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ANALOGY BETWEEN GAS ADSORPTION AND LIQUID ADSORPTION CHROMATOGRAPHY

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SUMMARY

The analogy in the theoretical representation between gas adsorption and liquid adsorption chromatography is considered. This analogy makes it possible to anticipate some parameters in liquid adsorption chromatography on the basis of the data for gas adsorption chromatography; as an example, adsorption isotherms and energy-distribution functions are discussed.

INTRODUCTION

Detailed studies^{1,2} of adsorption from vapours and from liquids has shown that the two phenomena are related: adsorption from liquids can be fully explained in terms of adsorption from their unsaturated vapours. As is well known, the processes of gas chromatography (GC) and liquid chromatography (LC) are based on dynamic equilibrium between solution and adsorption processes. In both methods, the stationary phase (solid porous particles or particles filled with stationary liquid, or both) is in dynamic contact with at least two species, the solute and the carrier fluid (gas or liquid).

Many theoretical papers have been published on the various chromatographic methods. From the point of view of their utility in complex physico-chemical studies of surface phenomena, the most interesting are those of Huber and Gerritse^{3,4}; the theoretical treatment of the chromatographic process given in these papers is convenient for comparing results obtained by GC and LC. Further, it is possible to study liquid-solid and liquid-liquid systems by means of parameters characterising the gas-solid and gas-liquid systems.

The purpose of this paper is to present the possible application of GC and LC to studies of liquid-solid systems. First, we shall consider the chromatographic process in general, then we shall discuss the application of adsorption chromatography to the studies mentioned above. Our considerations are based on the excellent papers of Huber and Gerritse^{3,4}; therefore, our purpose is to extend the theory of Huber and Gerritse to physico-chemical studies of surface phenomena.

GENERAL CONSIDERATIONS

The theoretical treatment of the chromatographic process by Huber and Gerritse^{3,4} is based on the mass-balance equation, and it results from generalisation of well-known papers on the mechanism of chromatography⁵⁻⁸. We assume that the stationary phase is heterogeneous, consisting of solid porous particles and particles filled with stationary liquid. Taking into consideration theoretical results derived for GC³ and LC⁴, it is possible to express for both methods the residence time t_{R_1} of the concentration c_1 in the chromatographic column in the following way:

$$t_{R_1} = t_{R_0} \left(1 + \frac{\varepsilon_\beta}{\varepsilon_\alpha} f_\beta + \frac{\varepsilon_\sigma}{\varepsilon_\alpha} f_\sigma + \frac{\varepsilon_\tau}{\varepsilon_\alpha} f_\tau \right) \quad (1)$$

where f_i ($i = \beta, \sigma, \tau$) are defined by

$$f_i = \frac{d}{dc_1} F_i(c_1, c_2, Q_{1,i}, Q_{2,i}) \quad (2)$$

The functions $F_i(c_1, c_2, Q_{1,i}, Q_{2,i})$, describing the concentration of component 1 in the surface phases, are treated as functions of four parameters: c_1 , the concentration of the solute in the mobile phase; c_2 , the concentration of the carrier fluid in the mobile phase; $Q_{1,i}$, the interaction energy of component 1 with the solid matrix (σ), the surface of the stationary liquid (τ) or in the volume of the stationary liquid (β); $Q_{2,i}$, the interaction energy of component 2 with the solid matrix or stationary liquid.

The other symbols in eqn. 1 have the following designations:

ε_α = the fraction of the column volume occupied by the mobile phase,

ε_β = the fraction of the column volume occupied by the stationary liquid,

ε_σ = the fraction of the column volume considered as the adsorbed phase on the surface of the solid matrix,

ε_τ = the fraction of the column volume considered as the adsorbed phase on the surface of the stationary liquid,

ε_m = the fraction of cross-sectional area occupied by the fluid stream,

$t_{R_0} = L/u_0$, the retention time of the carrier fluid,

$u_0 = v\varepsilon_m/\varepsilon_\alpha$, the migration velocity of the mobile phase, and

v , the linear velocity of the fluid.

Our treatment differs from that of Huber and Gerritse^{3,4} in two respects. First, we consider ε_σ as the ratio between the volume of the adsorbed phase on the surface of the solid matrix and the total volume of the column (the parameter ε_τ is similarly defined); secondly, we consider that the amount (concentration) of component 1 in the phase σ (or τ or β) is the function of the four parameters c_1 , c_2 , $Q_{1,i}$ and $Q_{2,i}$. By transforming eqn. 1 into the following form

$$\varepsilon_\alpha (t_{R_1} - t_{R_0})/t_{R_0} = \varepsilon_\beta f_\beta + \varepsilon_\sigma f_\sigma + \varepsilon_\tau f_\tau \quad (3)$$

and then multiplying eqn. 3 by the column volume (V), we obtain the expression for retention volume (V_N) derived by Conder *et al.*⁹ for GC

$$V_N = V_\beta f_\beta + V_\sigma f_\sigma + V_\tau f_\tau \quad (4)$$

where V_β , V_σ and V_τ are the volumes of the phases β , σ and τ , respectively.

As already mentioned, we shall consider adsorption effects and, particularly, adsorption effects on the solid matrix. It is possible to separate the contribution of the adsorption effect to the over-all retention volume (V_N) by using known methods^{9,10}.

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In the case of the adsorption effect on the solid matrix only, eqn. 4 is reduced to the expression

$$V_N = V_G f_G \quad (5)$$

Many authors have shown that the support surfaces are generally non-homogeneous, and many papers on adsorption GC show that heterogeneity of the support surface has a great effect on the sorption properties of the column packing¹¹⁻¹⁸. Assuming the well-known "patch" model of the heterogeneous surface, we can write eqn. 5 in the form:

$$V_N = \sum_{k=1}^n V_{G,k} f_{G,k}^* \quad (6)$$

or

$$V_N = \int_{V_G} f_G^* dV_G \quad (7)$$

where $V_{G,k}$ is the volume of the surface phase on the homogeneous patch "k" and $f_{G,k}^*$ is the "local function" characterizing the retention mechanism on the kth patch.

By introducing the differential function $\chi(Q_G) = (dV_G/dQ_G)$, we transformed eqn. 7 to the following form

$$V_N = \int_{\Omega} f_G^* \chi(Q_G) dQ_G \quad (8)$$

where $Q_G = Q_{1,\sigma} - Q_{2,\sigma}$ and Ω is the range of possible variations of Q_G . Assumption of the function F_G (as function of Q_G) is suitable for description of adsorption having concurrent character; this assumption is particularly necessary to describe the adsorption LC. For small concentrations of component 1 ($c_1 \ll c_2$), the function F_G (*i.e.*, the concentration of component 1 in the surface phase σ) can be expressed by the equation

$$F_G = K c_1 \exp\left(\frac{Q_G}{RT}\right) = K' x_1 \exp\left(\frac{Q_G}{RT}\right) \quad (9)$$

where $c = c_1 + c_2 \approx c_2$, $x_1 = c_1/c$ and K is the ratio of the molecular partition functions of the molecules of components 2 and 1 in the adsorbed phase^{19,20}. If we assume, for adsorption on homogeneous surface patches, the following equation

$$F_G = \begin{cases} K c_1 \exp\left(\frac{Q_G}{RT}\right) & \text{for } Q_G \geq Q_G^* \\ 1 & \text{for } Q_G < Q_G^* \end{cases} \quad (10)$$

where Q_{σ}^* is defined by

$$Q_{\sigma}^* = -RT \ln (K c_1) \quad (11)$$

then, from eqns. 2 and 7, we obtain

$$V_N = \int_{Q_{\sigma}^*}^{\infty} K \exp \left(\frac{Q_{\sigma}}{RT} \right) \chi(Q_{\sigma}) dQ_{\sigma} \quad (12)$$

Differentiating eqn. 12 with respect to Q_{σ}^* gives the equation

$$\frac{\partial V_N(c_1(Q_{\sigma}^*))}{\partial Q_{\sigma}^*} = K \exp \left(\frac{Q_{\sigma}^*}{RT} \right) \chi(Q_{\sigma}^*) \quad (13)$$

which gives the following relation for evaluation of the energy-distribution function

$$\chi(Q_{\sigma}^*) = \frac{1}{K} \exp \left(\frac{-Q_{\sigma}^*}{RT} \right) \cdot \frac{\partial V_N(c_1(Q_{\sigma}^*))}{\partial Q_{\sigma}^*} = -\frac{\partial V_N(c_1)}{\partial c_1} \cdot \frac{(c_1)^2}{RT} \quad (14)$$

Eqn. 14 is a general one, allowing us to determine the energy heterogeneity of adsorbent surfaces from the retention data obtained by both adsorption GC and LC. In GC, eqn. 14 can be transformed into a more convenient form. Taking into consideration the relation between concentration (c_1) and pressure (p_1) of gas 1 (we had previously assumed a low concentration of component 1, thus the free phase can be treated as an ideal phase),

$$p_1 = c_1 RT \quad (15)$$

Thus, from eqn. 14

$$\chi(Q_{\sigma}^*) = -\frac{\partial V_N(p_1)}{\partial p_1} \cdot \left(\frac{p_1}{RT} \right)^2 \quad (16)$$

In adsorption GC, an inorganic gas (e.g., argon or nitrogen) is most frequently the carrier, and volatile compounds are usually the chromatographed substances. Taking also into consideration the high temperatures of measurement (ranging from 300–400°K), we can assume that the effect of the carrier gas is very small as compared with that of the chromatographed substance. If the mechanism of localized adsorption seems to be appropriate for the chromatographed substance, then that of mobile adsorption should be applicable to the carrier gas. The assumption of mobility in the surface layer results in a considerably lower value of adsorption energy^{21,22}. These considerations lead to the conclusion that $Q_{1,\sigma}^* \gg Q_{2,\sigma}^*$. Finally, eqn. 16 for adsorption GC can be presented in the form

$$\chi(Q_{1,\sigma}^*) = -\frac{\partial V_N}{\partial p_1} \cdot \left(\frac{p_1}{RT} \right)^2 \quad (17)$$

where

$$Q_{1,\sigma}^* = -RT \ln (K \cdot p_1) \quad (18)$$

Eqn. 17 is identical with that obtained for adsorption GC by using Hobson's method (see refs. 11 and 21).

The function $\chi(Q_\sigma^*)$ can be determined from eqn. 14 or 17 by differentiating the retention volume presented as concentration or pressure function. Because of the accuracy of calculations, numerical approximation of the above retention function is more conveniently made by using the exponential equation

$$V_N = \exp \left(\sum_{k=0}^m A_k c_1^k \right) \quad (19)$$

which is reduced to the polynomial approximation

$$y = \sum_{k=0}^m A_k (c_1)^k \quad (20)$$

where

$$y = \ln V_N \quad (21)$$

Eqn. 19 generalizes the expression for retention volume that we obtain on assuming the Jovanović adsorption model in adsorption GC^{23,24}.

It appears that the Jovanović adsorption model gives much better results than the Langmuir model, because it takes into consideration mechanical contact of the free phase with the molecules of the surface phase; effects connected with mechanical contact are of great significance in chromatographic processes.

Eqn. 19 corresponds with the distribution function $\chi(Q_\sigma)$ expressed in the following way:

$$\chi(Q_\sigma^*) = \frac{(c_1)^2}{-RT} \left[\sum_{k=1}^m A_k (c_1)^{k-1} \right] \cdot \exp \left[\sum_{k=0}^m A_k (c_1)^k \right] \quad (22)$$

which has the following form for GC

$$\chi(Q_{1,\sigma}^*) = - \left(\frac{p_1}{RT} \right)^2 \left[\sum_{k=1}^m A'_k (p_1)^{k-1} \right] \exp \left[\sum_{k=0}^m A'_k (p_1)^k \right] \quad (23)$$

where the A_k terms are coefficients from eqn. 20; however, A'_k are coefficients from the following approximation

$$\ln V_N = y = \sum_{k=0}^m A'_k (p_1)^k \quad (24)$$

A simultaneous study of the interaction energy of molecules with the surfaces of adsorbents by means of GC and LC makes it possible to evaluate more accurately the energy effects on the liquid-solid border, as well as to predict retention data in LC on the basis of the data from GC.

EXPERIMENTAL

A comparison was made of data obtained by GC and high-pressure LC (HPLC) on silica gel (Merckosorb SI-100; particle size 10 μm ; E. Merck, Darmstadt,

G.F.R.). The GC measurements were made with a G. Ch. F. 18.3 chromatograph (W. Giede, G.D.R.), with thermal conductivity detection. The four-cell flow-through detector (single-cell volume 125 μ l) was specially constructed and built into the gas chromatograph.

A glass column (15.9 cm \times 1 mm I.D.) was used; it was packed by using ultrasonic vibration and inert-gas pressure, and was activated at 200° in a stream of dry carrier gas.

Samples of *n*-heptane, benzene and 1,2-dichloroethane (Spectrograde quality; Merck), in the volume range 0.05 to 1 μ l were introduced by means of a 1- μ l Hamilton micro-syringe. The carrier-gas (nitrogen) flow-rate was 4.76 ml/min at a column-inlet pressure of 5 atm. The detector response for each adsorbate was calibrated in order to avoid the influence of irreversible adsorption on the precision of measurement. The calibration procedure was carried out on a glass column (90.5 cm \times 1 mm I.D.) filled with 10% of squalane on Polsorb B. The revised calibration coefficients (detector constants) were used in calculating solute concentrations in the mobile phase. The concentrations in the stationary phase (adsorbed quantities) were calculated from retention data.

The HPLC measurements were carried out on an apparatus constructed at the Instrumental Analysis Laboratory of the Technical University of Eindhoven (The Netherlands) and fitted with an Orlita 1515 DMP pump and a Siemens differential-refractometer detector. The samples were introduced with Hamilton 1- μ l (7001 N) and 5- μ l (HP 305 N) micro-syringes and a 10- μ l (S.G.E., N. Melbourne, Australia) micro-syringe, through a PTFE SR-1 septum (Applied Science Labs., State College, Pa., U.S.A.).

Merckosorb SI-100 was activated at 200° during 4 h, and packed into a straight glass column (12.4 cm \times 4 mm I.D.) by the wet "balanced-slurry" technique. After packing, the columns were washed with acetone, 1,2-dichloroethane, benzene and *n*-heptane (150 ml of each).

All measurements were made at 30 \pm 0.01° (two steps ultrathermostat mode), and the mobile-phase flow-rate was kept at 0.5 ml/min. The internal $\epsilon_s = \epsilon_a - \epsilon_m$ and interstitial ϵ_m porosities of the columns were 0.339 and 0.387, respectively (these values were calculated from the retention time of *n*-hexane, a non-retarded compound, by assuming the pore volume of Merckosorb SI-100 to be 1 ml per g).

n-Hexane, *n*-heptane, 1,2-dichloroethane and benzene (Merck Spectrograde quality) were used as solvents and injected solutes. They were purified and dried (to a water content of 20–30 ppm) by the frontal-analysis technique (adsorptive filtration) over Merck silica gel for chromatography²⁵; the final drying was made statically with molecular sieves 5A and 3A. After drying, the water content was 0–3 ppm in *n*-hydrocarbons and 5–7 ppm in the other solvents (these values were controlled by Karl Fischer titration periodically during the whole cycle of LC measurements). To ensure a constant low water concentration in the mobile phase, a pre-column (volume ca. 17 ml) packed with well-activated molecular sieves 3A and 5A was used.

RESULTS AND DISCUSSION

The purpose of the numerical calculations was to examine the correlation between adsorption data obtained by GC and LC. The experimental retention data

were measured for the following systems by GC:

- (a) *n*-heptane on silica gel at 99.5°
- (b) benzene on silica gel at 99.5°
- (c) 1,2-dichloroethane on silica gel at 99.5° and for the following systems by LC:
- (d) benzene from *n*-heptane on silica gel at 30°
- (e) 1,2-dichloroethane from *n*-heptane on silica gel at 30°.

The experimental functions V_N vs. p_1 for the GC systems (a, b and c) are presented in Fig. 1; Fig. 2 shows the experimental functions V_N vs. c_1 for the LC systems d and e. The experimental results from Figs. 1 and 2 were approximated by using the

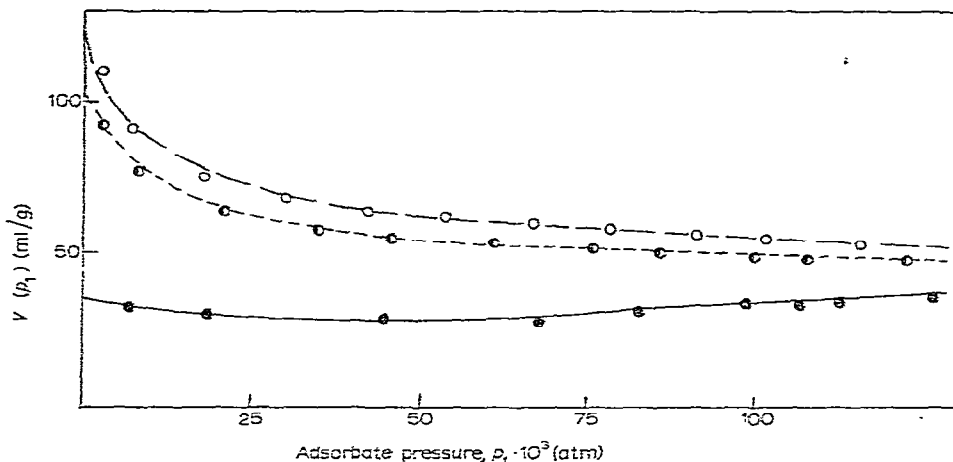


Fig. 1. Experimental functions $V_N(p_1)$ measured by GC at 99.5°. ●—●, $V_N(p_1)$ values obtained by using the approximation in eqn. 24 for system a; ●—● and ○—○, values for systems b and c, respectively. Circles denote the experimental values of retention volume.

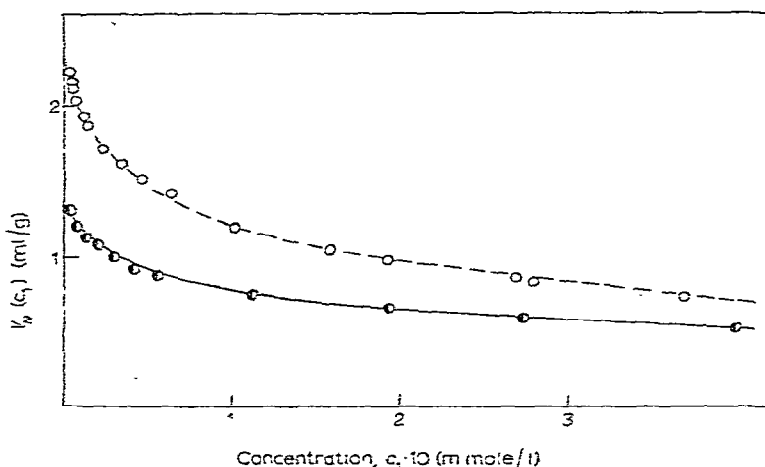


Fig. 2. Experimental functions $V_N(c_1)$ measured by HPLC at 30°. ●—●, $V_N(c_1)$ values derived by using the approximation in eqn. 20 for system d; ○—○, values for system e. Circles denote the experimental points.

numerical polynomial approximation procedure (experimental data for a, b and c were approximated according to eqn. 24; those for d and e were approximated according to eqn. 20).

As a criterion of the best approximation, we used the sum of the square deviations, which is defined by

$$S_m = \sum_{l=1}^L \left\{ V_N(c_{l,l}) - \exp \left[\sum_{k=0}^m A_k (c_{l,l})^k \right] \right\}^2 \quad (25)$$

where L is the number of experimental points. The degrees of the polynomials (m) and the sums of the square deviations for the best approximation (S_m) are presented in Table I.

TABLE I

DEGREE OF BEST-FIT POLYNOMIALS* AND SUM OF SQUARE DEVIATIONS FOR ADSORPTION ON SILICA GEL

Method	Adsorption system	Temperature, °C	Degree of polynomial, m	Sum of square deviations, S_m
GC	(a) <i>n</i> -Heptane	99.5	9	$1.01 \cdot 10^{-9}$
	(b) Benzene	99.5	10	$1.12 \cdot 10^{-9}$
	(c) 1,2-Dichloroethane	99.5	10	$2.13 \cdot 10^{-10}$
LC	(d) Benzene from <i>n</i> -heptane	30	10	$4.03 \cdot 10^{-6}$
	(e) 1,2-Dichloroethane from <i>n</i> -heptane	30	11	$2.02 \cdot 10^{-4}$

* Calculated from eqn. 20 or 24.

Figs. 3 and 4 present the adsorption isotherms calculated by means of the experimental data from Figs. 1 and 2, and according to the well-known equation^{3,11}:

$$N(c_1) = \int_0^{c_1} V_N(c_1) dc_1 \quad (26)$$

In Fig. 3, the adsorption isotherms for the systems a, b and c are shown; Fig. 4 presents the isotherms for the systems d and e. Fig. 3 shows that the highest adsorption is obtained with 1,2-dichloroethane; that for benzene is lower, and for *n*-heptane is least. For *n*-heptane, the adsorption isotherm obtained was of the third type. Thus, the interactions of the 1,2-dichloroethane and benzene molecules are much stronger than those of *n*-heptane molecules. From Fig. 3, it follows that, in LC, we should observe higher adsorption of 1,2-dichloroethane from *n*-heptane in comparison with that of benzene from *n*-heptane. This effect can be seen in Fig. 4.

Using the best-fit coefficients A_k , we calculated the energy-distribution functions. First, the energy-distribution function for GC systems were evaluated according to eqn. 23 (see Fig. 5). The constants K were determined according to the relationship proposed by Hobson (see refs. 11 and 26). The results indicated that the surface of silica gel exhibits the greatest heterogeneity towards 1,2-dichloroethane molecules, less heterogeneity towards benzene [the functions $\chi(Q_{1,\sigma}^*)$ show three maxima], and the least heterogeneity towards *n*-heptane molecules [the function $\chi(Q_{1,\sigma}^*)$ shows one maximum only]. The values of adsorption energies, and their ranges, are very similar for the adsorption of 1,2-dichloroethane and benzene, but the values for the adsorp-

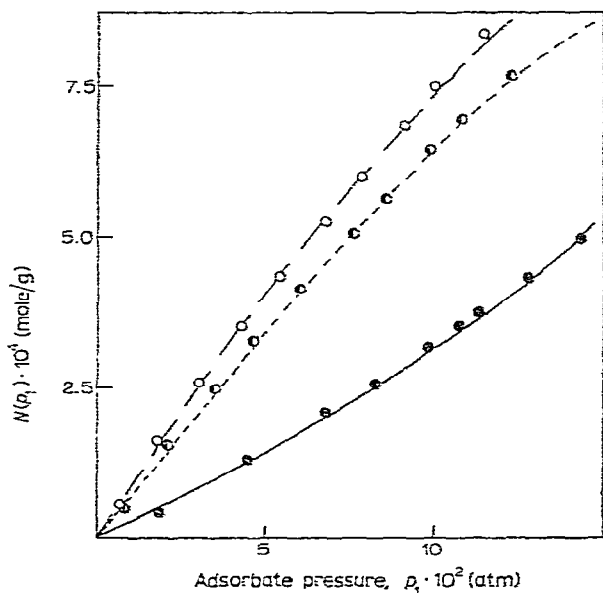


Fig. 3. Adsorption isotherms calculated from GC retention data. ●—●, Adsorption isotherms $N(p_1)$ calculated by using eqns. 26 and 24 for system a; ●—● and ○—○, values for systems b and c, respectively. Circles denote the points obtained by integrating the experimental curves $V_N(p_1)$ according to eqn. 26.

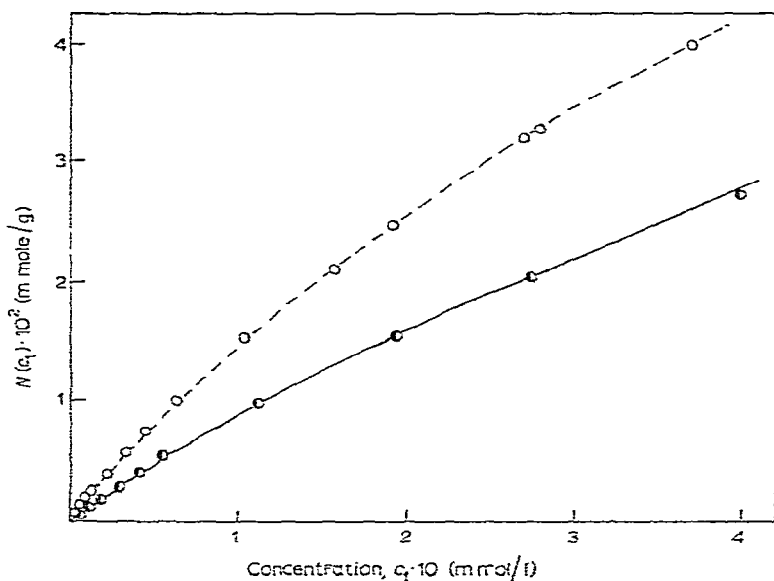


Fig. 4. Adsorption isotherms calculated from HPLC retention data. ●—● and ○—○, Adsorption isotherm $N(c_1)$ values calculated by using eqns. 26 and 20 for systems d and e, respectively. Circles denote the points obtained by integrating the experimental curves $V_N(c_1)$ according to eqn. 26.

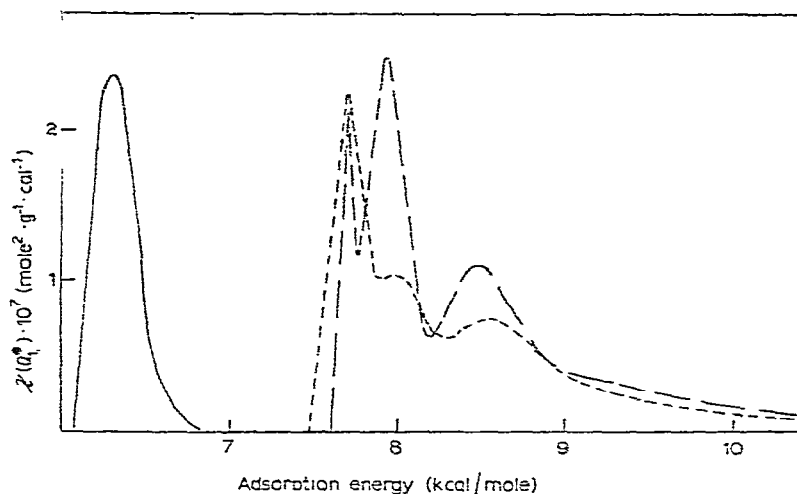


Fig. 5. Energy-distribution functions $\chi(Q_{1,c}^*)$ calculated from eqn. 23 by using GC retention data. —, $\chi(Q_{1,c}^*)$ for system a; --- and — · —, values for systems b and c, respectively.

tion of *n*-heptane are much lower in relation to that of 1,2-dichloroethane and benzene (the differences in minimum adsorption energies are about 1.6 kcal/mole).

The distribution functions $\chi(Q_c^*)$ for LC systems are presented in Fig. 6. In this case, the value for *K* was assumed to be 1.0 (this approximation has been used by several workers²⁷⁻³⁰). The distribution functions in Fig. 6 show one maximum, and their minimum differences in adsorption energies are about 2.2 kcal/mole. These values are similar to the differences in adsorption energies calculated from GC data (see Fig. 5). From a comparison of distribution functions calculated by using the GC

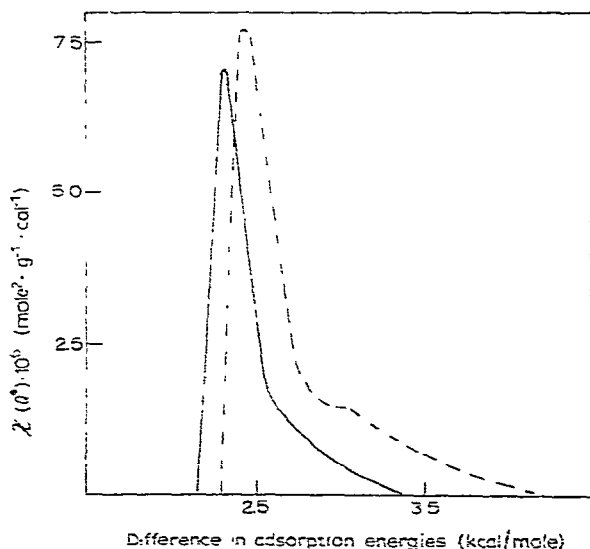


Fig. 6. Distribution functions $\chi(Q_c^*)$ calculated from eqn. 22 by using HPLC retention data. — and ---, functions for systems d and e respectively.

and LC data, it follows that, for LC (*i.e.*, liquid adsorption), the surface of the adsorbent shows less heterogeneity in relation to the adsorbing molecules.

The experimental data presented for GC and LC were measured at two different temperatures; from these studies, it follows that the influence of temperature on the results for adsorption energy is somewhat low³¹⁻³⁵. Therefore, our calculations chiefly concern the energetic effects of adsorption from gases and liquids.

It can be concluded that the data for GC systems give valuable information concerning adsorption isotherms and heterogeneity effects as regards analogous systems in LC. However, wider correlation could be obtained by suitable choice of measurement parameters and by adaptation of the apparatus for this purpose.

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