. Finally, Tenax is reported to be soluble in, for example, lower chlorinated hydrocarbons, tetrahydrofuran, carbon disulphide, dioxane, pyridine and cyclohexanone<sup>1</sup>.

Hence it seems reasonable to assume that after the adsorption step, absorption will also occur to a certain extent and, consequently, to interpret the linear section in terms of Henry's law with the magnitude  $S$  as the solute-gas equilibrium constant. Clarification of this question, however, needs further investigation.

#### REFERENCES

- 1 R. van Wijk, *J. Chromatogr. Sci.*, 8 (1970) 418.
- 2 R. H. Brown and C. J. Purnell, *J. Chromatogr.*, 178 (1979) 79.
- 3 N. van den Hoed and M. T. H. Halmans, *Am. Ind. Hyg. Assoc. J.*, 48 (1987) 364.
- 4 J. Vejrosta, M. Mikesova, A. Ansorgova and J. Drozd, *J. Chromatogr.*, 447 (1988) 170.
- 5 K. Schoene, J. Steinhanses and A. König, *J. Chromatogr.*, 455 (1988) 67.
- 6 K. Schoene, J. Steinhanses and A. König, *Fresenius' Z. Anal. Chem.*, 336 (1990) 114.
- 7 S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London, 2nd ed., 1982.
- 8 *Beilsteins Handbuch der Organischen Chemie*, Springer, Berlin, Göttingen, Heidelberg, 1958, E III: 1, 457 (*n*-octane), 664 (tetrachloroethene), 5, 808 (*o*-xylene).
- 9 R. C. Weast (Editor), *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 67th ed., 1986/1987, p. C-673.
- 10 J. Steinhanses and K. Schoene, *J. Chromatogr.*, 514 (1990) 273.