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## DETERMINATION OF THE ISOSTERIC HEAT OF ADSORPTION BY GAS ADSORPTION CHROMATOGRAPHY

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### SUMMARY

The determination of the isosteric heat of adsorption by means of polynomial approximation of an experimentally obtained function—retention volume *versus* adsorbate pressure—is discussed. The equation is proposed by means of which the isosteric heat of adsorption can easily be calculated by using the approximation coefficients. In order to illustrate theoretical considerations, experimental graphs of the isosteric heats of adsorption *versus* adsorbed amounts for benzene and *n*-hexane on porous glass beads are presented.

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### INTRODUCTION

In an earlier paper<sup>1</sup>, the following exponential expression

$$V_{N,t}(p) = \exp \left( \sum_{i=0}^n B_i p^i \right) \quad (1)$$

was proposed for approximating the retention volume  $V_{N,t}$  as a function of the adsorbate pressure  $p$ . In this equation,  $B_i$  is an opportune coefficient, the value of which may be calculated by using the polynomial approximation:

$$\ln V_{N,t}(p) = \sum_{i=0}^n B_i p^i \quad (2)$$

The best-fit polynomial for approximating the experimental function  $\ln V_{N,t}(p)$  may be found according to procedure recommended by Cole *et al.*<sup>2</sup>

A simplified form of eqn. 1, *viz.*,

$$V_{N,i}(\bar{p}) = \exp(B_0 + B_1 p) \quad (3)$$

may be obtained from the Jovanović adsorption isotherm<sup>1</sup>. Eqn. 3 describes the retention mechanism of gas adsorption chromatography for homogeneous adsor-

bents; heterogeneous adsorbents can be characterized by eqn. 1. The subscript "l" in eqn. 3 relates to homogeneous surfaces.

Suprynowicz *et al.*<sup>1</sup> discussed the application of eqn. 1 for determining energy-distribution functions, virial coefficients, adsorption isotherms and monolayer capacities, and use of this eqn. has been extended to liquid adsorption chromatography<sup>3</sup>. Recently, eqn. 1 was also used for evaluating the pre-exponential factor of Henry's constant and the average adsorption energy<sup>4</sup>.

In this paper we shall discuss the determination of the isosteric heat of adsorption ( $Q^{st}$ ) by means of eqn. 1. For this purpose, we shall propose an equation by means of which  $Q^{st}$  can easily be calculated from the coefficients  $B_i$ .

## THEORETICAL

The isosteric heat of adsorption is defined<sup>5-8</sup> by the expression

$$Q^{st}(p, T) = -R \left[ \frac{\partial \ln p}{\partial(1/T)} \right]_{N_t} \quad (4)$$

where  $N_t$  is the amount adsorbed.

By differentiating  $N_t(p, T)$  we obtain

$$dN_t = p \left[ \frac{\partial N_t}{\partial p} \right]_T d \ln p + \left[ \frac{\partial N_t}{\partial(1/T)} \right]_p d(1/T) \quad (5)$$

By using in eqn. 5 the well-known relationship

$$V_{N_t}(p, T) = FRT \left[ \frac{\partial N_t}{\partial p} \right]_T \quad (6)$$

and assuming the constancy of  $N_t$  we obtain the expression

$$Q^{st}(p, T) = \frac{FR^2T}{p V_{N_t}(p, T)} \left[ \frac{\partial N_t(p, T)}{\partial(1/T)} \right]_p \quad (7)$$

Eqn. 7 may be written in the slightly different form

$$Q^{st}(p, T) = \frac{FR^2T N_t(p, T)}{p V_{N_t}(p, T)} \left[ \frac{\partial \ln N_t(p, T)}{\partial(1/T)} \right]_p \quad (8)$$

where  $F$  is the James-Martin compressibility factor.

In the above equations,  $V_{N_t}(p, T)$  may be calculated analytically according to eqn. 1; however,  $N_t(p, T)$  can be determined by simple numerical integration:

$$N_t(p, T) = (FRT)^{-1} \int_0^p \exp \left( \sum_{i=0}^n B_i p^i \right) dp \quad (9)$$

In the case of linear chromatography

$$V_{N_t,1} = \exp(B_0) \quad (10)$$

so that

$$Q^{st} = R \left[ \frac{\partial \ln(V_{N_t,1}/T)}{\partial(1/T)} \right]_{N_t} = R \left[ \frac{\partial(B_0 - \ln T)}{\partial(1/T)} \right]_{N_t} \quad (11)$$

Let us now consider the correlation between  $Q^{st}$  and the energy-distribution function  $\chi(\varepsilon)$ . According to Van Dongen and Broekhoff<sup>5</sup>,  $Q^{st}$  on a heterogeneous surface may be expressed by:

$$Q^{st}(p,T) = \frac{\int_A \chi(\varepsilon) \cdot q^{st}(p,T,\varepsilon) \cdot (\partial N_1 / \partial \ln p)_T d\varepsilon}{\int_A \chi(\varepsilon) \cdot (\partial N_1 / \partial \ln p)_T d\varepsilon} \quad (12)$$

or

$$Q^{st}(p,T) = \frac{\int_A \chi(\varepsilon) \cdot q^{st}(p,T,\varepsilon) V_{N,1}(p,T,\varepsilon) d\varepsilon}{\int_A \chi(\varepsilon) \cdot V_{N,1}(p,T,\varepsilon) d\varepsilon} \quad (13)$$

where  $q^{st}$  is the local isosteric heat of adsorption and is defined by:

$$q^{st} = -R \left[ \frac{\partial \ln p}{\partial (1/T)} \right]_{N_1} \quad (14)$$

and

$$(\partial N_1 / \partial \ln p)_T = (FRT)^{-1} \cdot V_{N,1}(p,T,\varepsilon) \cdot p \quad (15)$$

In the above calculations,  $N_1(p,T,\varepsilon)$  is the local adsorption isotherm<sup>7</sup>. The local retention volume,  $V_{N,1}$  (see eqn. 3) is derived from the Jovanović adsorption isotherm<sup>6</sup>:

$$N_1 = N_m [1 - \exp(-ap)] \quad (16)$$

where

$$a = (1/K) \exp(\varepsilon/RT) \quad (17)$$

$N_m$  is the monolayer capacity,  $K$  is the pre-exponential factor of Henry's constant and  $\varepsilon$  is the adsorption energy. The adsorption isotherm (eqn. 16) may be used for evaluating the local isosteric heat of adsorption (eqn. 14):

$$q^{st} = R \frac{d \ln (1/K)}{d (1/T)} + \varepsilon \quad (18)$$

Thus by replacing the local retention volume  $V_{N,1}$  in eqn. 13 by:

$$V_{N,1} = (FRTN_m/K) \exp(\varepsilon/RT) \exp(-ap) \quad (19)$$

and substituting eqn. 18 for  $q^{st}$  we obtain:

$$Q^{st} = R \frac{d \ln (1/K)}{d (1/T)} + \frac{\int_A \chi(\varepsilon) \cdot \varepsilon \cdot \exp(-ap) \cdot \exp(\varepsilon/RT) d\varepsilon}{\int_A \chi(\varepsilon) \cdot \exp(-ap) \cdot \exp(\varepsilon/RT) d\varepsilon} \quad (20)$$

For the purpose of illustration, we have applied eqn. 8 to the adsorption data for benzene and *n*-hexane on porous glass beads at four temperatures (328, 343, 358 and 373 K); the appropriate experimental details of these adsorption systems have been reported<sup>4</sup>.

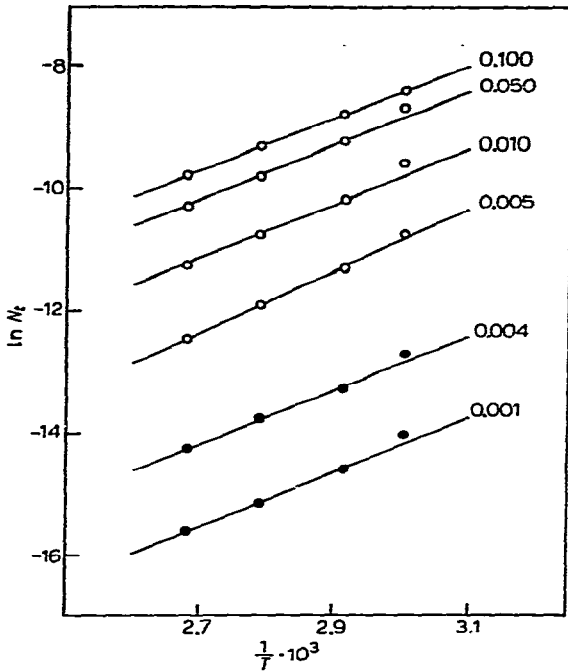


Fig. 1. Relationship between  $\ln N_i(p, T)$  and  $1/T$  for adsorption of benzene (○) and *n*-hexane (●) on porous glass beads; the numbers denote the adsorbate pressure.

Eqn. 8 was programmed in Algol 60 on an Odra 1204 computer. Starting from the coefficients  $B_i$  determining the best-fit polynomial (eqn. 2), we calculated the value of  $Q^{st}$  for a required pressure range.

In Fig. 1, graphs of  $\ln N_i(p, T)$  against  $1/T$  are presented for various adsorbate pressures. These graphs are rectilinear, and, if the dependence of  $\ln N_i$  on  $1/T$  is rectilinear, then  $Q^{st}$  can be calculated according to eqn. 8.

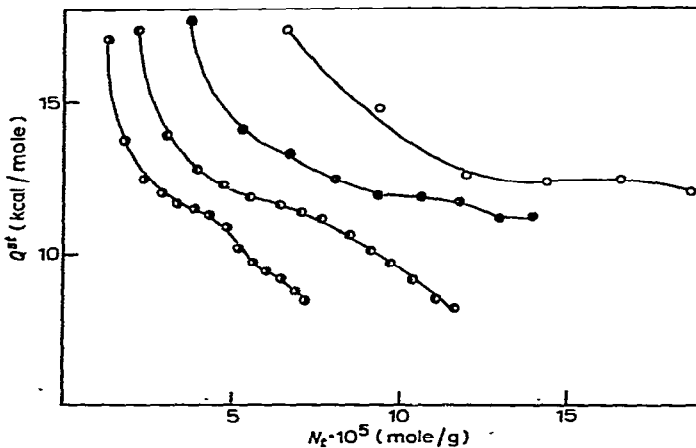


Fig. 2. Values of  $Q^{st}$  for benzene on porous glass beads at temperatures of 328 (○), 343 (●), 358 (◐) and 373 K (●).

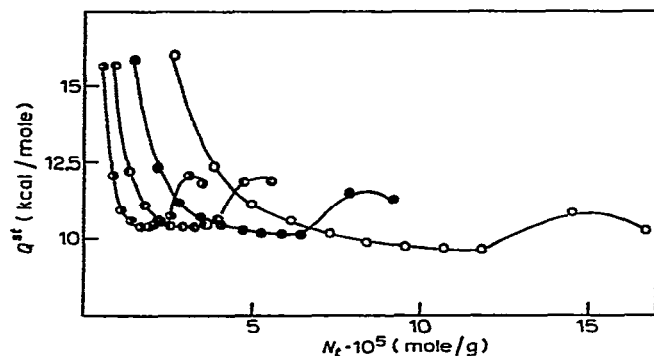


Fig. 3. Values of  $Q^{st}$  for *n*-hexane on porous glass beads (symbols as in Fig. 2).

Curves showing the relationship between  $Q^{st}$  calculated from eqn. 8 and  $N_s$  for the adsorption of benzene and *n*-hexane on porous glass beads at four temperatures are shown in Figs. 2 and 3; it can be seen that  $Q^{st}$  depends on the temperature. This problem was recently discussed by Koubek *et al.*<sup>8</sup>, who showed that the isosteric heat of adsorption on heterogeneous adsorbents may be a very variable function of the temperature and of the extent of coverage of the surface.

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