

Determination of adsorption isotherms on graphitized carbon black by zonal gas chromatography

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Abstract - A method for extracting the physico-chemical parameters from the analysis of the chromatographic elution peak profile is developed. From the set of differential equations of gas-chromatography, an analytical expression of the elution peak is given in the case of low concentrations, when the isotherm can be replaced by a two term expansion. The model is a function of 4 parameters: the sample size (peak area), the apparent axial dispersion (band broadening), the slope and the curvature of the isotherm at origin.

The variation of peak maximum with increasing amounts injected provides a convenient way of determining the first and second surface virial coefficients of the adsorption isotherm. We have examined the validity of the model by studying the elution behavior of benzene and hexane on graphitized carbon black at different temperatures. The parameters of the adsorption isotherm determined by chromatography are compared with those obtained from static methods (ref. 1). In the case of a Langmuir type isotherm, the monolayer capacity of the adsorbate can be measured.

INTRODUCTION

The theoretical models describing the propagation of the elution zone all rely on the resolution of the mass balance equations for the solute and the mobile phase, which are both involved in a transport and a partition process. At infinite dilution, the simplest chromatographic models assume that the partition is independent of solute concentration. This hypothesis is seldom verified, even at very low concentrations, especially in the case of gas adsorption chromatography. It is therefore interesting, from both theoretical and experimental aspects to study the importance of this phenomenon and to investigate the possibility of determining the adsorption isotherm from peak shape analysis.

Because of the complexity of the set of differential equations involved, several approximations are necessary; one can use either numerical integration (ref. 2-4) or approximate analytical solutions (ref. 5-8). Houghton (ref. 5) was the first to give an analytical solution of the second order solute differential equation, when deviation from linearity is small, with an expansion of the partition isotherm equation to its second term. In this model, the carrier gas mass balance is omitted and thence the sorption effect is neglected. Haarhoff and Van der Linde (ref. 6) improved the model by restoring the carrier gas mass balance, but the complexity of the set of reduced makes it uneasy to apply. In a previous work (ref. 7,8) we derived a theoretical model by modifying Houghton's equation to take into account the perturbation of the flow rate due to the solute exchanges between the mobile and the stationary phases.

In this work, we shall study the elution behavior of hexane and benzene at moderate finite concentration on graphitized carbon black and determine the first and second surface virial coefficients of the adsorption isotherm by zonal elution in gas chromatography.

THEORY

To describe the solute and carrier gas mass balances, one uses the set of two equations:

$$\frac{\partial C}{\partial t} [1 + k'(C)] = - \frac{\partial(uC)}{\partial z} + D \frac{\partial^2 C}{\partial z^2} \quad (1)$$

$$- \frac{\partial C}{\partial t} = \frac{\partial[u(\bar{C}_v - C)]}{\partial z} + D \frac{\partial^2 C}{\partial z^2} \quad (2)$$

where t is the time, z the abscissa along the column, D the apparent diffusion coefficient in the gas phase. $k' = \partial n_A / \partial n_G$ is the column capacity factor which is characteristic of the equilibrium between the gaseous (n_G moles) and the adsorbed (n_A moles) phase. $C_v = P/RT$ is

the average concentration of the carrier gas, \bar{P} the mean pressure inside the column, R the gas constant and T the column temperature. The carrier gas velocity u is a simple function of the solute concentration C , in eq. 2, when expanding it to the first order:

$$u = u_0 \frac{1 + k'}{1 + k' - 2k'_0 C / \bar{C}_V} \approx u_0 \left(1 + \frac{2k'_0 C}{(1 + k'_0) \bar{C}_V} \right) \quad (3)$$

where u_0 is the carrier gas velocity at zero solute concentration, $k'_0 = (t_R - t_0) / t_0$ the capacity factor for infinite dilution, t_R the corresponding solute retention time and t_0 , the retention time of an unretained compound. The system of eq. 1 and 2 can then be replaced by a single one:

$$\frac{\partial C}{\partial t} \left[1 + k'(C) \right] + u_0 \left(1 + \frac{2k'_0 C}{(1 + k'_0) \bar{C}_V} \right) \cdot \frac{\partial C}{\partial z} - D \frac{\partial^2 C}{\partial z^2} \quad (4)$$

The influence of the flow acceleration inside the solute zone, or sorption effect, is given by the corrective term $2k'_0 C / (1 + k'_0) \bar{C}_V$ and neglects the pressure drop inside the column.

If one assumes a slightly curved isotherm, the number of solute moles N_A per surface unit of adsorbent can be expressed as a two term series expansion in powers of the partial pressure p of the solute (ref. 9):

$$N_A \approx B_{AS} \frac{p}{RT} + C_{AAS} \left(\frac{p}{RT} \right)^2 \quad (5)$$

where B_{AS} and C_{AAS} are the surface virial coefficients, and p is the adsorbate partial pressure. Assuming a Dirac function for the injection profile, it may be shown (ref. 7,8) that, in this case, the elution profile is described by an equation which depends on four parameters: the peak area (a , $\mu\text{mol} \cdot \text{s} / \text{cm}^3$), the limit retention time at zero concentration (t_R , s), the global apparent dispersion coefficient in the gas phase (D , cm^2 / s), and the peak slant coefficient (λ , $\text{cm}^3 / \mu\text{mol}$):

$$C = \frac{2}{\lambda U} \left(\frac{D'}{\pi \tau} \right)^{\frac{1}{2}} \cdot \frac{e^{-\frac{\xi^2}{4D'\tau}}}{\coth\left(\frac{\mu}{2}\right) + \theta\left(\frac{\xi}{2\sqrt{D'\tau}}\right)} \quad (6)$$

The signal is measured at the column outlet where $z = L$ and $\xi = L - Ut$. The auxiliary variables are:

$$U = u_0 / (1 + k'_0) \quad D' = D / (1 + k'_0) \quad \mu = \lambda U^2 a / 2D' \quad (7)$$

$$\lambda = \frac{2}{1 + k'_0} \times \left(\frac{C_{AAS} A}{V_0} - \frac{k'_0 RT}{\bar{P}} \right) \quad (8)$$

where V_0 is the gas volume of the column. B_{AS} is related to the column capacity factor at infinite dilution, k'_0 by the equation:

$$B_{AS} = k'_0 V_0 / A \quad (9)$$

It may be shown (ref. 7,8) that the position of peak maximum, $t_M = f(C_M)$, is a straight line, for the range of validity of the model ($\lambda C_M \ll 1$):

$$t_M \approx t_R (1 + \lambda C_M) \quad (10)$$

Therefore, the peak slant coefficient may be either determined from the locus of the maximum of the elution peak according to eq. 10, or from fitting of the theoretical expression of the elution profile (eq. 6) to the experimental chromatogram obtained at finite concentrations and for the range of validity of the model. The retention time at infinite dilution, t_R , and the peak slant coefficient, λ , are related to the first two surface virial coefficients through eqs. 9 & 10. The contribution of the sorption effect ($-k'_0 RT / \bar{P}$, in eq. 9) tends to skew the elution peak.

EXPERIMENTAL

The gas chromatographic equipment utilizes a fluid sample switch injector (ref. 10) and a flame ionization detector. Helium is used as carrier gas and the inlet pressure (600 mbar) is controlled with a pressure regulator (Texas Instruments), working with reference to the outlet pressure. The column (50 cm long, 2.1 mm i.d.) is kept in an air-stirred oven the temperature of which is controlled within $\pm 0.1^\circ\text{C}$. It is packed with 1.51g of graphitized carbon black (Carbopack CHT, Supelco), of $10 \text{ m}^2 / \text{g}$ specific surface area, measured by the B.E.T. method.

The detector signal is amplified using a fast current amplifier (Model 427, Keithley), and the digitized data are stored on magnetic tape with a minicomputer (Model 21 MX 30, Hewlett Packard). The theoretical model is fitted to the experimental data, using a non-linear least square fit Fortran program with the computer of the Centre Interrégional de Calcul Electronique (C.I.R.C.E.).

RESULTS AND DISCUSSION

We have studied the modifications of peak shape observed at finite concentrations with a concave ($C_{AAS} < 0$) and a convex ($C_{AAS} > 0$) adsorption isotherm to the pressure axis.

The adsorption isotherm of benzene adsorbed on graphitized carbon black (ref. 1) is of the Langmuir type (Fig. 1), with a concave shape to the pressure axis. For the whole range of concentration studied (Fig. 2), a tailing peak is observed, with a retention time at peak maximum which decreases with the amount injected.

For hexane adsorbed on graphitized carbon black (ref. 1), the adsorption isotherm is first convex to the pressure axis, then passes through an inflection point for completing the formation of the first layer (Fig. 1). In the range of concentration studied, a fronting peak is observed (Fig. 3) and the retention time at peak maximum increases with the amount injected. This phenomenon is characteristic of a convex isotherm to p axis near origin.

The parameters of the two term expansion of the adsorption isotherm, can be determined either from fitting the theoretical elution profile to the analytical expression of the elution peak, or by fitting the coordinates of the maximum of the elution peak to eq. 10, as shown in Figs. 1 & 2. The range of validity of the model is easy to determine, since it coincides with the range of concentration where $C_M = f(t_M)$, is a straight line. The theoretical profiles (full lines of Fig. 2 & 3) are then defined by 4 parameters: the peak area, the limit retention time at zero concentration, the global apparent dispersion coefficient in the gas phase, and the peak slant coefficient.

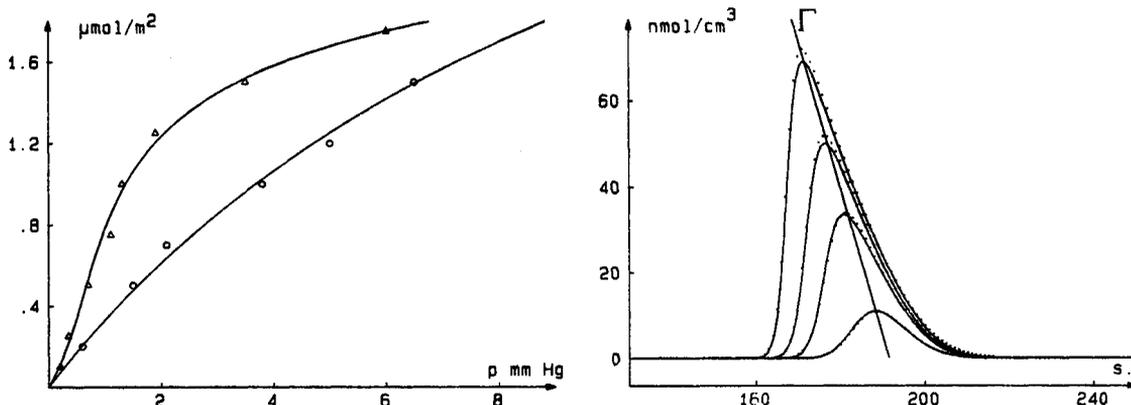


Fig. 1 Adsorption isotherm of benzene and hexane on graphitized carbon black at 70°C.

Experimental data from ref. 1: (o) benzene, (Δ) hexane.

Theoretical model: full lines.

$$N_A = 0.357 \cdot p / (1 + 0.085 \cdot p) \quad (\text{benzene})$$

$$\ln p = \ln N_A + 0.759 - 1.384 \cdot N_A + 0.943 \cdot N_A^2 \quad (\text{hexane})$$

Fig. 2 Elution of benzene on graphitized carbon black at 70°C.

..... : experimental data, — : theoretical model (eq. 6).

Γ : theoretical apex locus (eq. 10).

with $t_R = 191.4$ s, $D' = 0.0075$ cm²·s⁻¹, $\lambda = -1.5$ cm³/μmol.

masses injected: 60 μg, 40 μg, 25 μg, 7.5 μg.

Flow rate: 0.55 cm³/s.

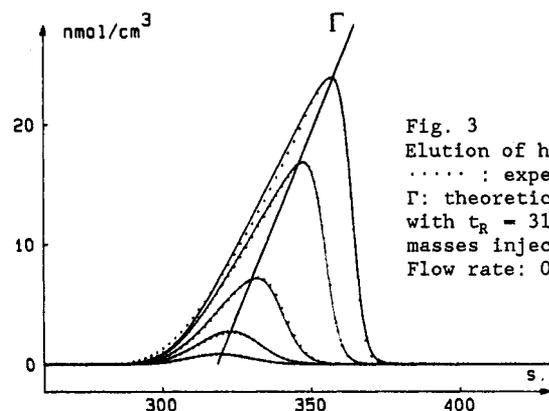


Fig. 3

Elution of hexane on graphitized carbon black at 70°C.

..... : experimental data, — : theoretical model (eq. 6),

Γ : theoretical apex locus (eq. 10).

with $t_R = 318.4$ s, $D' = 0.0035$ cm²·s⁻¹, $\lambda = 5.1$ cm³/μmol.

masses injected: 39 μg, 25 μg, 9.1 μg, 3.3 μg, 1.0 μg.

Flow rate: 0.55 cm³/s.

In a previous work, we have shown (ref. 7,8) that the slope and curvature of the isotherm at origin, determined from both methods coincide, within experimental errors. The surface virial coefficients measured from the peak apex method are given in Tables 1 & 2. The relative error at the 95% confidence level on B_{AS} is small ($\approx 1\%$), since it is measured from the retention time at infinite dilution. That on C_{AAS} measurement is larger ($\approx 10 - 15\%$) and depends largely on the flow rate stability during the whole experiment. The contribution of the sorption effect on the peak slant coefficient and therefore on C_{AAS} determination is negligible ($\approx 2\%$ of B_{AS} value (ref. 8)) with the carrier gas pressure drop used in this experiment (600 mbar).

If we assume that the adsorption isotherm of benzene on graphitized black is of the Langmuir type, we have:

$$N_A = \alpha p / (1 + \beta p) \quad (11)$$

where α and β are constants which are related to the surface virial coefficients:

$$B_{AS} = \alpha RT \quad C_{AAS} = -\alpha\beta (RT)^2 \quad (12)$$

The monolayer capacity $N_M = \alpha/\beta$ can then be calculated from the surface virial coefficients. The value measured at different temperatures by gas chromatography is listed in Table 1. Within experimental errors, in accordance with Langmuir model, it is independent of temperature. It may be compared with the value obtained from fitting Langmuir isotherm to the adsorption data published in the literature (ref. 1).

Table 1 shows that the first order surface virial coefficient B_{AS} (or retention volume per surface area of adsorbent at infinite dilution), measured by gas chromatography is in fair agreement, with that extrapolated at zero surface coverage from the static adsorption methods (ref. 1), considering the differences of the graphitized carbon black samples used. The monolayer capacity measured by chromatography is generally larger than the values from static adsorption determined at the same temperature. They are in good agreement, however, with the low temperature values, for which a higher precision was achieved. It is therefore possible from the gas chromatographic determination of the surface virial coefficients to measure the specific surface area of graphitized carbon black, for a given value of the molecular area of benzene.

Table 1. Surface virial coefficients for benzene adsorbed on graphitized carbon black.

T °K	Gas Chromatography			Static method (ref. 1)	
	B_{AS} $\text{cm}^3 \cdot \text{m}^{-2}$	C_{AAS} $\text{cm}^6 \cdot \mu\text{mol}^{-1} \cdot \text{m}^{-2}$	N_M $\mu\text{mol} \cdot \text{m}^{-2}$	B_{AS} $\text{cm}^3 \cdot \text{m}^{-2}$	N_M $\mu\text{mol} \cdot \text{m}^{-2}$
293				66.5	5.7
303				30.4	6.6
323				13.8	4.7
343	5.14	-4.0	6.6	7.6	4.2
353	3.65	-2.5	5.3		
363	2.59	-1.2	5.6		
373	1.94	-0.74	5.1	2.9	3.4
383	1.28	-0.29	5.6		

Table 2. Surface virial coefficients for hexane adsorbed on graphitized carbon black.

T °K	Gas Chromatography			Static method (ref. 1)	
	B_{AS} $\text{cm}^3 \cdot \text{m}^{-2}$	C_{AAS} $\text{cm}^6 \cdot \mu\text{mol}^{-1} \cdot \text{m}^{-2}$	B_{2D} $\text{m}^2 \cdot \mu\text{mol}^{-1}$	B_{AS} $\text{cm}^3 \cdot \text{m}^{-2}$	B_{2D} $\text{m}^2 \cdot \mu\text{mol}^{-1}$
293				92.1	-0.70
313				32.6	-0.65
323				20.7	-0.55
343	8.60	31	-0.21	10.0	-0.70
353	5.91	13	-0.19		
363	4.14	4.4	-0.13		
373	3.07	2.2	-0.11	4.4	-0.20
383	1.93	0.8	-0.11		

For hexane adsorbed on graphite, it is not possible to determine the monolayer capacity from the surface virial coefficients, since the adsorption isotherm is convex to the pressure axis for low adsorbate concentrations (Fig. 1). Table 2 compares the values of the surface virial coefficients measured by gas chromatography with those from the static methods and published in literature (ref. 1).

The parameters of Table 2, for the static method, were determined by fitting (Fig. 1) the virial form of the adsorption isotherm (Fig. 1) to the experimental data of ref. 1 :

$$\ln p = \ln N_A + C_1 + C_2 N_A + C_3 N_A + \dots \quad (13)$$

with $B_{AS} = RT \exp(-C_1)$, $C_{AAS} = - B_{AS}^2 C_2$. The two-dimensional second virial coefficient B_{2D} (ref. 9) was derived from the first two virial coefficients:

$$B_{2D} = - C_{AAS} / (2 B_{AS}^2) \quad (14)$$

The results are in fair agreement for the first virial coefficient B_{AS} , but only of the same magnitude order for B_{2D} . However, large experimental errors are made on B_{2D} determination with static measurements. Its value is then extrapolated for zero surface coverage, and is not from direct measurements, as in gas chromatography.

CONCLUSION

This work shows that it is possible to calculate the slope and the curvature at origin of the adsorption isotherm very easily from the plot of the maximum of the elution peak. Moreover, in the case of a Langmuir type isotherm and for moderate concentrations lying in the range of validity of the model, the method allows the determination of the monolayer adsorption capacity, as we have shown for benzene adsorbed on graphitized carbon black. Therefore the specific surface area of the adsorbent can be measured by zonal elution gas chromatography, if the molecular area of the adsorbate is known.

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