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Note

Some remarks on the characterization of gas–solid chromatographic systems

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In preceding papers[1,2], the application of an exponential approximation for analyzing the experimental data obtained from adsorption chromatography was considered. The experimental function V_N *versus* p, where V_N is the retention volume and p is the adsorbate pressure, was approximated by using the following exponential polynomial:

$$V_N = \exp\left(\sum_{i=0}^{m} B_i p^i\right) \tag{1}$$

where B_i ($i = 0,1,\ldots, m$) are the approximation coefficients. In linear chromatography, eqn. 1 can be reduced to the form

$$V_N = \exp(B_0) \tag{2}$$

The extrapolated retention volume, $\exp(B_0)$, is defined by the equation

$$\exp(B_0) = \frac{FRTN_m}{K} \sum_{j=1}^{n} \delta_j \exp\left(\frac{\varepsilon_j}{RT}\right) = \frac{FRTN_m}{K} \overline{\exp\left(\frac{\varepsilon}{RT}\right)} \approx$$

$$\approx \frac{FRTN_m}{K} \exp\left(\frac{\bar{\varepsilon}}{RT}\right) \tag{3}$$

where F is the James–Martin compressibility factor, N_m is the monolayer capacity, K is the pre-exponential factor of Henry's constant, connected with adsorption entropy, ε_j is the adsorption energy of the jth homogeneous surface patch, $\delta_j = N_{mj}/N_m$ is the fraction of adsorption sites having the adsorption energy ε_j and $\bar{\varepsilon}$ is the "exponential" mean adsorption energy. For a homogeneous surface, the sum in eqn. 3 can be replaced by $\exp(\varepsilon/RT)$, where $\varepsilon = \bar{\varepsilon}$ is the adsorption energy on the homogeneous surface.

The expression $\exp(B_0)$ corresponds to the second gas–solid virial coefficient[1] and it is characteristic of the given chromatographic system. Thus, if the exponential polynomial (1) approximates the experimental data V_N *versus* p well, then the expression $\exp(B_0)$ can be applied to characterize gas–solid chromatographic systems.

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It is well known that in gas–liquid chromatography (GLC) separation coefficients and retention indices are often used to characterize the GLC systems. The peaks of the chromatograms obtained in GLC are usually symmetrical, because in typical GLC systems the partition mechanism dominates. Therefore, the separation coefficient and retention index were defined for linear chromatography, *i.e.*, for symmetrical peaks. However, adaptation of these definitions to gas adsorption chromatography makes a comparison of gas–liquid and gas–solid chromatographic systems possible. Evidently, in gas–solid chromatography the retention indices can be used only to characterize the adsorbents with respect to the chromatographed substances.

We shall now discuss the separation coefficient from the point of view of adsorption chromatography. From the definition of Golbert and Vigdergauz[3] for the separation coefficient and using eqn. 2 in this definition, we obtain

$$K_c = 2 \cdot \frac{\exp(B_{0,\beta} - B_{0,\alpha}) - 1}{\exp(B_{0,\beta} - B_{0,\alpha}) + 1} \tag{4}$$

where $B_{0,k}$ ($k = \alpha, \beta$) is the retention coefficient of the kth substance. Substituting eqn. 3 into eqn. 4 we obtain

$$K_c = 2 \cdot \frac{A_{\beta,\alpha} \exp\left(\frac{\bar{\varepsilon}_\beta - \bar{\varepsilon}_\alpha}{RT}\right) - 1}{A_{\beta,\alpha} \exp\left(\frac{\bar{\varepsilon}_\beta - \bar{\varepsilon}_\alpha}{RT}\right) + 1} \tag{5}$$

where $A_{\beta\alpha} = N_{m\beta}K_\alpha/N_{m\alpha}K_\beta$. It follows from eqn. 5 that the coefficient K_c depends on the difference in the adsorption energies ($\bar{\varepsilon}_\beta - \bar{\varepsilon}_\alpha$) and on the ratio of the entropy factors, *i.e.*, $A_{\beta,\alpha}$. Eqn. 4 can be used to characterize chromatographic systems with small surface heterogeneity. Then, eqn. 1 satisfactorily describes the experimental function V_N *versus* p, which for this type of system is a slowly decreasing function. However, for strongly heterogeneous adsorbents, *i.e.*, when strongly asymmetric peaks are obtained, eqn. 4 is of little use. In discussing such systems, the asymmetry of peaks should be taken into account.

The adaptation of the retention index to adsorption chromatography seems to be more interesting. The retention index can be calculated from the equation

$$I = 100 \left(n + \frac{B_{0,x} - B_{0,n}}{B_{0,n+1} - B_{0,n}}\right) \tag{6}$$

which has been obtained from Kováts' definition[4] by replacing the retention volume by the expression $\exp(B_0)$. In eqn. 6, n is the carbon number of the first alkane used and $B_{0,n}$ and $B_{0,n+1}$ are the coefficients of the alkanes with n and $n + 1$ carbon atoms in the molecule, respectively. Substituting eqn. 3 into eqn. 6, we obtain

$$I = 100 \left[n + \frac{A^*_{x,n} + \frac{1}{RT}(\bar{\varepsilon}_x - \bar{\varepsilon}_n)}{A^*_{n+1,n} + \frac{1}{RT}(\bar{\varepsilon}_{n+1} - \bar{\varepsilon}_n)} \right] \tag{7}$$

TABLE I

CONTRIBUTION OF ENTROPY AND ENERGY EFFECTS TO RETENTION INDICES

Calculations performed with respect to *n*-hexane at 328 °K. ODS = Trichiorooctadecylsilane, G = porous glass beads, s = silanized, ns = not silanized.

No.	*Adsorbent*	*Substance*	*Ref.*	$A^*_{x,n}$	$\frac{\bar{\varepsilon}_x - \bar{\varepsilon}_n}{RT}$
1	Porous glass beads	Benzene	2	1.67	3.63
2	Porous glass beads	Cyclohexane	2	0.94	−0.84
3	ODS-ns-G	Benzene	5	−2.25	3.35
4	ODS-s-G	Benzene	5	−2.04	0.0

where $A^*_{x,n} = \ln A_{x,n}$. Eqn. 7 is more suitable than eqn. 6 for a theoretical discussion. It follows from eqn. 7 that the retention index depends on the difference in adsorption energies and the entropy factor $A^*_{x,n}$. The parameters $A^*_{x,n}$ are practically independent of temperature. The experimental studies confirm this conclusion.

In Table I the contributions of $A^*_{x,n}$ and $(\bar{\varepsilon}_x - \bar{\varepsilon}_n)/RT$ to the retention index are summarized. They were calculated for benzene and cyclohexane with respect to *n*-hexane on porous glass beads[3] and chromatographic packings with chemically bonded ODS phase[5]. It follows from Table I that the parameter $A^*_{x,n}$, connected with the adsorption entropy, gives a significant contribution to the retention index. The contribution of $A^*_{x,n}$ to the retention index is considerably smaller for chromatographed substances characterized by a large difference in adsorption energies (see systems 1 and 3 in Table I). However, for substances with similar adsorption energies (system 4 in Table I), the parameter $A^*_{x,n}$ chiefly determines the value of the retention index.

The problems outlined here require further detailed experimental studies.

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