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Note

Influence of the energetic heterogeneity of a column packing on the separation process in gas–solid chromatography

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The technique of gas–solid chromatography uses the differences in adsorption potentials of the constituents to separate a mixture of gases[1,2]. The problem of selectivity and separation has involved only quantitative studies so far, based on the assumption of the energetic homogeneity of the column packings. However, only a few adsorbents satisfy this assumption, and the problem of the influence of heterogeneity on selectivity and separation has not been discussed.

In the literature, the negative role of heterogeneity in chromatographic separations has generally been stressed. This results from the fact that heterogeneity causes the formation of asymmetric chromatographic bands, which are sometimes very broad[3,4]. However, it can be concluded from numerous data[5–7] that energetic heterogeneity of the adsorbent surface may favourably influence, and even determine, the separation of chromatographic substances. Rossi *et al.*[5] esterified silica gel with different alcohols, and separated C_1–C_4 hydrocarbons at room temperature, an optimum in selectivity and efficiency being obtained with benzyl alcohol in an autoclave at 200°. The best separation was obtained when only 25 % of the silica surface was covered with benzyl alcohol. Good separations of light C_1–C_4 hydrocarbons from a mixture containing saturated and unsaturated substances and their isomers were also obtained in our work[7], in which silica gels esterified with aliphatic alcohols were used; separation took place at the incompletely esterified surface silanol groups of the silica gel. Guillemin *et al.*[6] separated substances of different chemical character on Spherosil, *e.g.*, butane isomers on Spherosil (104 m²/g) silanized with trimethylchlorosilane and on non-silanized Spherosil. Better results were obtained on non-silanized than on silanized silica gel. Guillemin *et al.*[6] found that the better results were due to the presence of active hydroxyl groups on the surface of Spherosil.

Generally, the separation of chromatographic peaks is determined by the performance of the chromatographic column packings. Zhukhovitskii and Turkeltaub[8] propose the equation 1

$$k = \frac{\sqrt{2}}{4} \cdot k_c \sqrt{n} \tag{1}$$

where k_c is the selectivity coefficient, and n is the number of theoretical plates, which may account for the column efficiency. From eqn. 1 it follows, that the chromatographic separation is more dependent on k_c than n. Thus, we will discuss the influence of heterogeneity on the selectivity coefficient.

According to ref. 8, k_c is defined as follows

$$k_c = \frac{m-1}{m+1} \qquad (2)$$

where m (the separation factor) may be calculated from the ratio of the retention volumes $V_{N,\alpha}$ and $V_{N,\beta}$ of the separated species α and β:

$$m = \frac{V_{N,\beta}}{V_{N,\alpha}} \qquad (3)$$

The retention volume $V_{N,i}$ of the constituent i ($i = \alpha$ or β) is defined by the following equation[9,10]

$$V_{N,i} = F \cdot \frac{\partial N_{t,i}}{\partial \varrho_i} \qquad (4)$$

where F is the James–Martin compressibility factor, ϱ_i is the average density of the ith consituent in the gas phase and $N_{t,i}$ is the average number of the moles of type i in the surface phase.

In the case of linear chromatography, eqn. 4 may be reduced to[11,12]

$$V_{N,i} = B_{2,si} + 2B_{3,si}\,\varrho_i \qquad (5)$$

where $B_{2,si}$ and $B_{3,si}$ are the second and third gas–solid virial coefficients for component i, respectively. For a heterogeneous surface we have[13,14]

$$B_{2,si} = \frac{N_{m,i}\,RT}{K_i} \cdot \sum_{j \geqslant 1} S_{ij} \exp\left(\frac{\varepsilon_{ij}}{RT}\right) \qquad (6)$$

where $N_{m,i}$ is the monolayer capacity, S_{ij} is the proportion of the adsorbent surface having an adsorption energy equal to ε_{ij} and K_i is the pre-exponential factor of Henry's constant. Thus, in small density limits from eqns. 2, 3 and 6, we obtain[15]

$$k_c = \frac{\dfrac{N_{m,\beta}}{K_\beta} \cdot \sum_{j \geqslant 1} S_{\beta j} \exp\left(\dfrac{\varepsilon_{\beta j}}{RT}\right) - \dfrac{N_{m,\alpha}}{K_\alpha} \cdot \sum_{j \geqslant 1} S_{\alpha j} \exp\left(\dfrac{\varepsilon_{\alpha j}}{RT}\right)}{\dfrac{N_{m,\beta}}{K_\beta} \cdot \sum_{j \geqslant 1} S_{\beta j} \exp\left(\dfrac{\varepsilon_{\beta j}}{RT}\right) + \dfrac{N_{m,\alpha}}{K_\alpha} \cdot \sum_{j \geqslant 1} S_{\alpha j} \exp\left(\dfrac{\varepsilon_{\alpha j}}{RT}\right)} \qquad (7)$$

Eqn. 7 suggests that: (i) the selectivity of the column packing with a heterogeneous adsorbent depends on the relation between the individual types of adsorption centres and their adsorption energy; (ii) the average adsorption energy of the substance chromatographed on an energetically heterogeneous surface does not

affect the column selectivity. The above conclusions were to a great extent verified experimentally[15]. It was also found that energetically homogeneous surfaces may exhibit a lower selectivity than heterogeneous adsorbents having the same average adsorption energy in relation to the substances chromatographed.

REFERENCES

1 J. Janák, in E. Heftmann (Editor), *Chromatography*, Reinhold, New York, 3rd ed., 1975, p. 882.
2 S. Ross and J. P. Olivier, *On Physical Adsorption*, Wiley, New York, 1964.
3 A. V. Kiselev and I. Jashin, *Gas Adsorption Chromatography*, Nauka, Moscow, 1967.
4 J. C. Giddings, *Dynamics of Chromatography*, Marcel Dekker, New York, 1965.
5 C. Rossi, M. Munari, L. Cegarie and C. F. Tealdo, *Chim. Ind. (Milan)*, 42 (1960) 724.
6 C. L. Guillemin, M. La Page and A. J. de Vries, *J. Chromatogr. Sci.*, 9 (1971) 470.
7 A. Waksmundzki, R. Leboda and Z. Suprynowicz, *Chem. Anal. (Warsaw)*, 18 (1973) 727.
8 A. A. Zhukhovitskii and H. M. Turkeltaub, *Gazovaja Chromatografia*, Gostoptechizdat, Moscow, 1962.
9 J. R. Conder and J. H. Purnell, *Trans. Faraday Soc.*, 64 (1968) 3100.
10 A. Waksmundzki, W. Rudziński, Z. Suprynowicz, R. Leboda and M. Lasoń, *J. Chromatogr.*, 92 (1974) 9.
11 R. Leboda, *Chem. Anal. (Warsaw)*, in press.
12 R. Leboda, A. Waksmundzki and S. Sokołowski, *Ann. Soc. Chim. Polonorum*, in press.
13 R. A. Pierotti and J. Thomas, in *Surface and Colloid Science*, Vol. IV, Wiley, New York, 1971, pp. 98–215.
14 A. Waksmundzki, S. Sokołowski and W. Rudziński, *Z. Phys. Chem. (Leipzig)*, in press.
15 R. Leboda, *Ph. D. Thesis*, University MCS, Lublin, 1974.