

## Fullerene as an Adsorbent for Gases and Vapours

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Gas–solid partition coefficients of 22 solute gases and vapours on a sample of fullerene have been obtained by a chromatographic method, elution by characteristic point. Analysis of these coefficients by the solvation equation of Abraham shows that solute dipolarity/polarisability, and hydrogen-bond acidity, as well as general dispersion interactions can influence adsorption; the fullerene is weakly polarisable, and has some hydrogen-bond basicity, commensurate with its behaviour as a giant closed-cage alkene rather than an aromatic molecule.

Although measurable quantities of fullerenes were obtained by Kratschmer<sup>1</sup> in 1990, few reports exist of these materials as chromatographic phases. Jinno *et al.*<sup>2</sup> studied C<sub>60</sub> as a liquid-chromatographic stationary phase for the separation of polyaromatic hydrocarbons, and Stalling *et al.*<sup>3</sup> have recently used a number of C<sub>60</sub>/C<sub>70</sub> bonded polymeric materials as phases in liquid chromatography. No published studies exist on the use of fullerenes as solid adsorbents for gases and vapours, and we now report an investigation of a fullerene sample obtained from Polygon Enterprises, Waco, Texas, USA (83.9% C<sub>60</sub> and 16.1% C<sub>70</sub>).

The method was similar to that reported before,<sup>4</sup> in which the adsorbent is used as the stationary phase in a gas–solid chromatographic experiment. Adsorption isotherms were obtained by the method of elution by characteristic point (ECP),<sup>5</sup> as before, except that a flame ionisation detector was used instead of a katharometer. All experiments were carried out at 298 K with helium as the carrier gas. An example of an eluted peak is shown in Fig. 1. From the isotherms, gas–solid partition coefficients, defined by eqn. (1), were calculated. Here, C<sub>s</sub> and C<sub>g</sub> are the concentration of solute in the solid (g/g) and in the gas phase (g dm<sup>-3</sup>). K<sub>c</sub> values were obtained for 22 solutes.<sup>†</sup>

<sup>†</sup> Solutes used: *n*-decane, *n*-undecane, *n*-dodecane, 1,1,2,2-tetrachloroethane, tetrachloroethene, diiodomethane, di-*n*-butyl ether, octan-2-one, decan-2-one, *n*-butyl propanoate, octan-1-ol, dimethylsulfoxide, triethylphosphate, *n*-propylbenzene, 1,2-dichlorobenzene, 4-chlorotoluene, iodobenzene, nitrobenzene, *m*-cresol, 2-chlorophenol, benzyl alcohol, pyrrole.

$$K_c = (C_s/C_g); C_g \rightarrow 0 \quad (1)$$

The K<sub>c</sub> values, as logK<sub>c</sub>, were analysed through the solvation equation,<sup>6</sup> eqn. (2), where SP is a property of a series of solutes in a fixed phase. The descriptors are solute properties as follows: R<sub>2</sub> is an excess molar refraction, π<sub>2</sub><sup>H</sup> is the solute dipolarity/polarisability, Σα<sub>2</sub><sup>H</sup> and Σβ<sub>2</sub><sup>H</sup> are the solute summation hydrogen-bond acidity and basicity, and logL<sup>16</sup> is derived from the solute gas–hexadecane partition coefficient at 298 K.<sup>6</sup>

$$\log(\text{SP}) = c + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2^H + l\log L^{16} \quad (2)$$

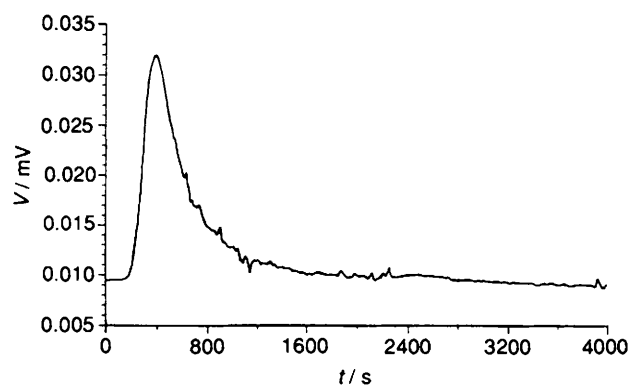


Fig. 1 Eluted peak from benzyl alcohol

Because the descriptors in eqn. (2) refer to particular properties of the solutes, the coefficients in the equation will correspond to specific properties of the phase concerned. Hence eqn. (2) not only provides information on the ability of a phase to separate solutes, but also on the phase itself. The  $r$  constant refers to the ability of the phase to interact with solute  $\pi$ - and  $n$ -electron pairs,  $s$  to the phase dipolarity/polarisability,  $a$  to the phase hydrogen-bond basicity,  $b$  to the phase acidity, and  $l$  to the phase lipophilicity. Application of eqn. (2) to the  $\log K_c$  values leads to eqn. (3), where  $n$  is the number of data points,  $\rho$  is the correlation coefficient,  $\sigma$  is the standard deviation, and  $F$  is the Fisher  $F$ -statistic. The goodness-of-fit in eqn. (3) is about as expected in adsorption work. Although we were restricted by practical considerations in the choice of solutes, the descriptors for the 22 solutes cover a good range of values ( $R_2$  from 0.00 to 1.46,  $\pi_2^H$  from 0.00 to 1.74,  $\Sigma\alpha^H$  from 0.00 to 0.57, and  $\log L^{16}$  from 2.86 to 5.70). Furthermore, inter-correlations between the descriptors are minimal, the largest being between  $R_2$  and  $\pi_2^H$  ( $\rho = 0.469$ ) and between  $\pi_2^H$  and  $\log L^{16}$  ( $\rho = -0.427$ ).

$$\log K_c = -1.58 - 0.24 R_2 + 0.72 \pi_2^H + 1.04 \Sigma\alpha^H + 0.48 \log L^{16}$$

$$n = 22; \rho = 0.951; \sigma = 0.12; F = 40 \quad (3)$$

The fullerene will separate gases and vapours mainly through interactions with solutes that are dipolar/polarisable ( $s = 0.72$ ), and are hydrogen-bond acids ( $a = 1.04$ ), as well as through general dispersion interactions ( $l = 0.48$ ). Conversely, it can be deduced that the fullerene is rather weakly polarisable, behaves as a hydrogen-bond base, and is rather weakly lipophilic. The negative coefficient of  $R_2$  probably arises through lone pair-lone pair repulsions. It might be thought odd that the fullerene seems to be but weakly polarisable, but this is exactly as expected if fullerenes behave not as highly aromatic molecules, but as giant closed-cage alkenes.<sup>7</sup> Compare the  $s$  constant of 0.72 with that of 0.49 for

the solubility of gases and vapours in poly(butadiene), estimated from results at higher temperatures,<sup>8</sup> and of 1.24 for the solubility of gases and vapours in chlorobenzene at 298 K.<sup>9</sup>

It is not surprising that comparison with carbonaceous adsorbents such as Carbotrap, a graphitised carbon, shows marked differences in the solvation equation. For Carbotrap the main term in eqn. (2) is the general dispersion interaction,  $l \log L^{16}$ , there being no terms in dipolarity/polarisability, or in acidity or basicity.<sup>10</sup>

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