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MODEL INVESTIGATIONS ON THE EFFECT OF ENERGETIC HETEROGENEITY OF COLUMN PACKINGS ON THE SEPARATION PROCESS IN GAS-SOLID CHROMATOGRAPHY

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SUMMARY

The influence of energetic heterogeneity of adsorbents on their resolution ability, characterized by the separation coefficients, was investigated. Two analytical distribution functions were considered: the exponential function, corresponding to the Freundlich isotherm, and the quasi-gaussian function, corresponding to the Dubinin–Radushkewich isotherm. The numerical studies were concerned with the determination of selectivity coefficients for two consecutively eluted substances, which were characterized by the same analytical form of the energy distribution but by different parameters, determining the shape of the distribution. The numerical results were compared with those obtained from a homogeneous surface.

In some instances the separation coefficient calculated for a heterogeneous surface is greater than that calculated for a homogeneous surface, characterized by the same value of the average adsorption energy.

INTRODUCTION

The selectivity of chromatographic separations in gas–solid chromatography (GSC) is based on the differences in the intermolecular interactions of the components with the surface of the adsorbent. Therefore, the theory of selectivity is based on the theory of intermolecular interactions. This theory is relatively simple for adsorption on homogeneous surfaces, but, apart from graphitized carbons, such ideal surfaces are rarely found in chromatographic practice.

The first advanced attempts to describe quantitatively the effects of surface heterogeneity in GSC were those by Roginskij *et al.*¹ and Wojciechowski and Rudziński², who investigated the effect of surface heterogeneity on the shape of elution curves. Dougharty³ developed expressions for peak moments in GSC systems with heterogeneous surfaces.

The problem of adsorbent heterogeneity is also important in respect of the industrial production of chromatographic packing. Some experimental and theoretic-

cal results of studies on the energetic heterogeneity of adsorbent surfaces were presented in earlier papers⁴⁻⁸.

The aim of this work was to investigate the effect of the shape of the energy distribution function for two substances separated on a heterogeneous adsorbent and the influence of the relative positions of the functions on the energy axis (the influence of adsorption energy represented by adsorptive centres of a heterogeneous surface) on the value of the selectivity coefficient. The results obtained are compared with corresponding data for energetically homogeneous surfaces.

THEORETICAL

In GSC the following relationship between the retention volume, V_N , of a substance being chromatographed and number of moles, N_t , at pressure p , corresponding to a density ρ in the free gas phase is valid⁹:

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

where F is the James–Martin compressibility factor. Assuming ideality of the gas phase, eqn. 1 can be rewritten as follows:

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

According to Zhukhovitskij and Turkeltaub¹⁰, the selectivity, k_c , of a chromatographic column is determined by the equation

$$k_c = \frac{|m - 1|}{m + 1} \quad (3)$$

where m is the separation factor and is defined as the ratio of the retention volumes, $V_{N,A}$ and $V_{N,B}$, of separated species A and B, respectively:

$$m = \frac{V_{N,A}}{V_{N,B}} \quad (4)$$

From eqns. 2, 3 and 4, we obtain

$$k_c = \frac{|V_{N,A} - V_{N,B}|}{V_{N,A} + V_{N,B}} = \frac{\frac{\partial}{\partial p} (N_{t,A} - N_{t,B})}{\frac{\partial}{\partial p} (N_{t,A} + N_{t,B})} \quad (5)$$

Eqn. 5 does not have a limiting value, except when $V_{N,A} = V_{N,B}$, to which a minimum with $k_c = 0$ corresponds.

The analytical forms of the expressions for retention volume and k_c depend on the adsorption model assumed (local adsorption isotherm) and on the form of the energy distribution function.

Numerous investigations have shown that energy distribution functions for most adsorption systems are similar to an exponential^{1,11-18} or quasi-gaussian distribution^{8,19-29}. Because of this, we shall confine our considerations to these two cases. An exponential distribution of adsorption energy corresponds to the Freundlich (F) isotherm¹¹ and a quasi-gaussian distribution to the Dubinin-Radushkevich (DR) isotherm^{30,31}.

In the former instance the amount of adsorbed chromatographed substance, N_t , at its vapour pressure p can be expressed as

$$N_t = \left(\frac{p}{p + K} \right)^C \quad (6)$$

where

$$\frac{1}{K} = \frac{1}{K'} \cdot \exp \left[- \frac{\varepsilon - \varepsilon_0}{RT} \right] \quad (7)$$

C is a heterogeneity parameter varying in the interval $0 \leq C \leq 1$, K is Henry's constant, K' is the pre-exponential factor of Henry's constant, ε is the adsorption energy and ε_0 is the adsorption energy on the lowest energetic centres. For simple gases³²

$$K' = 1.76 \cdot 10^4 (MT)^{\frac{1}{2}} \quad (8)$$

where K' is expressed in Torr and M is the molecular weight of the adsorbate.

Freundlich's isotherm corresponds to the following distribution of adsorption energy, $\chi(\varepsilon)$:

$$\chi(\varepsilon) = \begin{cases} 0 & \text{for } \varepsilon < \varepsilon_0 \\ \frac{\sin \pi C}{\pi RT} \left[\exp \left(\frac{\varepsilon - \varepsilon_0}{RT} \right) - 1 \right]^{-C} & \text{for } \varepsilon > \varepsilon_0 \end{cases} \quad (9)$$

From eqns. 2, 5 and 6 we obtain the following expression for the selectivity factor:

$$k_c = \frac{C_A \cdot \frac{K_A}{(p + K_A)^2} \cdot \left(\frac{p}{p + K_A} \right)^{C_A - 1} - C_B \cdot \frac{K_B}{(p + K_B)^2} \cdot \left(\frac{p}{p + K_B} \right)^{C_B - 1}}{C_A \cdot \frac{K_A}{(p + K_A)^2} \cdot \left(\frac{p}{p + K_A} \right)^{C_A - 1} + C_B \cdot \frac{K_B}{(p + K_B)^2} \cdot \left(\frac{p}{p + K_B} \right)^{C_B - 1}} \quad (10)$$

From eqn. 10 it follows that k_c depends on K_A , C_A , K_B and C_B .

In the latter instance (DR) the equation for an isotherm has the form

$$N_t = \exp \left[- B \ln^2 \frac{p}{K} \right] \quad (11)$$

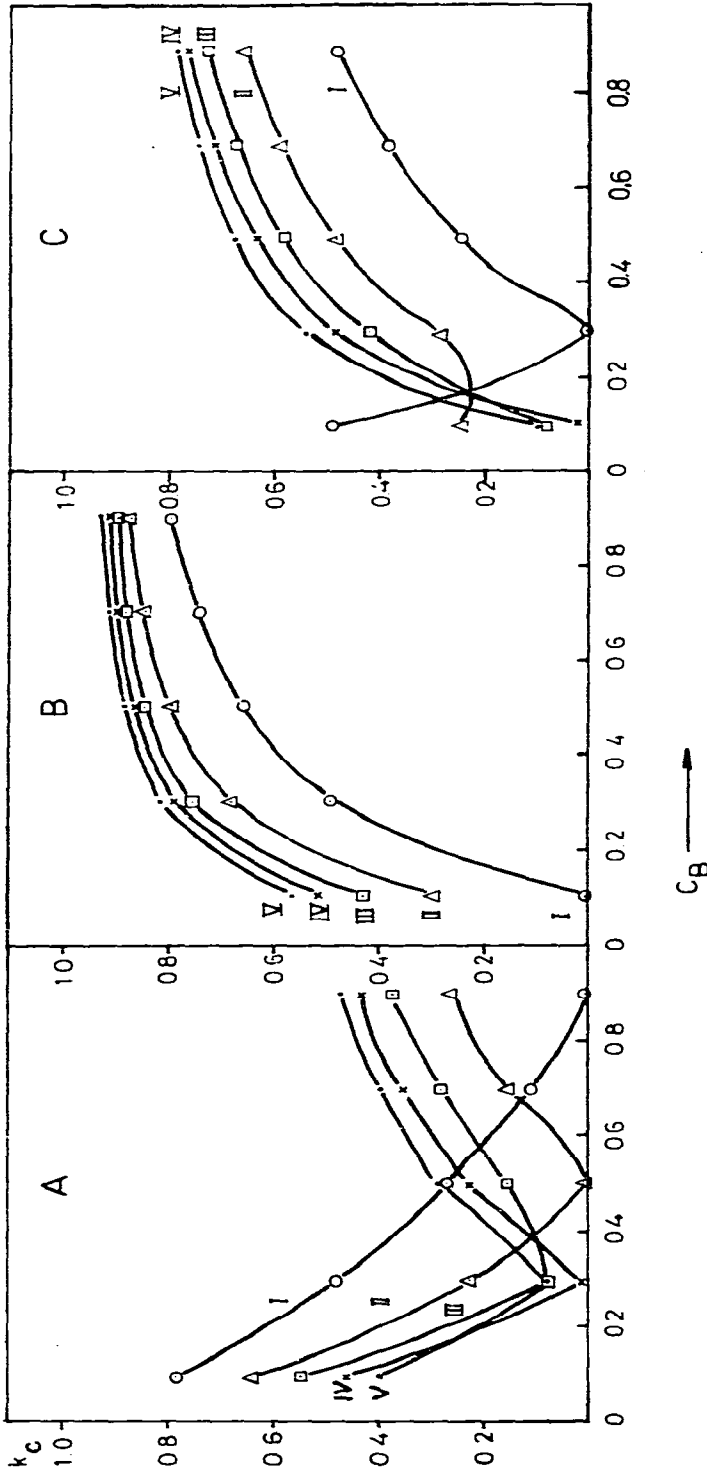


Fig. 1. Dependences of k_c on C_B . (A) $C_A = 0.9, K_A = 2$; (B) $C_A = 0.1, K_A = 2$; (C) $C_A = 0.3, K_A = 2$. $K_B = 2$. $C_A = 2$ (I), 4 (II), 6 (III), 8 (IV) or 10 (V).

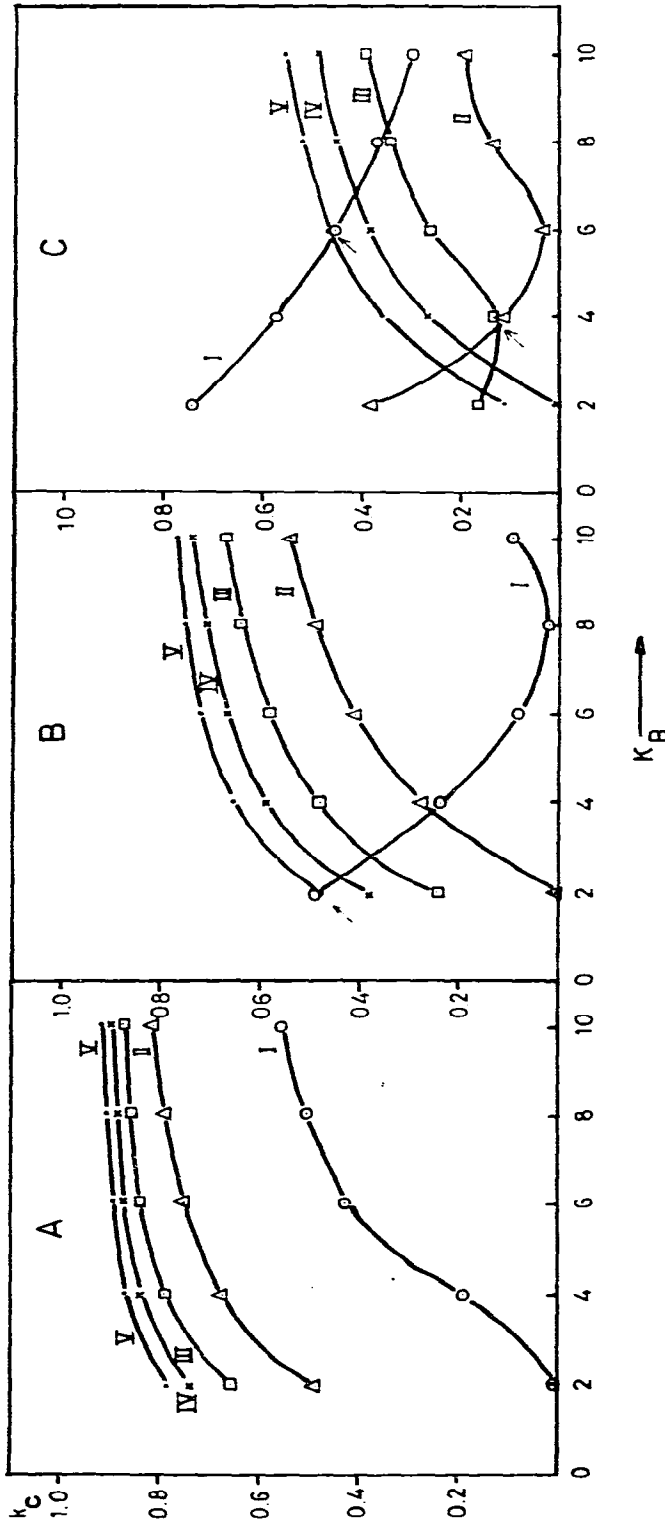


Fig. 2. Dependences of k_c on K_B . (A) $C_A = 0.1, K_A = 2$; (B) $C_A = 0.3, K_A = 2$; (C) $C_A = 0.7, K_A = 2$. $C_B = 0.1$ (I), 0.3 (II), 0.5 (III), 0.7 (IV) or 0.9 (V).

which corresponds to the following distribution energy $\chi(\varepsilon)$:

$$\chi(\varepsilon) = \begin{cases} 0 & \text{for } \varepsilon < \varepsilon_0 \\ 2B(\varepsilon - \varepsilon_0) \exp[-B(\varepsilon - \varepsilon_0)^2] & \text{for } \varepsilon > \varepsilon_0 \end{cases} \quad (12)$$

In the above, $B > 0$ is the heterogeneity parameter.

As in the former instance, from eqns. 2, 5 and 11 we obtain

$$K_c = \frac{B_A \cdot \ln \frac{p}{K_A} \left\{ \exp \left[-B_A \left(\ln \frac{p}{K_A} \right)^2 \right] \right\} - B_B \cdot \ln \frac{p}{K_B} \left\{ \exp \left[-B_B \left(\ln \frac{p}{K_B} \right)^2 \right] \right\}}{B_A \cdot \ln \frac{p}{K_A} \left\{ \exp \left[-B_A \left(\ln \frac{p}{K_A} \right)^2 \right] \right\} + B_B \cdot \ln \frac{p}{K_B} \left\{ \exp \left[-B_B \left(\ln \frac{p}{K_B} \right)^2 \right] \right\}} \quad (13)$$

The selectivity coefficient is determined mainly by B and K .

In order to investigate the influence of energetic heterogeneity of an adsorbent on the coefficient of selectivity (k_c) of two substances (A and B), numerical calculations were carried out according to eqns. 10 and 13 based on model systems. Suitable values of the heterogeneity parameters K , C and B were assumed for the system. The assumed model of adsorption on a heterogeneous surface was as follows: (i) a heterogeneous surface of an adsorbent consists of homogeneous patches; (ii) adsorption of substances A and B on the homogeneous patches occurs according to the Langmuir equation; and (iii) in an adsorption process no attracting interactions takes place, adsorption being localized. Such assumptions allow the overall isotherm of adsorption to be described by the Freundlich and Dubinin–Radushkewich equations.

In numerical calculations the following parameters were assumed:

$C \in [0.1]$, $p = 2$ Torr and $K \in [0, 10]$ for the Freundlich isotherm and $B \in [1 \cdot 10^{-8}, 1 \cdot 10^{-7}]$ and $[1 \cdot 10^{-6}, 1 \cdot 10^{-5}]$ and $K \in [0, 100]$ for the Dubinin–Radushkewich isotherm. The values are typical of chromatographic systems. This paper deals with the most representative results of the numerical calculations.

RESULTS AND DISCUSSION

We shall first discuss the results of calculations for the exponential distribution function, $\chi(\varepsilon)$. Such a distribution of energy is characteristic, of, e.g., silica-carbon adsorbents, Carbonsils¹⁵ and some unmodified silica gels^{13,14,16}.

The results of numerical calculations for an exponential distribution of energy are presented in Figs. 1–7. Fig. 1 shows the dependence of the selectivity coefficients, k_c , on C_B , determining the shape of the energy distribution function $\chi(\varepsilon)$. The higher the value of the constant C , the more energetically homogeneous the adsorbent is. The shape of the $\chi(\varepsilon)$ function depends on the topography of adsorptive centres on the surface of an adsorbent.

The individual curves in Fig. 1 correspond to a constant value of C_A and definite values of K_A and K_B . The values of K_A and K_B determine the mutual positions of curves $\chi(\varepsilon)$ of substances A and B on the energy axis, ε . From Fig. 1 it follows that k_c is considerably dependent on the energetic heterogeneity parameters on the surface

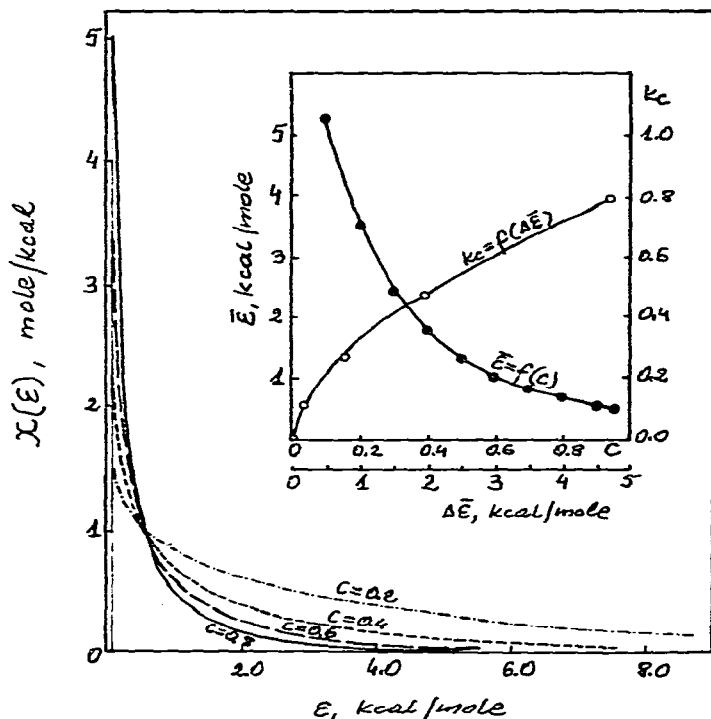


Fig. 3. Energy distributions, $\chi(\varepsilon)$, calculated according to eqn. 9 for curve I in Fig. 1A ($K_A = K_B$). The inset shows the dependence of $\bar{\varepsilon}$ on C (●), and the dependence of k_c on $\Delta\bar{\varepsilon} = |\bar{\varepsilon}_A - \bar{\varepsilon}_B|$, where $\bar{\varepsilon}_A$ and $\bar{\varepsilon}_B$ denote the average adsorption energies calculated from eqn. 14 with $C_A = 0.9$ and $C_B = 0.2, 0.4, 0.6$ or 0.8 .

of adsorbents (C and K). The value of k_c can either increase or decrease on passing through the minimum, depending on the shape of the $\chi(\varepsilon)$ function of substances A and B (C_A and C_B) and on the mutual positions of the $\chi(\varepsilon)_A$ and $\chi(\varepsilon)_B$ curves (K_A and K_B) on the ε axis. Minima on the plots in Figs. 1 and 2, for which $k_c = 0$, correspond to the situation when $A = B$ [$C_A = C_B$ and $K_A = K_B$; the energy distribution functions $\chi(\varepsilon)$ of the two substances overlap]. Also for the curves in Fig. 2 [$k_c = f(K_B)$, C_A , C_B and K_B values being established] a clear dependence of k_c on the heterogeneity parameters can be observed. The coefficient k_c can either increase or decrease with increase in K_B , depending on the assumed values of C_A and C_B .

The above dependences are presented in more detail in Figs. 3–7. They contain the energy distributions functions $\chi(\varepsilon)$ for various values of C_A , C_B , K_A and K_B examined in Figs. 1 and 2. For the sake of simplification we investigated the relative positions of the $\chi(\varepsilon)$ function for substances A and B. Fig. 3 corresponds to curve I in Fig. 1A and Fig. 4 to curve I in Fig. 1C. In the first instance (Fig. 3) the minimal adsorption energies, ε_0 , of substances A and B are similar ($K_A = K_B$), and it is only the shape of the $\chi(\varepsilon)$ function of substance B (C_B) which changes at a constant shape of the $\chi(\varepsilon)$ function of substance A ($C_A = \text{constant}$).

Comparing the course of the curves in Fig. 1A and C with the course of the $\chi(\varepsilon)$ function for substances A and B (Figs. 3 and 4), one can conclude that the smaller is the overlap of the $\chi(\varepsilon)$ curves for the two separated substances, the higher is k_c . This

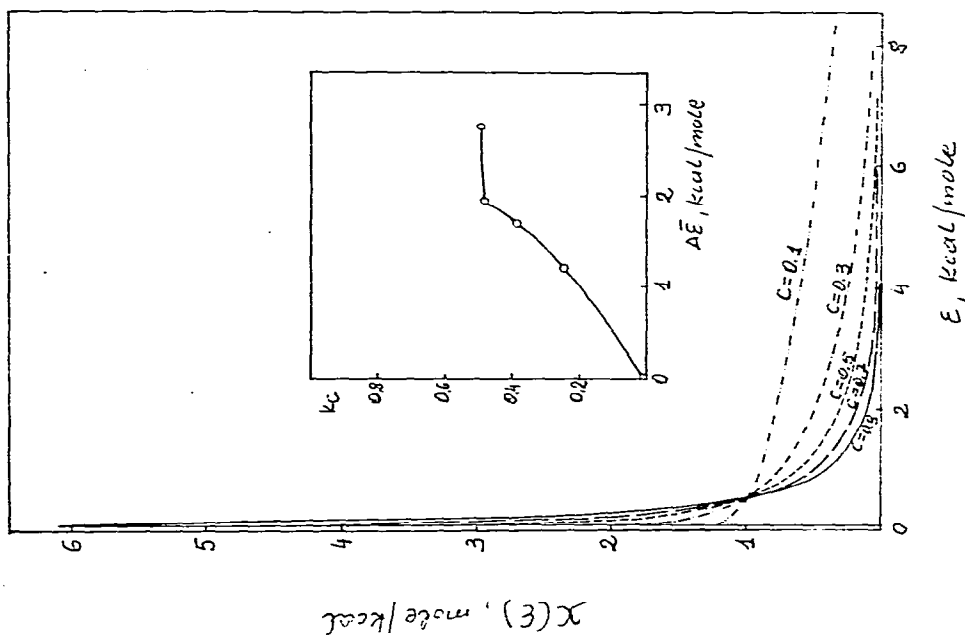
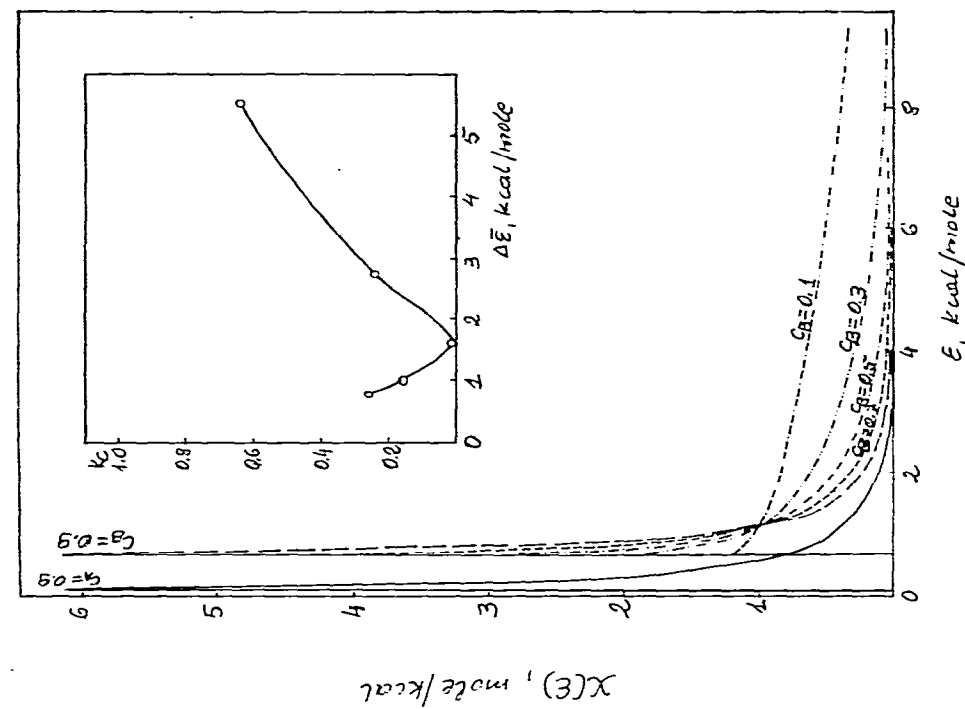


Fig. 4. Energy distributions, $\chi(E)$, calculated for curve I in Fig. 1C ($K_A = K_B$). In the inset, $\Delta \bar{E}$ was calculated with $C_A = 0.3$ (\bar{E}_A) and with $C_B = 0.1, 0.3, 0.5, 0.7$ or 0.9 (\bar{E}_B).

Fig. 5. Energy distributions, $\chi(E)$, calculated for curve II in Fig. 1A ($K_A = 2$ and $K_B = 4$). The inset shows k_c versus $\Delta \bar{E}$, where $\Delta \bar{E}$ was calculated with $C_A = 0.9$ (\bar{E}_A) and $C_B = 0.3, 0.5, 0.7$ or 0.9 (\bar{E}_B).

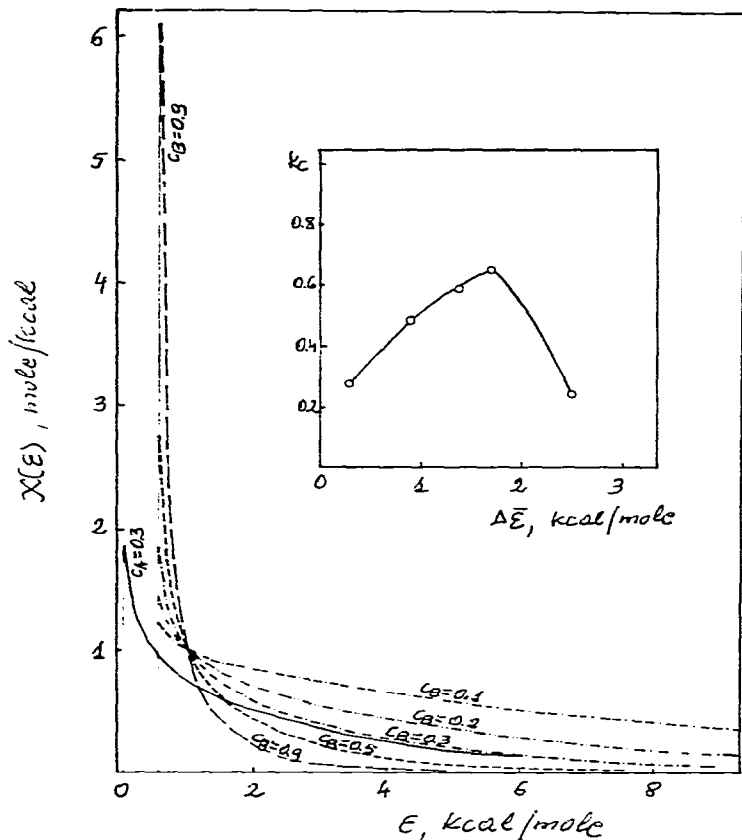


Fig. 6. Energy distributions, $\chi(\epsilon)$, calculated for curve II in Fig. 1C ($K_A = 2$ and $K_B = 4$). The inset shows k_c versus $\Delta\bar{\epsilon}$, where $\Delta\bar{\epsilon}$ was calculated with $C_A = 0.3$ ($\bar{\epsilon}_A$) and $C_B = 0.1, 0.3, 0.5, 0.7$ or 0.9 ($\bar{\epsilon}_B$).

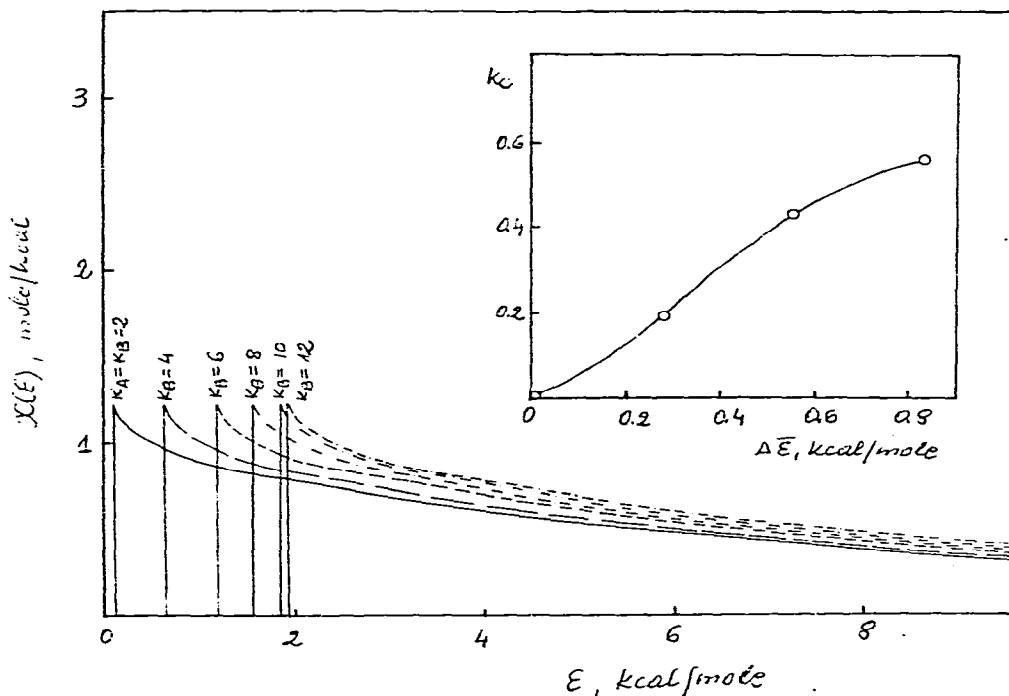


Fig. 7. Energy distributions, $\chi(\epsilon)$, calculated for curve I in Fig. 2A ($C_A = C_B = 0.1$). The inset shows k_c versus $\Delta\bar{\epsilon}$, where $\Delta\bar{\epsilon}$ was calculated with $K_A = 2$ ($\bar{\epsilon}_A$) and $K_B = 2, 4, 6$ or 8 ($\bar{\epsilon}_B$).

situation arises when C_A and C_B differ considerably from each other or when K_A and K_B differ even at similar or identical C_A and C_B values (see Figs. 5–9). The areas of the overlap of the curves for substances A and B will be small if they have considerably different properties. In analytical practice the separation of such substances is usually easy.

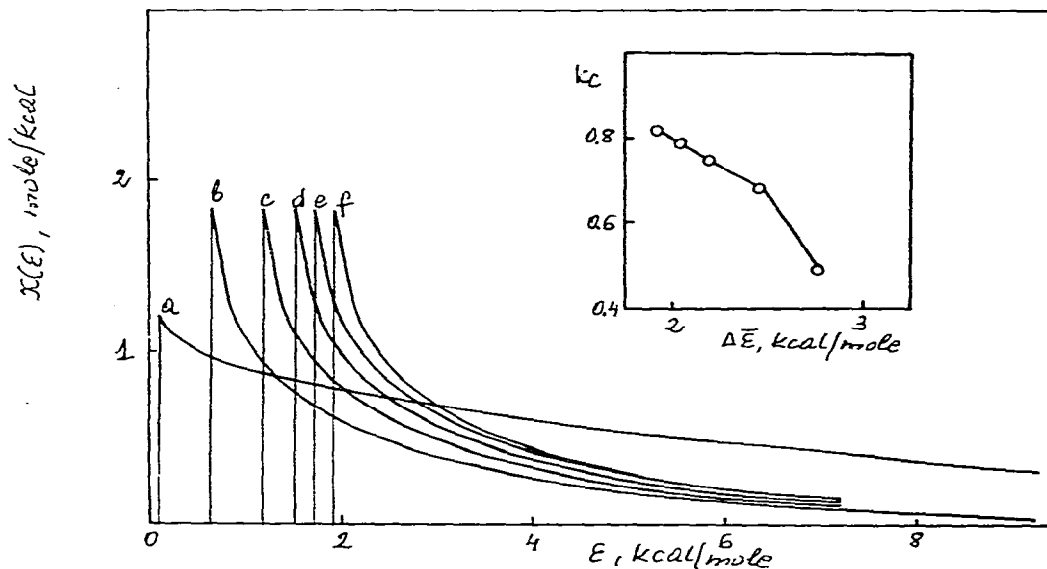


Fig. 8. Energy distributions, $\chi(\epsilon)$, calculated for curve II in Fig. 2A. $C_A = 0.1$ (a); $C_B = 0.3$ (b–f); $K_A = 2$ (a); $K_B = 4$ (b), 6 (c), 8 (d), 10 (e) or 12 (f). The inset shows k_c versus $\Delta\bar{\epsilon}$, where $\Delta\bar{\epsilon}$ is the difference between the average adsorption energy of curve a ($\bar{\epsilon}_A$) and curves b–f ($\bar{\epsilon}_B$).

As the shape of the energy distribution function, $\chi(\epsilon)$, determines the mean energy of adsorption, $\bar{\epsilon}$, it could be concluded that k_c is determined by the differences in the values of mean energies of adsorption, $\Delta\bar{\epsilon} = |\bar{\epsilon}_A - \bar{\epsilon}_B|$, and not by their distribution, $\chi(\epsilon)_A$ and $\chi(\epsilon)_B$. Let us examine the problem assuming energetic homogeneity of an adsorbent. The adsorbent will have an energy of adsorption relative to substances A and B, equal to the means $\bar{\epsilon}_A$ and $\bar{\epsilon}_B$ on the surface of a heterogeneous adsorbent.

The curve with solid symbols in the inset in Fig. 3 shows the dependence of $\bar{\epsilon}$ on C (for $K_A = K_B = \text{constant}$) for all the functions $\chi(\epsilon)$ shown in the figure. $\bar{\epsilon}$ values were calculated numerically from the following equation:

$$\bar{x} = \bar{\epsilon} - \epsilon_0 = \frac{\sin \pi C}{\pi RT} \int_0^{\infty} x \left[\exp\left(-\frac{x}{RT}\right) - 1 \right]^{-C} dx \quad (14)$$

$\bar{\epsilon}$ decreases with decrease in C and at $C = 1$ (homogeneous surface) $\bar{\epsilon}$ reaches the value ϵ_0 . The greater is the difference between C_A and C_B the higher is the value $\Delta\bar{\epsilon} = |\bar{\epsilon}_A - \bar{\epsilon}_B|$ and the smaller are the areas of overlap of the $\chi(\epsilon)_A$ and $\chi(\epsilon)_B$ functions. It is obvious that if k_c value is determined by $\Delta\bar{\epsilon}$, then the function $k_c = f(\Delta\bar{\epsilon})$ should have the same course (and shape) as the functions $k_c = f(C_B)$ and $k_c = f(K_B)$.

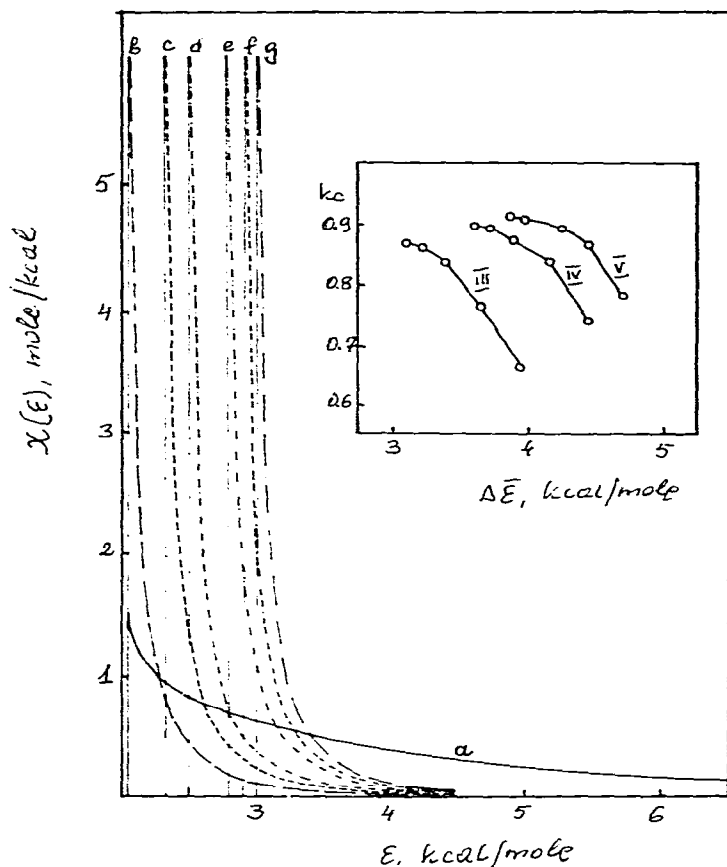


Fig. 9. Energy distributions, $\chi(\epsilon)$, calculated for curve V in Fig. 2A. $C_A = 0.1$ (a); $C_B = 0.9$ (b-g); $K_A = 2$; $K_B = 2$ (b), 4 (c), 6 (d), 8 (e), 10 (f) or 12 (g). The inset shows the dependence of k_c on $\Delta \bar{\epsilon}$ for curves III, IV and V in Fig. 2A.

Fig. 3 also presents the courses of the $k_c = f(\Delta \bar{\epsilon})$ dependences. As expected, k_c increases with increase in $\Delta \bar{\epsilon}$. The curve does not correspond closely to the plot of $k_c = f(C_B)$ presented in Fig. 1A, curve I. From Fig. 4 it follows that although k_c increases with increase in $\Delta \bar{\epsilon}$, the shape of the function is slightly different than in the previous instance. The curve $k_c = f(\Delta \bar{\epsilon})$ in Fig. 4 also does not correspond closely to the plot of $k_c = f(C_B)$ presented in Fig. 1C, curve I. Differences in the courses of the function $k_c = f(\Delta \bar{\epsilon})$ in Figs. 3 and 4 and $k_c = f(C_B)$ in Fig. 1A, curve I, and Fig. 1C, curve I, result from different values of C_A (0.9 and 0.3) for the two cases investigated. This means that k_c is determined not only by the differences in the mean energies of adsorption, $\bar{\epsilon}_A$ and $\bar{\epsilon}_B$, but also by the courses of the functions $\chi(\epsilon)_A$ and $\chi(\epsilon)_B$. Further analysis of the curves $k_c = f(\Delta \bar{\epsilon})$ in Figs. 5, 6 and 9 compared with the corresponding curves $k_c = f(C_B)$ and $k_c = f(K_B)$ (see the figure legends) also allows such a conclusion. The influence of the shape of the function $\chi(\epsilon)$ for substances A and B on the course of the investigated dependences is clear.

In Fig. 5 the shape of $k_c = f(\Delta \bar{\epsilon})$ curve corresponds closely to the curve $k_c = f(C_B)$ in Fig. 1A, curve II. In this instance the value of k_c is determined by $\Delta \bar{\epsilon} =$

$|\bar{\varepsilon}_A - \bar{\varepsilon}_B|$, whereas in the other instances (Figs. 6–9) the value of k_c seems to be influenced not only by $\Delta\bar{\varepsilon}$ but also by the parameters of heterogeneity, C_A , C_B and K_B . Further confirmation of this conclusion is provided by Figs. 10, which shows the dependence of k_c on K_B for an energetically homogeneous surface. The values of k_c were calculated from eqn. 10 assuming $C_A = C_B = 1$. Then the energy distribution function, $\chi(\varepsilon)$, becomes Dirac's delta function. As follows from Fig. 10, the plot of k_c versus K_B (with K_A constant) is linear and does not correspond with any curve presented in Fig. 2.

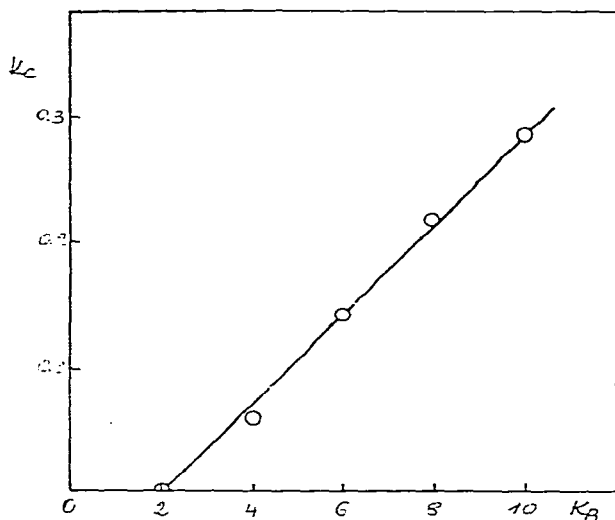


Fig. 10. Dependences of k_c on K_B ($K_A = 2$) for an energetically homogeneous surface ($C_A = C_B = 1$).

Now we shall discuss the quasi-gaussian energy distribution function of the adsorption energy. Adsorbents that show an energy distribution of this type are characterized by a more regular distribution of adsorptive centres on the surface in comparison with an exponential distribution. A quasi-gaussian distribution is characteristic of some unmodified^{8,19} and chemically modified silica gels^{6,8,19} and other adsorbents^{17,18,28}.

Fig. 11 presents plots of $k_c = f(B_B)$ for $K_A = K_B = 10$, and Fig. 12 plots of $k_c = f(K_B)$ for $K_A = 50$. In general, for the energy distribution functions discussed here k_c depends on the shape of the functions $\chi(\varepsilon)$, *i.e.*, on B_B (B_A constant) and on K_B . Further data, which we have omitted here, indicate that the course and absolute value of k_c are closely dependent on the relationship between K_A , K_B , C_A and C_B . However, the courses of the functions $\bar{\varepsilon} = f(B)$ and $k_c = f(\Delta\bar{\varepsilon})$ seem interesting. Fig. 13 shows plots of these functions and functions $\chi(\varepsilon)$ illustrating curve I in Fig. 11. The values of $\bar{\varepsilon}$ were calculated from the equation

$$\bar{x} = 2B \int_0^{\infty} x^2 \exp(-Bx^2) dx = \frac{1}{2} B \sqrt{\pi} B^{-3/2} \quad (15)$$

$$\bar{x} = \bar{\varepsilon} - \varepsilon_0$$

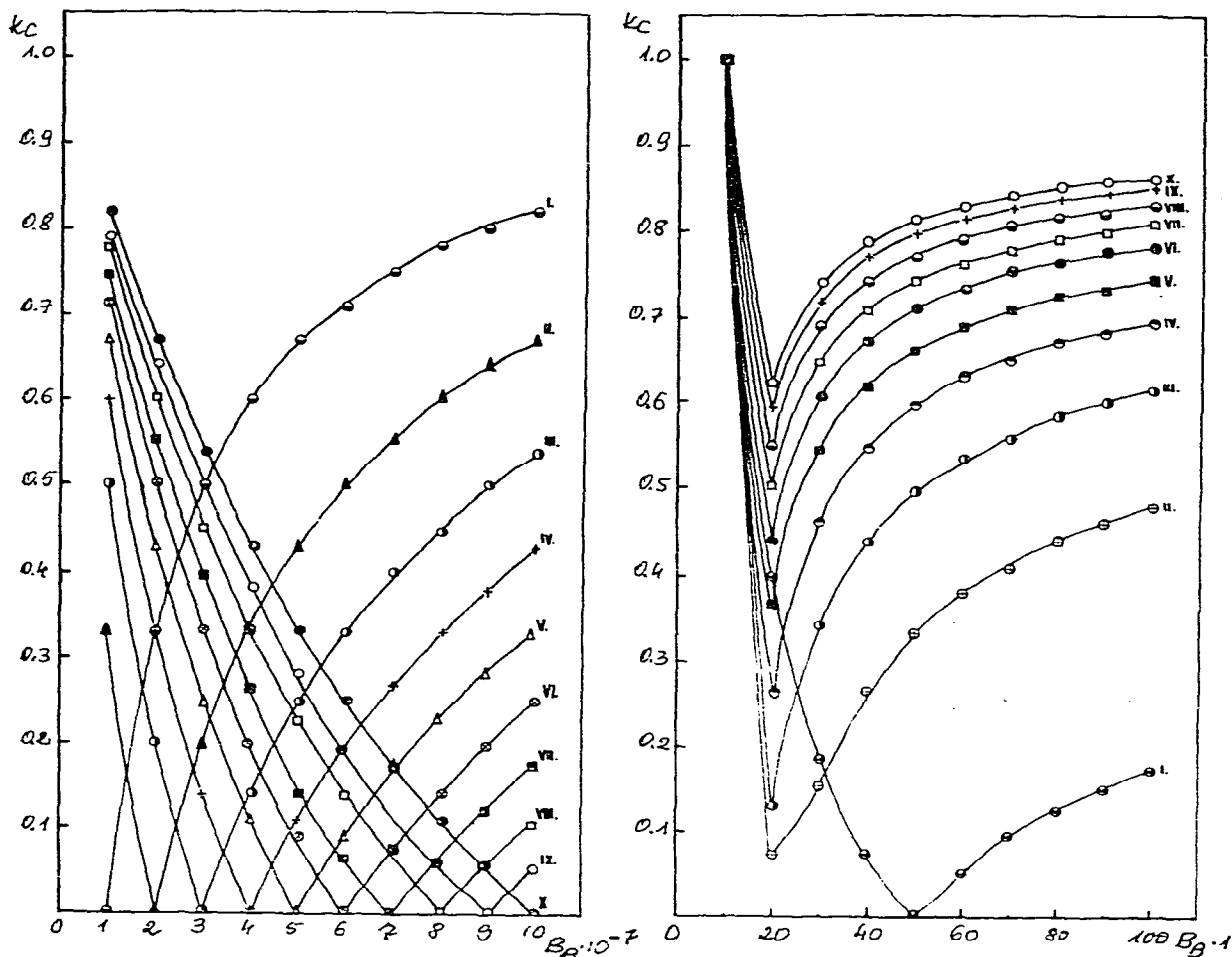


Fig. 11. Dependence of k_c on B ($K_A = K_B = 10$). Curve I corresponds to $B = 1 \cdot 10^{-8}$; the other curves (II, III, etc.) were calculated for subsequent B values increasing in steps of $1 \cdot 10^{-8}$ up to $1 \cdot 10^{-7}$ (curve X).

Fig. 12. Dependence of k_c on K_B ($K_A = 50$). Curves I-X as in Fig. 11.

From Fig. 13, it follows that mean energy, $\bar{\epsilon}$, depending on the shape of the function $\chi(\epsilon)$ (parameter B), changes in a similar manner to that in the case of an exponential distribution, but the dependence $k_c = f(\Delta\bar{\epsilon})$ is different. The curve does not correspond with the plot of $k_c = f(B_B)$ presented in Fig. 11 curve I. This indicates a clear influence of energetic heterogeneity of the surface of an adsorbent on k_c . The effects of heterogeneity become clearer when further dependences $k_c = f(\Delta\bar{\epsilon})$ are examined.

Table I shows the data illustrating the dependence $k_c = f(\Delta\bar{\epsilon})$ for curve II in Fig. 12. In this instance the increase in K_B is related to an increase in k_c , but a simultaneous slight decrease in $\Delta\bar{\epsilon}$ is observed.

So far we have been dealing with strongly heterogeneous adsorptive systems, *i.e.*, for which the differences between the minimal and maximal energies of adsorption are 3–10 kcal/mole. Great differences between the energies are disadvantageous

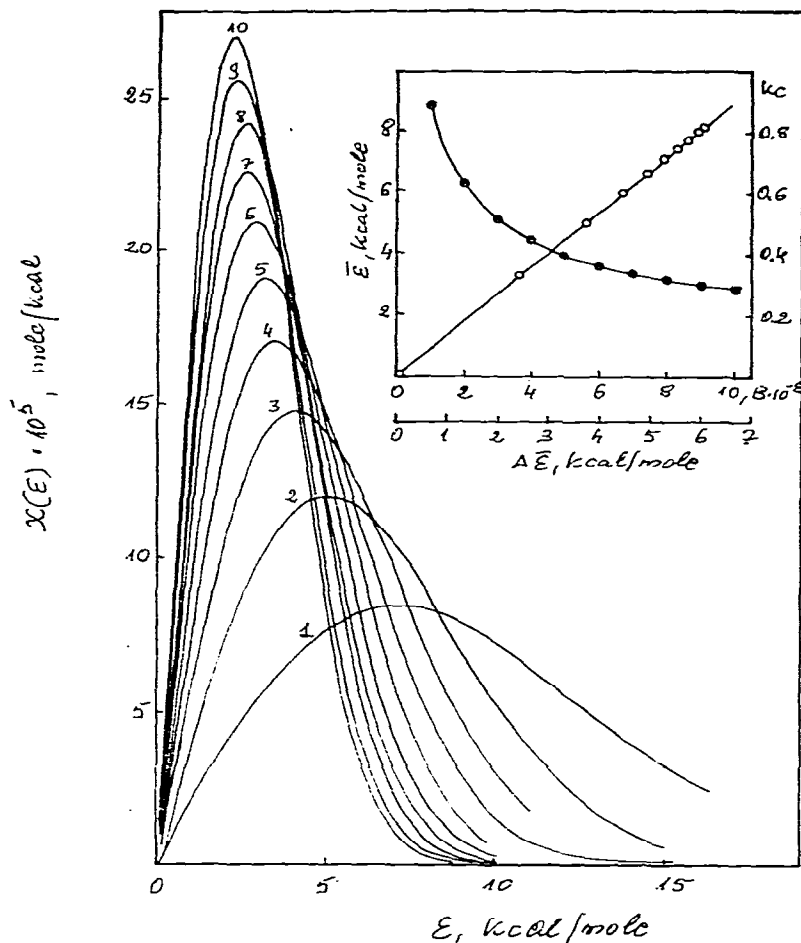


Fig. 13. Energy distributions functions, $\chi(\epsilon)$, for curve I in Fig. 11 ($K_A = K_B = 10$). Numbers on curves indicate the values of B multiplied by 10^{-8} . The inset shows the dependence of the average adsorption energy, $\bar{\epsilon}$, calculated from eqn. 15 for curves 1-10 versus B (●), and dependences of k_c on $\Delta \bar{\epsilon} = |\bar{\epsilon}_A - \bar{\epsilon}_B|$. (○), where $\bar{\epsilon}_A$ denotes the average adsorption energy for the energy distribution 1, whereas $\bar{\epsilon}_B$ denotes values for energy distributions 2-10.

TABLE I

DEPENDENCES OF SELECTIVITY COEFFICIENT, k_c , ON VALUES OF $\Delta \bar{\epsilon}$ FOR CURVE II IN FIG. 12 ($K_A = 50$)

k_c	$\Delta \bar{\epsilon} = \bar{\epsilon}_A - \bar{\epsilon}_B $ (kcal/mole)	K_B
0.07	2.92	20
0.15	2.72	30
0.26	2.62	40
0.33	2.52	50
0.38	2.58	60
0.41	2.42	70
0.44	2.37	80
0.46	2.32	90
0.48	2.32	100

for analytical purposes, as they may result in considerable broadening of chromatographic bands³³. Therefore, we shall now deal with adsorptive systems in which the differences between the minimal and maximal energies of adsorption are much smaller.

Fig. 14 shows the courses of the dependences $k_c = f(B_B)$ when $K_A = K_B$, $\varepsilon_{0A} = \varepsilon_{0B}$ and B changes within the range $1 \cdot 10^{-6} - 1 \cdot 10^{-5}$. The differences between the minimal and maximal adsorption energies on plots of the function $\chi(\varepsilon)$ are 0.9–2.6 kcal/mole. The surface of an adsorbent is homogeneous, and this type of adsorbent includes some chemically modified ones^{8,19}. From Fig. 14 it follows that the course of the function $k_c = f(B_B)$ depends on the heterogeneity parameter B_A . The dependences differ slightly from those in Figs. 11 and 12, and show minima and maxima.

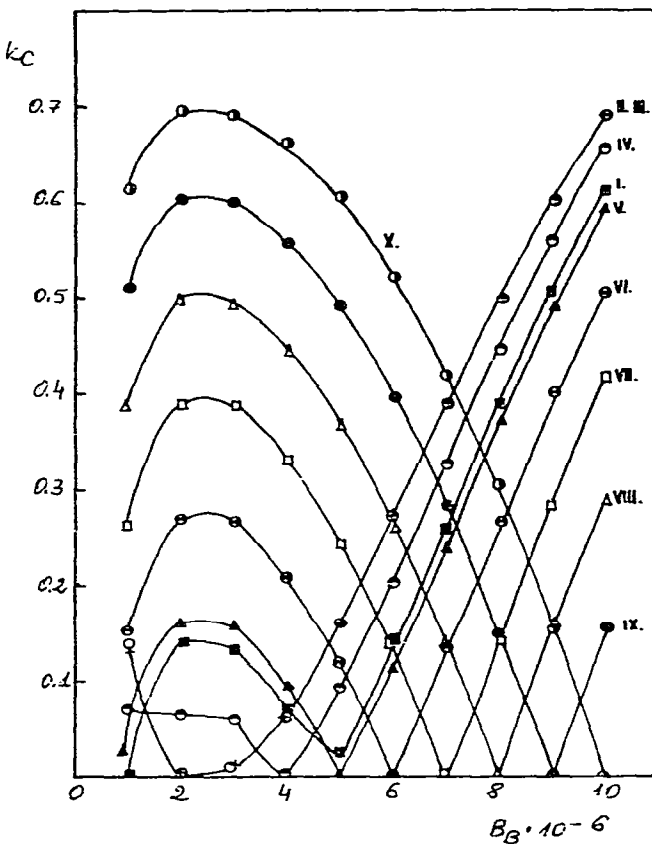


Fig. 14. Dependence of k_c on B_B ($K_A = K_B = 10$). B_A varies in the range $1 \cdot 10^{-5} - 1 \cdot 10^{-6}$. Curve I corresponds to $B = 1 \cdot 10^{-6}$; the other curves correspond to increasing B in steps of $1 \cdot 10^{-6}$ up to $9 \cdot 10^{-6}$ (curve X).

Fig. 15 shows the dependence of the mean energy of adsorption, $\bar{\varepsilon}$, on B in the range $1 \cdot 10^{-6} - 1 \cdot 10^{-5}$, and $k_c = f(\Delta\bar{\varepsilon})$ for some selected systems illustrated in Fig. 14. The course of $\bar{\varepsilon} = f(B)$ is the same as in Fig. 13, but the plots of $k_c = f(\Delta\bar{\varepsilon})$ are different, although in both instances (Figs. 13 and 15) $K_A = K_B$.

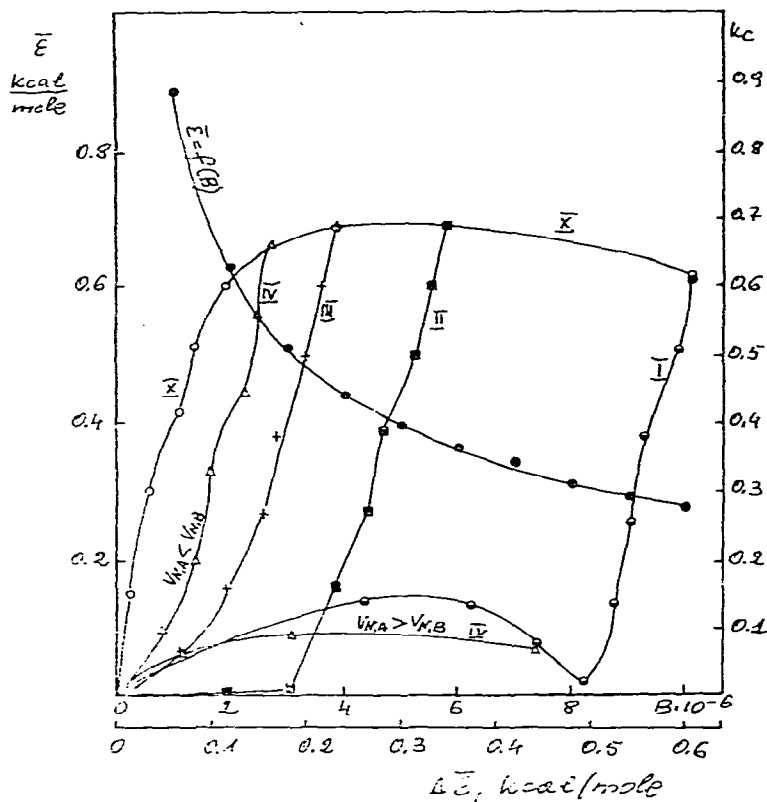


Fig. 15. Dependences of average adsorption energies, \bar{E} , on B (●) and dependences of k_c on $\Delta\bar{E}$ for curves I-IV and X in Fig. 14.

In Fig. 14, curves II and III [$k_c = f(B_B)$] virtually coincide, whereas in Fig. 15 the dependences $k_c = f(\Delta\bar{E})$ corresponding to them are not convergent. The differences in the courses of the investigated functions in Figs. 11-13, 14 and 15 indicate not only the influence of energetic heterogeneity of an adsorbent surface on the value of k_c , but also a complex character of the dependences.

CONCLUSIONS

From the data presented, it follows that energetic heterogeneity of an adsorbent surface can be a positive factor in chromatographic separations. However, the heterogeneity may also result in broadening of chromatographic bands³³, which, in turn, decreases the column efficiency, *i.e.*, the number of theoretical plates, n . Thus, the problem of separation is complex and should be considered as such, taking into account, *e.g.*, equations for resolution or for the criterion of separation. However, some experimental and theoretical data^{2,4,6,15} suggest that the problem might not be so complex and difficult. It should be noted that from the equation for the criterion of separation, K_s , connecting the selectivity coefficient, k_c , and the column efficiency, n ,

$$K_s = \frac{\sqrt{2}}{4} \cdot \sqrt{n} \cdot k_c \quad (16)$$

it follows that the chromatographic separation is more dependent on k_c than on n .

Broadening of chromatographic bands will occur mainly with adsorbents on the surface of which there are adsorptive centres with very different energies of adsorption and with a very irregular arrangement on the surface. This conclusion follows from the kinetics of the adsorption-desorption process. A strong heterogeneity of an adsorbent surface can be decreased by physical or chemical modification of the adsorbent. In addition, symmetry of the peaks can be improved by using small amounts of the dosed samples and relatively high temperatures. In this way lateral interactions of the adsorbate molecules in the chromatographic band can be weakened or prevented.

Thus, in speaking about a positive effect of energetic heterogeneity of an adsorbent on the separation of chromatographed substances, we should mean the influence of moderate heterogeneity, *i.e.*, at which the differences between the minimal and maximal energies of adsorption are very small. Examples of heterogeneous adsorbents that permit complete separations of various hydrocarbons are given elsewhere^{6,8,19}.

It is also worth stressing that a theoretical description of the problem of selectivity may be more complicated for chemically modified adsorbents. This problem is discussed in another paper⁶.

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