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INVESTIGATIONS OF ADSORBENT HETEROGENEITY BY GAS CHROMATOGRAPHY

II. EVALUATION OF THE ENERGY DISTRIBUTION FUNCTION

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SUMMARY

This second part is devoted to the application of gas chromatographic data in evaluating the differential distribution of adsorption energies on heterogeneous surfaces. To this purpose we have chosen Hobson's method for evaluating the energy distribution function. It is shown that the function $V_N = V_N(p)$, obtained directly in gas chromatography, is extremely useful in evaluating the energy distribution function.

INTRODUCTION

In the first part of this series we discussed the great importance of adsorbent heterogeneity in physical adsorption. The heterogeneity effects are responsible for many interesting and important phenomena in physical adsorption, because of the predominant role of the gas–solid interactions in the majority of adsorption systems.

A review of the most interesting solutions concerning this problem was given previously[1], but while this first part was devoted to investigations of the adsorption mechanism on heterogeneous surfaces, the present paper is devoted to the exact evaluation of the adsorption energy distribution from chromatographic data alone. This function is defined as equal to $(\partial V/\partial \varepsilon)$, where ε is the energy of adsorption and V is the volume of adsorption space, or the number of adsorption sites, depending upon the adsorption model assumed.

We may distinguish two possible methods of evaluation, *viz.* (1) investigations of the temperature dependence of retention data and (2) investigations of the pressure dependence of retention data. The first method is connected with the virial description of physical adsorption[2–5]. The second method is connected with the fact that the retention volume V_N has the following simple relationship to the adsorption isotherm[6]:

$$V_N(p_0) = F \frac{\partial N_t}{\partial p_0} \tag{1}$$

where ρ_0 is the adsorbate density in the free gas (mobile) phase, N is the number of the adsorbed molecules and F is the James–Martin compressibility factor.

There has been published a great number of papers on the possibility of employing the pressure dependence of adsorption data to evaluate the function $x(\varepsilon)$. but only a small number of these offers useful methods for evaluating $x(\varepsilon)$. These are the papers of Adamson and Ling[7] and Adamson and Dormant[8], Harris[9], Takizawa[10], Hobson[11] and Rudziński *et al.*[12].

In addition to the methods enumerated above, we may recall here the comparatively great success of the methods proposed by D'Arcy and Watt[13] and Jaycock and Waldsax[14]. These methods are based on numerical calculations in which best-fit procedure is applied.

However, from the point of view of gas chromatography Hobson's method is of exceptional importance, because the data needed are directly obtained by gas chromatography, whereas all the other methods mentioned require the graphical evaluation of the adsorption isotherm from the function $V_N = V_N(p)$.

THEORETICAL

Consider the basic assumptions about the adsorption model accepted by Hobson[11].

The local isotherm θ_1 on each area with energy ε follows the relation

$$\theta_1(\varepsilon,p,T) = \frac{p}{K}\exp\left(\frac{\varepsilon}{RT}\right) \qquad \text{for } p<p' \tag{2}$$

$$\theta_1(\varepsilon,p,T) = 1 \qquad \text{for } p \geqslant p' \tag{3}$$

$$K = 1.76\cdot 10^4 (MT)^{\frac{1}{2}} \tag{4}$$

where $\theta(\varepsilon,p,T)$ is the relative coverage of areas with energy ε, p is the pressure in Torr, (p') is defined below, T is the absolute temperature, R the universal gas constant and M the molecular weight of the adsorbate.

At a pressure given by

$$p = p' = K\exp\left[-(\varepsilon+\varepsilon_0)/RT\right] \tag{5}$$

the isotherm for each ε_0 is assumed to rise vertically (condensation occurs) and continues at $\theta_1 = 1$ for all higher p. Thus ε_0 represents the interaction energy between adsorbate molecules. The form of the function θ_1, expressing the local isotherm equation required by eqn. 3 is for fixed values of p and T and variable ε'. This form may be expressed by

$$\theta(\varepsilon,p,T) = \frac{p}{K}\exp\left(\frac{\varepsilon}{RT}\right) \qquad \text{for } \varepsilon<\varepsilon' \tag{6}$$

$$\theta(\varepsilon,p,T) = 1 \qquad \text{for } \varepsilon \geqslant \varepsilon' \tag{7}$$

where

$$\varepsilon' = -RT\ln\left(\frac{p}{K}\right) - \varepsilon^0 \tag{8}$$

It has been pointed out by Hobson that the choice of ε^0 has only a small influence on the form of $x(\varepsilon)$ obtained. In the case $\varepsilon^0 = 0$, Hobson's method leads to

$$x(\varepsilon') = -\left(\frac{\partial \theta_t}{\partial \varepsilon'}\right)_T - RT\left(\frac{\partial^2 \theta_t}{\partial \varepsilon'^2}\right)_T \tag{9}$$

which we shall use in our calculations. Eqn. 9 may be rewritten in the form

$$x(\varepsilon) = -\left(\frac{\partial \theta_t}{\partial p}\right)_T \left(\frac{-p}{RT}\right) - RT\left\{\frac{\partial}{\partial p}\left[\left(\frac{-p}{RT}\right)\left(\frac{\partial \theta_t}{\partial p}\right)\right]_T\right\}\left(\frac{-p}{RT}\right) \tag{10}$$

which after reduction yields

$$x(\varepsilon) = -\frac{p^2}{RT}\left(\frac{\partial^2 \theta_t}{\partial p^2}\right)_T \tag{11}$$

Now

$$V_N = F\left(\frac{\partial N_t}{\partial \rho_0}\right)_T = FN_\infty\left(\frac{\partial \theta_t}{\partial \rho_0}\right)_T = N_\infty FRT\left(\frac{\partial \theta_t}{\partial p}\right)_T \tag{12}$$

when ideality of the free gas phase is assumed. Further, N_∞ is the monolayer capacity. From eqns. 11 and 12 it follows that

$$x(\varepsilon) = \left(-\frac{1}{FN_\infty}\right)\left(\frac{p}{RT}\right)^2\left(\frac{\partial V_N}{\partial p}\right)_T \tag{13}$$

Thus, one has only to express the right-hand side of eqn. 13, in terms of ε to obtain the desired function $x(\varepsilon)$.

The advantage of gas chromatographic data when using Hobson's method is that, whereas in order to use the experimental data in the form of an adsorption isotherm two graphical differentiations are required, only one graphical differentiation is needed when using retention data, *i.e.* the function $V_N(p)$.

Successive graphical differentiations introduce greater errors, apart from the fact that they are very laborious.

RESULTS AND DISCUSSION

We have evaluated the energy distribution function $x(\varepsilon)$ for the four adsorption systems investigated. Strictly speaking, we have evaluated the functions $x'(\varepsilon) = FN_\infty x(\varepsilon)$, as the problem of finding N_∞ (monolayer capacity) requires some additional investigations. Following Cerofolini[15], one most reliable estimation of N_∞ for heterogeneous surfaces is the use of the *DR* isotherm, proposed originally by Kaganer[16]. However, it has been pointed out by Misra[17], using the method of Stieltjes' transform, that the *DR* isotherm is essentially related to the Gaussian distribution multiplied by the first power of adsorption energy. Thus, the use of N_∞ calculated from the *DR* isotherm to evaluate the energy distribution is not an entirely consistent procedure, as it assumes, *a priori*, the character of the energy distribution.

We shall not go into details here of the evaluation of N_∞, and confine ourself to the evaluation of $x'(\varepsilon)$, giving the character of the energy distribution. It will be shown that the function $x'(\varepsilon)$ allows for extracting not only qualitative, but also quantitative, information about the nature of adsorbent heterogeneity.

Consider Figs. 1–4. Each of these figures consist of one continuous plot (below) and a number of other plots (above). The lower continuous plots present the whole energy distribution, whereas the upper ones portray this function in an appropiate scale, in order to give details

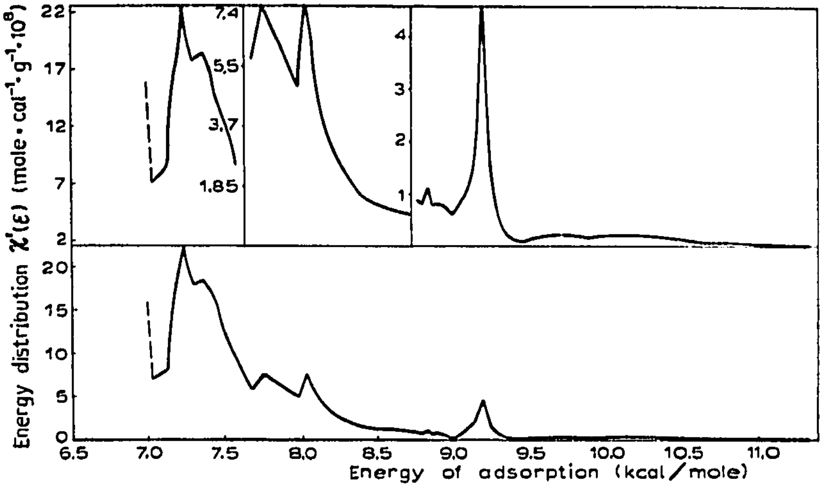

Fig. 1. Distribution of adsorption energy for cyclohexane adsorbed on wide-pore silica gel.

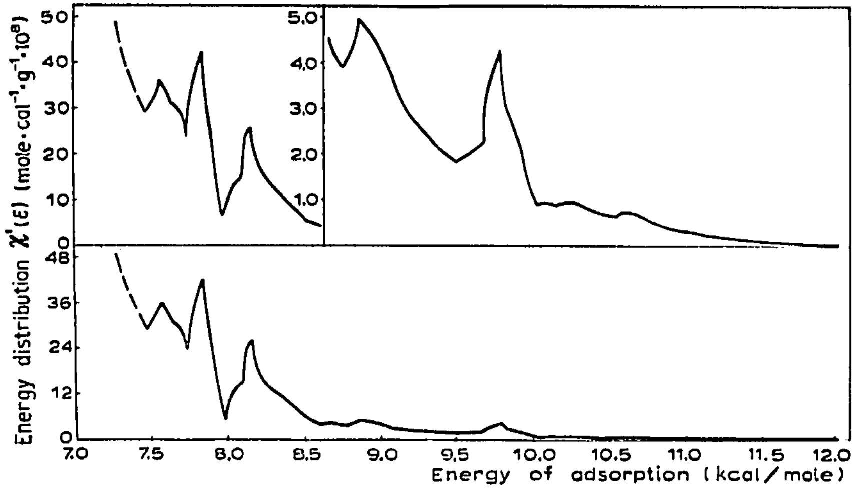

Fig. 2. Distribution of adsorption energy for cyclohexene adsorbed on wide-pore silica gel.

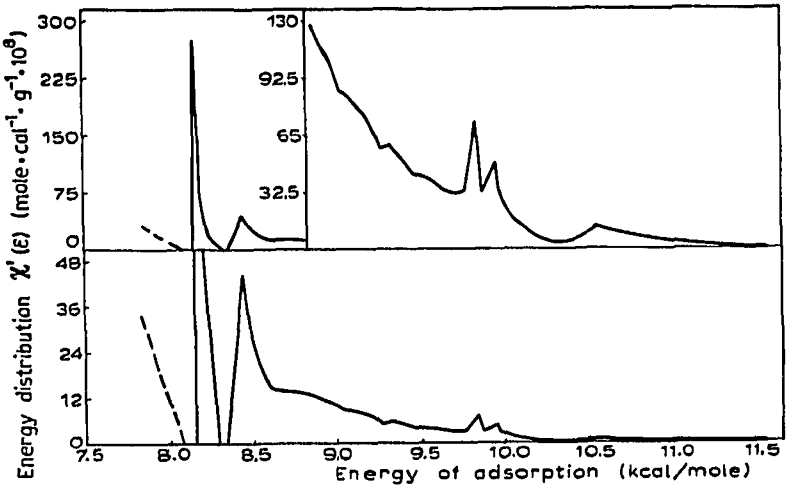

Fig. 3. Distribution of adsorption energy for cyclohexane adsorbed on narrow-pore silica gel.

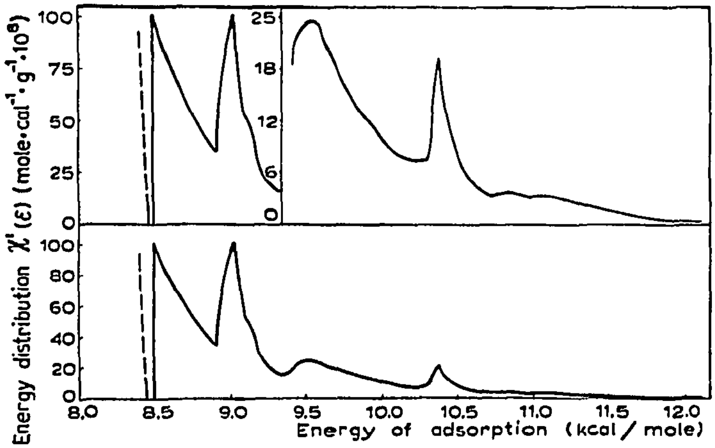

Fig. 4. Distribution of adsorption energy for cyclohexene adsorbed on narrow-pore silica gel.

At first sight it appears that there are always five marked peaks on these figures. We have denoted them by the Roman numbers I, II, III, IV and V. The natural assumption would be that these peaks correspond to five different types of adsorption sites on the investigated silica gel surfaces[1]. If so, then the energy intervals connected with these peaks should correspond to the energy intervals related to the pressure intervals shown by the appropriate peaks on the plot ($\partial \ln p/\partial \ln N_t$) (relation given by eqn. 8 for the case $\varepsilon^0 = 0$).

We have estimated this relationship, and the results are presented in Tables I–IV.

It is seen from these tables that there exists an excellent agreement between appropriate energy intervals for all the investigated adsorption systems. The differences which appear are smaller than the interaction depth between two adsorbate

TABLE I

ADSOPTION SYSTEM CYCLOHEXANE/WIDE-PORE SILICA GEL

Area of surface	*Energy interval estimated from the function ($\partial \ln p/\partial \ln N_t$) in cal/mole*	*Energy interval estimated from the function $x(\varepsilon)$ in cal/mole*
I	9280–11330	9000–11500
II	8550–9280	8000–9000
III	7620–8550	7700–8000
IV	6990–7620	7350–7700
V	6500–6990	7100–7350

TABLE II

ADSORPTION SYSTEM CYCLOHEXENE/WIDE-PORE SILICA GEL

Aera of surface	*Energy interval estimated from ($\partial \ln p/\partial \ln N_t$) in cal/mole*	*Energy interval estimated from the function $x(\varepsilon)$ in cal/mole*
I	9970–11490	9500–12000
II	8460–9970	8600–9500
III	7930–8460	8000–8600
IV	7420–7930	7720–8000
V	7050–7420	7500–7720

TABLE III

ADSORPTION SYSTEM CYCLOHEXANE/NARROW-PORE SILICA GEL

Area of surface	*Energy interval estimated from the function ($\partial \ln p/\partial \ln N_t$) in cal/mole*	*Energy interval estimated from the function $x(\varepsilon)$ in cal/mole*
I	10140–11560	10300–11500
II	9730–10140	9750–10300
III	8590–9730	8600–9750
IV	8260–8590	8370–8600
V	7870–8260	8100–8370

molecules in the bulk phase[18]. The above comparison provides strong support for the assumption that these peaks in fact represent the energy distribution within the adsorption patches existing on the silica gel surfaces.

It provides additionally an explanation for the origin of the success when describing the energy distribution within every area by the exponential distribution

TABLE IV

ADSORPTION SYSTEM CYCLOHEXENE/NARROW-PORE SILICA GEL

Area of surface	*Energy interval estimated from the function ($\partial \ln p/\partial \ln N_t$) in cal/mole*	*Energy interval estimated from the function $x(\varepsilon)$ in cal/mole*
I	10690–12110	10730–12000
II	10100–10690	10250–10730
III	9180–10100	9340–10250
IV	8710–9180	8900–9340
V	8420–8710	8470–8900

of Sips[19], as was shown in the first part of this series, *i.e.* for the majority of peaks on Figs. 1–4 the calculated function $x(\varepsilon)$ is like a left-hand-side limited exponential distribution, while we have assumed a non-limited exponential distribution. Thus, we have assumed the right-hand-side character of the energy distribution in developing the function ($\partial \ln p/\partial \ln N_t$) in Part I. The left-hand-side limitation plays a small rôle in the adsorption mechanism, when assumed to be ideally stepwise.

It may be further expected that the more characteristic is an adsorption patch (more expressively marked peak on the plot $x(\varepsilon)$) the more expressive will be the appropriate linear part on the plot ($\partial \ln p/\partial \ln N_t$), corresponding to the adsorption on this area. Consider for instance the distribution of adsorption energy within the third area of surface in the case of cyclohexane adsorbed on narrow-pore silica gel (see Part I). This is a very slightly marked peak. Consider now the part of the function ($\partial \ln p/\partial \ln N_t$), corresponding to the adsorption on this area (Fig. 4 of Part I). It is seen that this peak also is only slightly marked.

The adsorption energies for all areas and adsorption systems are greater in the case of wide-pore silica gel than in the case of narrow-pore silica gel. This is probably due to the different methods of their preparation.

The reason for which the left-hand sides of the functions $x(\varepsilon)$ have been drawn in the figures as slightly dashed lines is connected with the basic property of Hobson's method: that at overall coverages greater than unity the function $x(\varepsilon)$ is still an increasing one and its plot is then physically meaningless, as eqn. 3, underlying Hobson's method, requires the existence of areas on which Henry's adsorption actually occurs.

CONCLUSIONS

In the first and second parts of this publication series we have demonstrated the utility of gas chromatographic data in investigating the energetic heterogeneity of adsorbents. Two theoretical procedures were chosen, one giving the adsorption mechanism on heterogeneous surfaces, the other the exact distribution of adsorption energy. It has been shown that the function $V_N = V_N(p)$, measured directly in gas chromatography, is extremely useful in the chosen theoretical procedures.

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