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Note

A modification of the chromatographic Hobson method for studying heterogeneity of adsorbents

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The problem of energetic heterogeneity of adsorbents with regard to gas chromatography has been widely discussed¹⁻⁴, and it has been shown that the heterogeneity of adsorbents greatly affects the adsorptive properties of chromatographic packings¹⁻⁴. The problem of adsorbent heterogeneity is also important from the point of view of the industrial production of chromatographic packings (testing adsorbents).

Existing methods for studying adsorbent heterogeneity are most frequently based on utilisation of experimental adsorption isotherms⁵⁻⁹. For chromatographic purposes, however, the most useful methods would be those utilising chromatographic data and characterised by simplicity and rapidity of calculation. These aspects are important from the point of view of computerisation of industrial processes, and some methods (based on experimental adsorption isotherms) for studying heterogeneity of adsorbents can be easily adapted to chromatographic data. For this purpose, the known relationship between the retention volume V_N and the amount adsorbed N_t is used¹⁰

$$V_N = F \left(\frac{\partial N_t}{\partial Q_0} \right)_T \quad (1)$$

which, assuming ideality of the gas phase, reduces to

$$V_N = FRT \left(\frac{\partial N_t}{\partial p} \right)_T \quad (2)$$

In eqn. 1, Q_0 is the adsorbate density in the free gas phase, and F is the James-Martin compressibility factor.

In this way, Hobson's method⁵ has been adapted to chromatographic data. The equation, in its final version, reduces to calculation of the energy distribution function, $\chi(\varepsilon)$, from the following equation^{2,3}

$$\chi(\varepsilon) = - \frac{1}{F} \cdot \left(\frac{p}{RT} \right)^2 \cdot \left(\frac{\partial V_N}{\partial p} \right)_T \quad (3)$$

where

$$p = K \exp \left(\frac{-\varepsilon}{RT} \right) \quad (4)$$

Hobson's method was developed on the basis of the following integral equation for the over-all adsorption isotherm $N_t(p)$

$$N_t(p) = \int_0^{\infty} \theta_l(p, \varepsilon) \chi(\varepsilon) d\varepsilon \quad (5)$$

on assuming Henry's equation for the local adsorption isotherm θ_l . Therefore, by analogy with the chromatographic method², Hobson's method is somewhat limited by the equation taken for local adsorption.

We suggest here an extremely simple method, which, in effect, is a modification of the Hobson method. The energy distribution function $\chi(\varepsilon)$ is evaluated by using the well-known method of "condensation approximation"^{6,7}. In the first approximation, the function $\chi(\varepsilon)$ is given by the simple equation

$$\chi(\varepsilon) = \frac{p}{F(RT)^2} \cdot V_N \quad (6)$$

However, the second approximation leads to an expression similar to eqn. 3

$$\chi(\varepsilon) = \frac{-1}{F} \cdot \left(\frac{p}{RT}\right)^2 \cdot \left(\frac{\partial V_N}{\partial p}\right)_T \quad (7)$$

where p is treated as function of ε

$$p = f(\varepsilon) \quad (8)$$

The relationship expressed by eqn. 8 is dependent on the choice of expression for the local adsorption isotherm θ_l , and eqn. 8 can be evaluated for different local adsorption isotherms from the Cerofolini equation¹¹

$$\varepsilon(\theta_l, p) = \varepsilon\left(\frac{1}{2}, p\right) \quad (9)$$

Eqn. 9 can be written in the form

$$\varepsilon = \varepsilon_L + \varepsilon_0 \quad (10)$$

where ε_L is the relationship between p and ε calculated from the Langmuir eqn. (this relationship is identical with eqn. 4). However, ε_0 depends on assuming the local adsorption isotherm θ_l . In Table I are summarised the energies ε_0 for different local adsorption isotherms calculated according to eqns. 9 and 10.

It would be interesting to study the function $\chi(\varepsilon)$ given by eqn. 7 for more realistic local adsorption isotherms. First, we shall consider the adsorption model (localised or mobile). As is well known, the constants K for both adsorption models are different^{12,13}. We shall denote this constant by K_l for localised adsorption and by K_m for mobile adsorption. Both constants satisfy the relationship $K_m < K_l$; thus,

$$K_m = c K_l \quad (11)$$

where $c < 1$. We can therefore deduce the contribution ε_0^* to the energy ε_0 , by assuming mobile adsorption

$$\varepsilon_0^* = RT \ln c < 0 \quad (12)$$

TABLE I

SHIFT VALUES OF THE FUNCTION $\chi(\epsilon)$ FOR DIFFERENT LOCAL ADSORPTION ISOTHERMS CALCULATED WITH REGARD TO FUNCTION $\chi(\epsilon)$ FOR THE LANGMUIR EQUATION

Adsorption model	Local isotherm equation	Shift value of the function $\chi(\epsilon)$ in cal/mole
Localised adsorption	Langmuir	0.0
	Jovanovic	$RT \ln (\ln 2)$
	Fowler-Guggenheim	$-2RT_c \approx -RT_k$
Mobile adsorption	Volmer	$RT \ln c$
	Jovanovic	$RT \ln c + RT \ln (\ln 2)$
	Hill-DeBoer	$RT \ln c + RT - (27/8) RT_c \approx$ $RT \ln c + RT - (27/16) RT_k$

Taking into consideration the mechanical contact between molecules from the free and the adsorbed phases (*i.e.*, assuming the Jovanovic eqn. for local adsorption¹⁴⁻¹⁶), we obtain the function $\chi(\epsilon)$, which is shifted to the left along the energy axis; this shift is equal to $\epsilon_0 = RT \ln (\ln 2) < 0$ (see Table I).

A much larger shift of the function $\chi(\epsilon)$ is obtained for eqns. that take into consideration interactions in the surface phase (*i.e.*, the relationship of Hill-DeBoer¹⁷ or Fowler-Guggenheim¹⁸). The shift of the function $\chi(\epsilon)$ for the Hill-DeBoer eqn. equals $RT - (27/8)RT_c$, whereas for the Fowler-Guggenheim eqn. it equals $-2RT_c$; T_c is the two-dimensional critical temperature¹³, and

$$T_c \approx 0.5T_k \quad (13)$$

where T_k is the three-dimensional temperature.

It appears from Table I and from the given considerations that the choice of equation for local adsorption has a considerable influence on the position of the function $\chi(\epsilon)$ on the energy axis, and thereby also on the precision of determining the energetic heterogeneity of an adsorbent. The knowledge of these effects makes possible a more accurate determination of the surface heterogeneity of the adsorbent.

The choice of the model for local adsorption requires separate consideration, with regard to which the following rule may be helpful: if the chromatographed substance is an organic vapour, then localised adsorption is more probable (there are strong interactions of the adsorbate with the adsorbent), whereas for chromatography of an inorganic gas mobile adsorption is more likely. Of course, the probability of mobile adsorption increases with rise in temperature. The qualitative standard can be ratio of the adsorption energy to RT ; for values of $\epsilon/RT \geq 8$, localised adsorption can be assumed.

The above considerations are illustrated by Fig. 1, which shows a comparison of the function $\chi(\epsilon)$ for cyclohexane on silica gel at 126.3°C calculated from eqn. 7 by using the Langmuir isotherm (dashed line) and the Fowler-Guggenheim isotherm (solid line). The shift of the function $\chi(\epsilon)$ obtained with the Fowler-Guggenheim isotherm in relation to that obtained with the Langmuir isotherm equals -1108 cal per mole ($T_k = 554$ °K). The function $\chi(\epsilon)$ denoted by the dashed line in Fig. 1 was published in our previous paper².

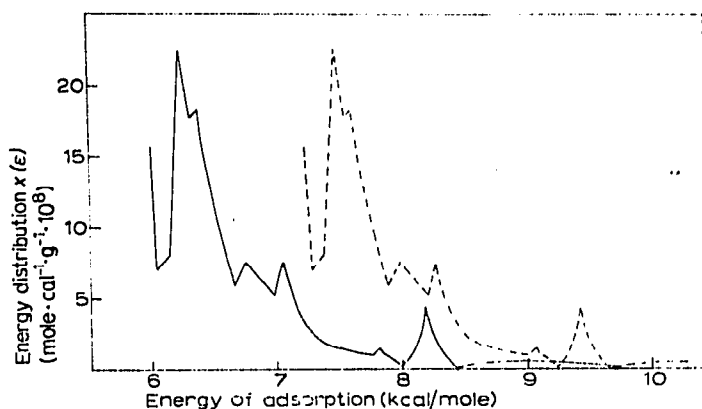


Fig. 1. Distribution of adsorption energy for cyclohexane adsorbed on wide-pore silica gel at 126.3°C. The solid line denotes the function $\chi(\epsilon)$ calculated by using the Fowler-Guggenheim local adsorption isotherm; the dashed line denotes $\chi(\epsilon)$ for the Langmuir isotherm.

The value of the shift of $\chi(\epsilon)$ (-1108 cal per mole) reflects the value of the interactions in the adsorption phase (*i.e.*, the interactions between adsorbed molecules), which result in weakening of the molecule-surface action.

In our opinion, the choice of a suitable sorption model in gas adsorption chromatography is important for quantitative evaluation of the properties of chromatographic packings.

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