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## POROUS POLYAROMATIC BEADS

### IV\*. A STUDY OF THEIR INTERACTIONS WITH ADSORBATES IN GAS CHROMATOGRAPHY

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#### SUMMARY

The separation of adsorbates on porous aromatic polymers is discussed in terms of interaction energies. Six adsorbents have been prepared based on the polymerisation of styrene, or a 4-substituted styrene, and divinylbenzene. The substituted styrenes are 4-bromo-, 4-methoxy-, 4-carbomethoxy- and 4-nitrostyrene, and 4-vinylbiphenyl. Retention times for a wide range of aliphatic and aromatic compounds are given and are related to the attractive forces between adsorbates and adsorbents. A semi-quantitative approach is used to account for the relative proportions of dipole and induced-dipole interactions.

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#### INTRODUCTION

An understanding of the physico-chemical processes that occur in gas chromatography (GC) is of importance to those who are interested in complex analytical problems, for in this way, the ability to select and develop stationary phases is enhanced.

There have been many interesting attempts to describe solute-solvent and adsorbate-adsorbent interactions in GC both in terms of thermodynamic and molecular energy functions, principally the former. However, in recent studies, Kiselev *et al.*<sup>1</sup> and Kalashnikova *et al.*<sup>2</sup> have investigated the interactions of various adsorbates on the surface of graphitized thermal carbon black. The intermolecular interaction potential functions between hydrocarbon adsorbates and carbon have been calculated<sup>3</sup> and many of the calculations are in good agreement with experimentally determined retention data, although there are some discrepancies resulting from uncertainties in the calculations, for example concerning the geometry of the adsorbates in the process of adsorption<sup>4</sup>.

However, much of the work done to elucidate the interactions occurring when porous polymer beads are used in GC has been confined to relating retention data

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on commercial polymers to the carbon number of the adsorbate<sup>5-7</sup>, to the relative molecular mass of the adsorbate<sup>7-9</sup>, to thermodynamic functions such as enthalpies<sup>5-7,10-14</sup> and free energies of adsorption<sup>5,6,12</sup>. There have also been attempts to relate retention data to the electron polarizability<sup>7,8,14</sup> of the adsorbate and the dipole moment<sup>7,8</sup> and some of the commercial polymers have been classified<sup>5,8</sup> in terms of specific and non-specific interactions<sup>15</sup>. All these treatments have, in general, been based on polymers with chemical compositions which are not precisely known and whose retention data vary from batch to batch<sup>16-19</sup>.

Due to the difficulties in obtaining consistent results from different batches of commercially available porous aromatic polymers, materials for this work have been prepared from styrene and divinylbenzene and give consistent results<sup>20,21</sup>. Subsequently, a series of polymers was synthesised in which the only change was the substitution of a functional group in the 4-position of the styrene molecule.

Although, by this means, polymers were obtained which gave consistent and reproducible results, it is not yet possible to use Kiselev's method to rationalise retention data, for their chemical nature is complex and their surfaces are not homogeneous. Nevertheless, we have attempted to produce an empirical semi-quantitative explanation of the interactions between the polymers and adsorbates.

## EXPERIMENTAL

Six porous aromatic polymers have been prepared from styrene or a 4-substituted styrene, and divinylbenzene as cross-linking agent (Table I).

All GC results were determined isothermally on Pye Series 104 chromatographs equipped with dual flame ionization or thermal conductivity detectors. Columns were made of 42 × 4 cm I.D. Pyrex glass. As sample size of adsorbate affects the retention time, a standard procedure of injection was used<sup>20</sup>.

TABLE I  
POROUS AROMATIC POLYMERS PREPARED IN THIS STUDY  
DVB = divinylbenzene; EVB = ethylvinylbenzene.

Symbol	Composition (mole %)	Analysis (%)			HETP (mm)	Surface area (m <sup>2</sup> /g)
		C	H	N		
SD	Styrene, DVB, EVB (55,40,5)	91.93	8.02	—	25.0	223
SD-Br	4-Bromostyrene, DVB, EVB (40, 55, 5)	74.86	6.41	—	7.3	424
SD-Ph	4-Vinylbiphenyl, DVB, EVB (42, 53, 5)	92.40	7.60	—	10.4	372
SD-OMe	4-Methoxystyrene, DVB, EVB (48, 47, 5)	85.18	7.87	—	1.4	433
SD-CO <sub>2</sub> Me	4-Carbomethoxystyrene, DVB, EVB (25, 67, 8)	86.19	7.40	—	3.0	494
SD-NO <sub>2</sub>	4-Nitrostyrene, DVB, EVB (45, 50, 5)	78.50	6.27	4.47	2.3	81
SD-Br/Br	SD-Br brominated <sup>20</sup> with Br <sub>2</sub> /CCl <sub>4</sub>	56.33	4.64	—	6.2	392

## RESULTS

The adjusted retention times relative to that of pentane for a selection of aliphatic compounds at 151° on the porous polymers prepared in the study are given in Table II. Adjusted retention times for some aromatic compounds relative to hexane at 193° and relative to benzene at 220° are given in Table III.

TABLE II

ADJUSTED RETENTION TIMES (RELATIVE TO PENTANE) OF ALIPHATIC ADSORBATES ON SOME POROUS AROMATIC POLYMERS

Carrier gas: nitrogen, 50 ml/min. Glass column: 42 × 0.4 cm I.D. Temperature: 151°.

Adsorbate	SD	SD-Ph	SD-OMe	SD-CO <sub>2</sub> Me	SD-Br	SD-NO <sub>2</sub>
Butane	0.38	0.38	0.41	0.36	0.38	0.37
Pentane	1.00	1.00	1.00	1.00	1.00	1.00
Hexane	2.54	2.52	2.64	2.48	2.69	2.65
Heptane	6.46	6.43	6.45	6.52	7.25	6.76
2,2,3-Trimethylbutane	4.62	4.10	4.91	4.72	5.06	—
Octane	15.69	14.48	14.73	16.69	19.31	17.24
But-1-ene	0.35	0.36	0.36	0.33	0.33	0.37
Pent-1-ene	0.94	0.88	1.00	0.90	0.91	1.00
Hex-1-ene	2.42	2.48	2.55	2.33	2.44	2.68
Hept-1-ene	6.31	5.76	6.09	6.10	6.56	6.80
Oct-1-ene	15.15	13.14	14.09	15.21	17.75	17.47
Methanol	0.23	0.21	0.27	0.17	0.19	0.41
Ethanol	0.46	0.48	0.55	0.45	0.44	1.00
Propan-1-ol	1.23	1.24	1.41	1.24	1.19	2.65
Butan-1-ol	3.31	3.24	3.64	3.41	3.38	7.18
Pentan-1-ol	9.08	7.52	8.91	9.34	10.00	19.53
2-Methylbutan-2-ol	4.00	3.62	4.18	4.38	4.59	8.06
Propan-1,2-diol	6.23	6.52	6.82	6.90	5.56	24.71
Formic acid	0.73	0.90	0.86	0.71	0.47	0.76
Acetic acid	1.62	2.52	1.77	1.72	1.25	5.41
Propionic acid	4.69	4.19	2.73	2.83	4.63	13.00
2-Methylpropionic acid	7.62	6.52	6.82	6.45	7.00	24.35
Dichloromethane	0.92	1.00	1.00	0.81	0.72	1.38
Trichloromethane	2.00	2.19	2.18	1.93	1.75	3.15
Tetrachloromethane	2.92	3.19	3.41	2.79	2.94	3.88
1,2-Dichloroethane	2.77	2.95	2.91	2.62	2.50	5.21
1-Bromo-2-methylpropane	4.77	5.00	5.27	4.93	5.31	7.82
2-Bromobutane	4.69	4.76	5.27	4.79	5.19	7.97
Specific retention volume of pentane (ml/g)	27.0	36.7	26.1	50.3	38.5	35.9

## DISCUSSION

In the following treatment, the principal interactions between an adsorbate molecule and a polymer are assumed to be due to the interactions that occur between dipoles and induced dipoles.

The polymer can be considered, as we shall discuss further in more detail, as consisting of a polystyrene "backbone" (in which there are free vinyl groups) to which functional groups are attached. The retention data obtained on the different polymers are related in such a way that the interactions can be approximated to those between the adsorbate molecule and C<sub>6</sub>H<sub>5</sub>X, where X is the functional group on the polymer. However, the latter is constrained and cannot undergo free rotation, and it has been shown that for such a dipolar molecule, able only to undergo rotational oscillations, the contribution to the orientational moment is decreased by half<sup>22-24</sup>, and so the total average intermolecular potential energy,  $-U_T$ , can be obtained by the following relation:

$$-U_T = \frac{1}{4\pi\epsilon_0^2} \left[ \frac{1}{3kT} \cdot \frac{\mu_1^2\mu_2^2}{r^6} + \frac{1}{2} \cdot \frac{\mu_1^2\alpha_2 + \mu_2^2\alpha_1}{r^6} + \frac{3}{2} \cdot \frac{I_1 I_2}{I_1 + I_2} \cdot \frac{\alpha_1 \alpha_2}{r^6} \right] \quad (1)$$

where  $\mu$  is the dipole moment, and  $\alpha$  is the polarizability and  $I$  is the ionization energy of a molecule,  $r$  is the intermolecular distance between two molecules and  $\epsilon_0$  is the permittivity in free space.

TABLE III

ADJUSTED RETENTION TIMES OF AROMATIC ADSORBATES ON SOME POROUS AROMATIC POLYMERS RELATIVE TO HEXANE AND BENZENE

Carrier gas: nitrogen, 50 ml/min. Glass column: 42 × 0.4 cm I.D.

Adsorbate	SD	SD-Ph	SD-OMe	SD-CO <sub>2</sub> Me	SD-Br	SL-NO <sub>2</sub>
<i>Relative to hexane, at 193°</i>						
Hexane	1.00	1.00	1.00	1.00	1.00	1.00
Cyclohexane	1.40	1.37	1.37	1.27	1.27	1.57
Benzene	1.54	1.49	1.43	1.30	1.23	2.04
Toluene	3.14	2.90	2.96	2.79	2.79	4.29
Ethylbenzene	6.29	5.69	5.71	5.58	6.05	8.27
<i>o</i> -Xylene	7.35	6.97	6.99	6.82	6.93	10.57
<i>m</i> -Xylene	6.49	6.25	6.24	5.97	6.30	9.00
<i>p</i> -Xylene	6.42	5.93	6.24	5.94	6.21	8.84
Styrene	7.63	7.30	7.20	7.05	6.85	11.43
Bromobenzene	8.83	8.87	8.47	7.94	8.21	14.49
Nitrobenzene	22.20	23.97	21.80	19.95	22.06	61.96
Phenol	10.97	11.24	11.21	11.22	9.80	31.82
Aniline	10.20	11.19	11.21	12.10	12.58	—
Specific retention volume of hexane (ml/g)	17.1	22.3	25.1	37.8	33.1	20.7
<i>Relative to benzene at 220°</i>						
Benzene	1.00	1.00	1.00	1.00	1.00	1.00
Toluene	1.85	1.89	1.93	1.96	2.29	1.87
Nitrobenzene	11.08	11.47	11.00	12.07	13.29	20.74
<i>o</i> -Nitrotoluene	16.31	16.63	16.57	18.22	20.71	29.16
<i>m</i> -Nitrotoluene	19.85	20.74	19.71	22.07	26.86	39.89
<i>p</i> -Nitrotoluene	22.46	23.58	22.29	25.85	30.57	46.42
Phenol	5.54	5.79	6.00	6.52	6.29	10.84
<i>o</i> -Cresol	8.77	9.05	9.43	10.52	10.00	15.47
<i>m</i> -Cresol	9.85	10.21	10.71	12.44	11.71	19.58
<i>p</i> -Cresol	9.85	10.21	10.71	12.30	11.86	19.37
Aniline	5.23	5.89	6.57	6.81	6.86	—
Specific retention volume of benzene (ml/g)	14.7	17.7	18.7	25.5	19.1	21.0

It is possible to obtain approximate values for the interaction distance, at a minimum value for  $U_T$ ,  $r^*$ :

$$r^* = r_1 + r_2 \quad (2)$$

where  $r_1$  and  $r_2$  are the radii of the adsorbent and adsorbate molecules. Approximate values of  $r_1$ , in turn, can be obtained from the molar volume of the compounds, as-

suming that the molecules are spherical. Of the methods available for calculating molar volume, density, molar refraction, equations of state, and calculation from bond lengths and angles and contact distances<sup>25</sup>, the first was chosen because of ease in obtaining the data. (The values of molar volumes for 35 molecules, typical of those used in this study were calculated by the four methods. Each set of values is self-consistent and although the absolute values do not agree this does not affect the subsequent argument). Values of  $r_2$ , for the polymer, were obtained by assuming that the adsorbate molecule would interact with a specific group on the polymer which could be regarded as benzene (when styrene was the monomer used) or a substituted benzene [diphenyl, anisole, methyl benzoate, bromobenzene and nitrobenzene for (see Table I) SD-Ph, SD-OMe, SD-CO<sub>2</sub>Me, SD-Br, SD-NO<sub>2</sub>, respectively].

The polymers contain different proportions of free vinyl groups and this is due, in part, to the fact that the reactivity ratios of the different monomers, in the polymerisation process, vary<sup>26,27</sup>. Thus there is a different amount of cross-linking in the polymers and the number of unreacted vinyl groups, from the second group in divinylbenzene, varies. This variation was accounted for in calculations of total average energy of attraction by the following means, and tested on two other systems of different adsorbates at two temperatures.

The specific retention volume,  $V_m$ , is related to  $U_T$ :

$$V_m = ae^{BU_T} \quad (3)$$

where  $a$  and  $B$  are constants. By using adjusted retention volumes (or times) relative to that of a reference adsorbate the effect of other parameters such as surface area of the packing material and errors inherent in the calculations of  $V_m$  are eliminated. Thus for two adsorbates on an adsorbent

$$\frac{V_{m_2}}{V_{m_1}} = \frac{t'_{R_2}}{t'_{R_1}} = \frac{a_2 \exp(BU_{T_2})}{a_1 \exp(BU_{T_1})} \quad (4)$$

where  $t'_R$  is the adjusted retention time for an adsorbate. Eqn. 4 can be expressed in an alternative way:

$$\log Rt'_R = K\Delta U_{T_{21}} \quad (5)$$

$Rt'_R$  is the adjusted retention time of an adsorbate relative to a second adsorbate,  $\Delta U_{T_{21}}$  is the difference in energies of attraction of the two adsorbates on a polymer and  $K$  is a constant.

In eqn. 4 the values of  $a$  are assumed to be the same for the two adsorbates on the packing material, and this is only true if the interaction distances,  $r^*$ , have been calculated correctly. Thus  $a$  can be considered as a measure of error in calculating  $r^*$ , as shall be seen later. Nevertheless, eqns. 4 and 5 are helpful, for they can be used to obtain the proportional contribution of vinyl groups in the adsorbent. Eqn. 5 is first used to calculate  $\Delta U_T$  for a particular adsorbate as, in this case,  $a$  and  $B$  are constants.

$K$  was calculated by assuming that  $\Delta U_T$  has two components: potential energy contributions from the functional groups and from the free vinyl groups in the polymer. Thus two attractive energy terms are derived as if they were composed of interactions between an adsorbate and the relevant substituted benzene molecule and the adsorbate and styrene. In the calculations, these energies were expressed as  $\Delta U_{T_x}$ , the contribution due to the functional groups and  $y\Delta U_{T_y}$ , the contribution due to the free vinyl groups:

$$\log Rt'_R = K(\Delta U_{T_x} + y\Delta U_{T_y}) \quad (6)$$

Values of  $\Delta U_{T_x}$  and  $\Delta U_{T_y}$  were calculated for each polymer and an adsorbate. Values of  $y$  were varied in 0.05 increments from 0.05 to 1.15 (*i.e.* allowing for contributions of 5–115% from the vinyl groups). Values greater than 1.00 were used to test whether or not the contribution of free vinyl groups could overcome that of the substituted benzene. For each polymer, 23 values of  $K$  were obtained for an adsorbate, and a value of  $y$  could then be chosen and tested for other adsorbates (Table III). Ideally, values for  $K$  for all the adsorbates should be the same, but the results show the limitations of the spherical molecule model (Table IV). Nevertheless, the contribution of the vinyl groups to  $\Delta U_T$  can be obtained (Table V).

TABLE IV

MEAN VALUES OF  $K$  (EQN. 6) FOR SOME ADSORBATES ON SOME POROUS AROMATIC POLYMERS CORRESPONDING TO A CONSTANT CONTRIBUTION OF FREE VINYL GROUPS TO  $-U_T$

Absorbate	$10^{21} \times K$ (J molecule <sup>-1</sup> ) ( $\pm$ standard deviation)
Cyclohexane	1.82 $\pm$ 0.17
Benzene	0.88 $\pm$ 0.19
Toluene	3.36 $\pm$ 0.49
Ethylbenzene	6.25 $\pm$ 0.24
<i>o</i> -Xylene	6.32 $\pm$ 0.49
<i>m</i> -Xylene	6.54 $\pm$ 0.54
<i>p</i> -Xylene	7.01 $\pm$ 0.65
Styrene	4.67 $\pm$ 0.33
Phenol	5.07 $\pm$ 0.30
Bromobenzene	3.77 $\pm$ 0.12
Nitrobenzene	3.46 $\pm$ 0.26

Subsequent calculations of  $\Delta U_T$  were made for which the contribution of vinyl groups in the polymer were allowed. Thus eqns. 5 and 6 could be rephrased for reference adsorbate 1 and adsorbate 2 as

$$\log Rt'_R = a' + b'\Delta U_{T_{21}} \quad (7)$$

Using data from Table IV, a plot of  $\log Rt'_R$  and  $\Delta U_{T_{21}}$  gives series of straight lines in which  $b'$  is a constant, but there are different values of  $a'$  (Fig. 1, Table VI). Table VI also gives values of  $r^*$  calculated from the spherical molecule model, and  $r^{*a'}$ , the

TABLE V

CONTRIBUTION (%) OF THE FREE VINYL GROUPS IN THE POLYMERS TO THE TOTAL ATTRACTION ENERGIES BETWEEN ADSORBATES AND ADSORBENTS

Polymer	Contribution ( $\pm 5\%$ )
SD	40
SD-Ph	55
SD-OMe	30
SD-CO <sub>2</sub> Me	15
SD-Br	10
SD-NO <sub>2</sub>	30

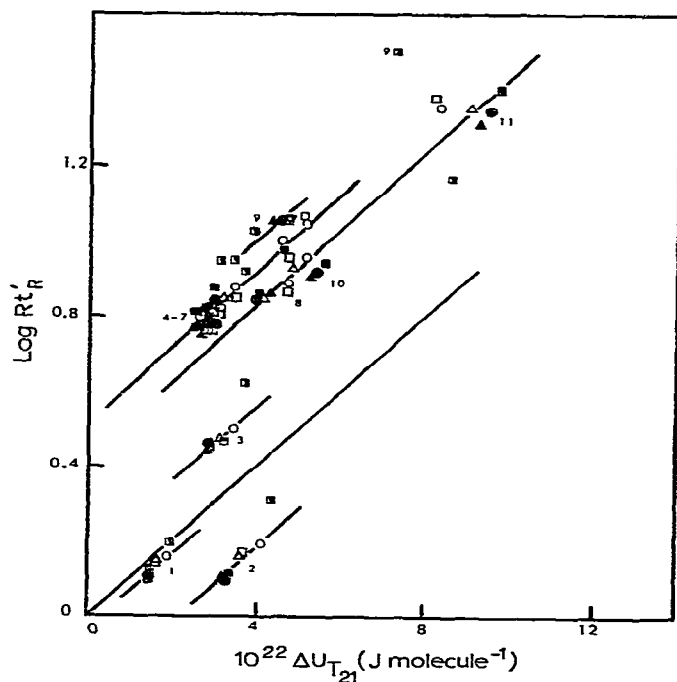


Fig. 1. Plots of  $\log Rt'_R$  and  $\Delta U_{T_{21}}$  on some porous aromatic polymers. Adsorbates: 1 = cyclohexane; 2 = benzene; 3 = toluene; 4 = ethylbenzene; 5 = *o*-xylene; 6 = *m*-xylene; 7 = *p*-xylene; 8 = styrene; 9 = phenol; 10 = bromobenzene; 11 = nitrobenzene. Polymers:  $\circ$  = SD;  $\square$  = SD-Ph;  $\triangle$  = SD-OMe;  $\blacktriangle$  = SD-CO<sub>2</sub>Me;  $\bullet$  = SD-Br;  $\blacksquare$  = SD-NO<sub>2</sub>;  $\blacksquare$  = SD-Br/Br. Temperature, 193°.

intermolecular distance calculated assuming that  $a' = 0$ . It is found that  $a'$  is dependent on  $\Delta r^*$  by the simple relation

$$\Delta r^* = ma' + c \quad (8)$$

where  $m$  and  $c$  are constants, found by a least mean squares treatment (correlation coefficient 0.999) to be 0.067 and 0.009. Using this method of calculation,  $a'$  is a measure of the error in calculating  $r^*$  using a spherical molecular model.

TABLE VI

INTERCEPTS  $a'$  (EQN. 7) OBTAINED FROM FIG. 1. FOR SOME ADSORBATES AT 193° AND INTERACTION DISTANCES,  $r^*$ ,  $r^*_{a'}$ , AND THE DIFFERENCE BETWEEN THE TWO VALUES,  $\Delta r^*$

SD is taken as an adsorbent for the calculations of  $r^*$ .

Adsorbate	$a'$	$r^*$ (nm)	$r^*_{a'}$ (nm)	$\Delta r^*$ (nm)
Benzene	-0.22	0.656	0.673	-0.017
Cyclohexane	-0.02	0.678	0.680	-0.002
Toluene	0.17	0.676	0.664	0.012
Styrene	0.43	0.685	0.658	0.027
Bromobenzene	0.43	0.674	0.649	0.025
Nitrobenzene	0.43	0.671	0.648	0.023
<i>o</i> -Xylene	0.52	0.691	0.656	0.035
<i>m</i> -Xylene	0.52	0.693	0.658	0.035
<i>p</i> -Xylene	0.52	0.693	0.658	0.035
Ethylbenzene	0.52	0.693	0.658	0.035
Phenol	0.55	0.654	0.623	0.031
Phenol*	0.55	0.693	0.661	0.032

\* SD-CO<sub>2</sub>Me is taken as another example.

The result for the closest approach  $r^*_{a'}$ , between benzene and SD is similar to that found, by static measurements, for benzene and phenanthrene<sup>28</sup>. Values of  $r^*_{a'}$ , for the aromatic hydrocarbons are almost constant, which agrees with the generally accepted view that they are adsorbed along the planar surface of the benzene ring<sup>29</sup> and  $r_1$  will not change significantly with methyl substitution since  $r_1$  is relatively large, for it represents half the thickness of the aromatic ring.

The values of  $r^*_{a'}$  for phenol appear, at first sight, to be anomalous. However, it has been found that while "flat adsorption" is the preferred configuration for many aromatic compounds, phenols prefer "vertical adsorption" in liquid-solid chromatography, using alumina<sup>30,31</sup> and a wide range of other polar porous solids, such as silica<sup>31</sup> and thus one would indeed expect  $r^*_{a'}$  for phenol to be smaller than that for benzene and other aromatic hydrocarbons.

Values for  $\Delta U_{T_{21}}$  on SD-NO<sub>2</sub> (Fig. 1) appear to be consistently low. However, the polymer can be regarded as a nitrobenzene molecule attached to the polymer surface via the 4-position of its aromatic ring. The powerful dipole moment of the nitro group, which has a major contribution to  $\Delta U_T$ , is located so that the interaction distance can be visualised as being between the adsorbate and the centre of the nitro group and not, as assumed earlier in this argument, between the adsorbate and the centre of the nitrobenzene molecule. Thus  $r^*_{a'}$  has been overestimated leading to an artificially lower value of  $\Delta U_{T_{21}}$ .

Fig. 2 shows a plot of  $\log Rt'_R$  against  $\Delta U_{T_{21}}$  taking into account values of  $a'$  obtained from Table VI.

The method by which  $\Delta U_{T_{21}}$  was calculated was then checked by applying it to two other sets of adsorbates at different column temperatures (Tables II and III). The results from plotting  $\log Rt'_R$  for the aliphatic compounds, using pentane as the reference adsorbate (Table II), and the aromatic compounds, using benzene as reference adsorbate (Table III), against  $\Delta U_{T_{21}}$ , are shown in Fig. 3. the values of  $a'$ ,  $r^*$ ,  $r^*_{a'}$  and  $\Delta r^*$  being given in Table VII.



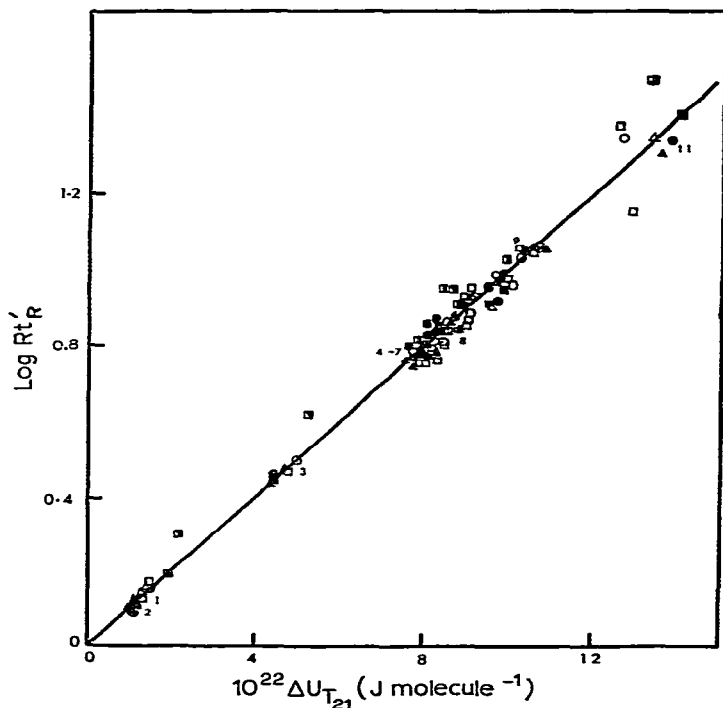


Fig. 2. Plots of  $\log Rt'_R$  and  $\Delta U_{T_{21}}$  on some porous aromatic polymers, after allowing for values of  $a'$ , shown in Table VI. For key and conditions, see Fig. 1.

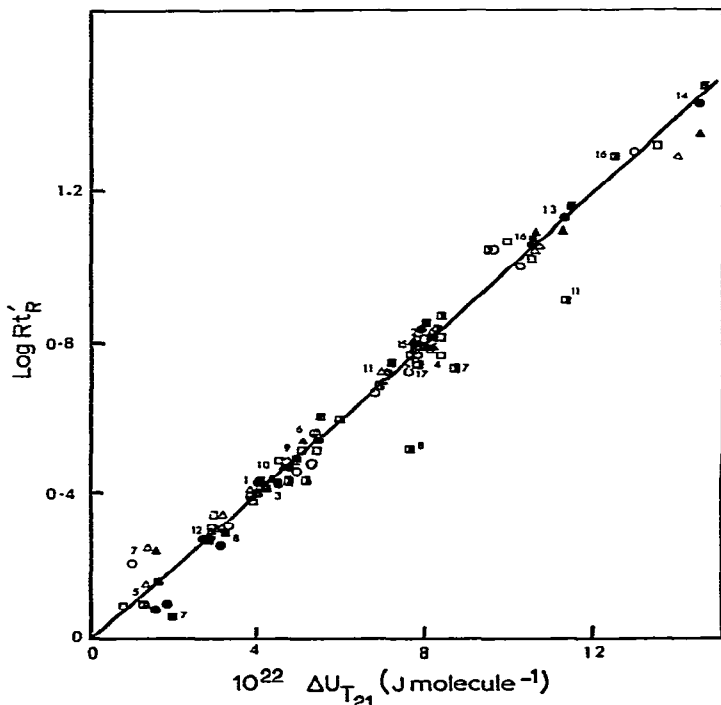


Fig. 3. Plot of  $\log Rt'_R$  and  $\Delta U_{T_{21}}$  on some porous aromatic polymers, after allowing for values of  $a'$ , shown in Table VI. Adsorbates: 1 = hexane; 2 = heptane; 3 = hex-1-ene; 4 = hept-1-ene; 5 = propan-1-ol; 6 = butan-1-ol; 7 = acetic acid; 8 = trichloromethane; 9 = tetrachloromethane; 10 = 1,2-dichloroethane; 11 = 2-bromobutane; 12 = toluene; 13 = nitrobenzene; 14 = *m*-nitrotoluene; 15 = phenol; 16 = *m*-cresol; 17 = aniline. Polymers: for key, see Fig. 1. Temperature: 151° (1-11); 220° (12-17).

TABLE VII

INTERCEPTS,  $a'$ , (EQN. 8) OBTAINED FOR SOME ADSORBATES AT 151° AND 220° AND INTERACTION DISTANCES,  $r^*$ ,  $r^*_{a'}$ , AND THE DIFFERENCE BETWEEN THE TWO VALUES,  $\Delta r^*$

Calculation of  $r^*$  on SD unless otherwise stated.

Adsorbate	$a'$	$r^*$ (nm)	$r^*_{a'}$ (nm)	$\Delta r^*$ (nm)
151°				
Hexane	0.35	0.700	0.671	0.029
Hexane*	0.35	0.739	0.710	0.029
Hexane**	0.35	0.716	0.692	0.026
Heptane	0.73	0.715	0.661	0.054
Heptane*	0.73	0.754	0.700	0.054
Octane	1.13	0.729	0.654	0.075
Hex-1-ene	0.35	0.695	0.666	0.029
Hept-1-ene	0.73	0.710	0.657	0.053
Ethanol	-0.37	0.613	0.651	-0.038
Propan-1-ol	-0.03	0.637	0.640	-0.003
Butan-1-ol	0.35	0.659	0.634	0.025
Butan-1-ol*	0.35	0.698	0.672	0.026
Butan-1-ol**	0.35	0.675	0.653	0.022
1,2-Dichloroethane*	0.03	0.683	0.681	0.002
Trichloromethane	-0.16	0.645	0.659	-0.014
Tetrachloromethane	0.03	0.665	0.663	0.002
2-Bromobutane	0.35	0.679	0.654	0.025
220°				
Toluene	0.32	0.676	0.654	0.022
Nitrobenzene	0.52	0.671	0.644	0.027
Aniline	0.66	0.658	0.621	0.037
Phenol	0.66	0.654	0.617	0.037
<i>m</i> -Cresol	0.95	0.674	0.622	0.052
<i>m</i> -Nitrotoluene	0.95	0.690	0.640	0.050

\* Calculation of  $r^*$  on SD-CO<sub>2</sub>Me.

\*\* Calculation of  $r^*$  on SD-NO<sub>2</sub>.

Comparing the interaction distances between the polymers and the alkanes, alkenes and alcohols, the values for  $r^*_{a'}$  are similar (although naturally values for  $r^*$  vary) suggesting that adsorption is taking place along the chain. The values of  $\Delta r^*$  for 1,2-dichloroethane and tetrachloromethane are very small, as would be expected for these molecules can be regarded in this context as spherical. However, for trichloromethane, while  $\Delta r^*$  is negative,  $r^*_{a'}$  is similar to that of tetrachloromethane, suggesting that both molecules have adopted similar adsorption configurations with three chlorine atoms facing the adsorbent surface. Indeed, the cross-sectional areas of adsorbed trichloromethane and tetrachloromethane on graphite are 0.279 and 0.289 nm<sup>2</sup>, respectively<sup>32,33</sup>.

There are anomalous results for acetic acid, probably because the molecule adopts different adsorption configurations on the polymers due to the strongly acidic hydrogen atom. This leads to deviations in the values of  $r$  and hence  $\Delta U_{T,21}$ .

The arguments developed earlier for the adsorption configurations for phenols on the polymers, and for all adsorbates on SD-NO<sub>2</sub> are supported by the results recorded in Tables II, III and VII, and plotted in Fig. 3.

Figs. 2 and 3 can be superimposed to produce a single straight line representing the dependence of  $\log R'_R$  on  $\Delta U_{T_{21}}$  for a wide range of adsorbates on different porous polymers. Thus, although it is not possible to devise a molecular-statistical treatment of retention data analogous to that attempted for the interactions between hydrocarbons and graphite, a semi-quantitative average potential energy of attraction has been calculated for a wide range of non-polar and polar adsorbates and six polymers. This approach, although not ideal, gives good agreement with experimental results. A more sophisticated approach is now needed to calculate interaction distances. The empirical method is being developed to account for solute-solvent interactions in gas-liquid chromatography<sup>34</sup>. A known relationship between retention data and the difference in interaction energies that occur between a solvent and different solutes can lead to a precise way of selecting and developing stationary phases.

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