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Note

The cluster expansion for retention volume in gas–solid chromatography

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Rudziński and co-workers[1,2] discussed the possibility of evaluating the second and third gas–solid virial coefficients from gas chromatographic data, and also derived the following relationship between retention volume, V_N, and average density in the free gas phase, ϱ:

$$V_N = B_{2,s} + B_{3,s}\varrho \tag{1}$$

where $B_{i,s}$ are the gas–solid virial coefficients.

The aim of this paper is to derive an analytical expression for retention volume in gas–solid chromatography. It is known that the retention volume, V_N, bears the following simple relationship to the adsorption isotherm[1–3]:

$$V_N = F \frac{\partial_N}{\partial \varrho_0} \tag{2}$$

where N is the number of the adsorbed molecules and F is the James–Martin compressibility factor.

Let us consider an assembly of mutually interacting molecules trapped in a fixed volume, V, bounded by a non-porous solid surface which exerts an adsorptive field of force on the gas. The logarithm of overall partition function for this system can be expanded into powers of the activity, α:

$$\ln \Xi = \sum_{1}^{\infty} B_l \alpha^l \tag{3}$$

where B_l are the cluster integrals:

$$l! B_l = \int_V \prod^{l} g_i \sum_{i,j}^{l} \prod^{l} f_{ij(c)} \mathrm{d}r^l \tag{4}$$

where $g_i = \exp\left[-v(r_i)/kT\right]$ and $f_{ij} = \exp\left[-u(r_i,r_j)/kT\right] - 1$. The term $v(r_i)$ is the adsorptive potential energy of a gas molecule at r_i and $u(r_i,r_j)$ is the mutual potential

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energy of two molecules at r_i and r_j. Further, we have assumed that $u(r_i,r_j) = u(|r_i - r_j|)$. In eqn. 4, the subscript (c) means that, to each particular product $f_{ij(c)}$ there corresponds a connected graph of l vertices. It can be shown relatively easily[4,5] that

$$l^2 B_l = (V + W_1) \sum_{[n_k]} \prod_k \frac{(l\beta_k)^{n_k}}{n_k!} + \sum_{[m,n_k]} m W_m \prod_k \frac{(l\beta_k)^{n_k}}{n_k!} \tag{5}$$

$$\Sigma n_k k = l-1 \qquad \Sigma n_k k = l-m$$

where the β_ks are the irreducible Mayer integral and W_m are defined in the same topological way as the superficial cluster integrals introduced by Bellemans[4,5]:

> W_m = {the sum of the contributions of all connected graphs of m distinct square vertices such that the basic part of these graphs consists of white squares and their terminal subparts of black squares}

and the contribution from a given graph of m distinct squares has been calculated as follows:

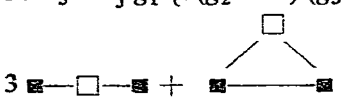
(a) to each white square associate a factor g_i;
(b) to a terminal sub-part of λ black squares associate a factor $\overset{\lambda}{\Pi} g_i - 1$;
(c) to each line joining two squares associate a factor f_{ij};
(d) integrate over V.

For example:

$$1!W_1 = \int_V (g_1 - 1)\,\mathrm{d}r_1 = \blacksquare$$

$$2!W_2 = \int_V g_1 (g_2 - 1) f_{12}\,\mathrm{d}r_1 \mathrm{d}r_2 = \square\!-\!\blacksquare \tag{6}$$

$$3!W_3 = \int g_1 \{3(g_2 - 1)(g_3 - 1) f_{12} f_{13} + (g_2 g_3 - 1) f_{12} f_{13} f_{23}\}\,\mathrm{d}r_1 \mathrm{d}r_2 \mathrm{d}r_3 =$$



From eqns. 3 and 5 we obtain

$$N = \frac{\sum\limits_{2} m W_m \varrho^m}{1 - \sum\limits_{1} k \beta_k \varrho^k} + W_1 \varrho \tag{7}$$

and, according to eqn. 2

$$V_N/F = W_1 \varrho + \frac{\sum\limits_{m=2} m^2 W_m \varrho^{m-1} + \sum\limits_{m=2} \sum\limits_{k=1} mk W_m \beta_k (k-m) \varrho^{m+k-1}}{(1 + \sum\limits_{k=1} k \beta_k \varrho^k)^2} \tag{8}$$

Eqn. 8 is the cluster expansion for retention volume in gas–solid chromatography. The cluster integral, W_1, is in fact the second gas–solid virial coefficient[6].

Finally, it should be noted that eqn. 8 was derived with superficial effects being neglected[4] (*i.e.*, effects of surface tension on N); the last assumption is very often made[6,7].

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