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LIQUID ADSORPTION CHROMATOGRAPHY WITH MIXED MOBILE PHASES

II. EFFECTS OF ADSORBENT HETEROGENEITY

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SUMMARY

An analytical expression for the capacity ratio of a chromatographed compound, involving the energetic heterogeneity of the adsorbent surface, has been derived in terms of the liquid chromatography theory of Snyder. This expression has been examined by using the experimental data obtained from high-performance liquid chromatography with two- and three-component mobile phases.

INTRODUCTION

In the first part of this series[1] we discussed the effects of nonideality of the mobile phase in liquid adsorption chromatography. The analytical expressions for the capacity ratio, containing the activity coefficients of the components appearing in the mobile phase, have been discussed. These expressions were derived by using Snyder's relationship[2,3]

$$k'_{(1,2,\ldots,n)s} = \sum_{i=1}^{n} k'_{(i)s} y_i \tag{1}$$

where y_i is the mole fraction of the ith component in the surface phase, n is the number of the components in the mobile phase, the subscripts s and i refer to the sth compound chromatographed and the ith component of the mobile phase, respectively, $k'_{(i)s}$ is the capacity ratio for the sth compound and ith pure solvent and $k'_{(1,2,\ldots,n)s}$ is the capacity ratio for the sth compound and an n-component mobile phase.

It follows from ref. 3 that eqn. 1 may be transformed to the form

$$1/k'_{(1,2,\ldots,n)s} = \sum_{i=1}^{n} x_i/k'_{(i)s} \tag{2}$$

where x_i is the mole fraction of the ith component in the mobile phase. Eqn. 2 is obtained from eqn. 1 by replacing y_i by the expression

$$y_i = (x_i/k'_{(i)s})/(\sum_{j=1}^{n} x_j/k'_{(j)s})$$ (3)

which is valid for ideal mobile and adsorbed phases, and also for homogeneous adsorbents. For two-component mobile phases eqn. 2 becomes

$$1/k'_{(1,2)s} = x_1/k'_{(1)s} + x_2/k'_{(2)s}$$ (4)

This equation was discussed previously[4] in connection with the logarithmic dependence of the capacity ratio on composition of the mobile phase. The linear form of eqn. 4 is formally identical with that obtained by Scott and Kucera[5]

$$1/k'_{(1,2)s} = a + b \cdot x_2$$ (5)

where the constants a and b are functions of $k'_{(1)s}$ and $k'_{(2)s}$.

In this paper the analytical eqns. 2 and 4 for the capacity ratio have been generalized by assuming the energetic heterogeneity of the adsorbent surface. The case of liquid chromatography (LC) with a two-component mobile phase will be discussed in detail.

THEORETICAL

Let us consider a chromatographic system with an ideal n-component mobile phase on a heterogeneous solid surface. According to Snyder's theory of LC[2] the capacity ratio for the whole adsorbent surface is

$$k'_{(1,2,\ldots,n)s} = \sum_{l=1}^{L} f_l \, k'_{(1,2,\ldots,n)s,l}$$ (6)

where $k'_{(1,2,\ldots,n)s,l}$ is the capacity ratio of the lth type of adsorption site, f_l is the ratio of the number of lth type adsorption sites to the total number of adsorption sites and L is the number of types of adsorption sites. According to eqn. 1, the capacity ratio for the lth type of adsorption sites may be expressed as

$$k'_{(1,2,\ldots,n)s,l} = \sum_{i=1}^{n} k'_{(i)s,l} \, y_{i,l}$$ (7)

where $y_{i,l}$ is the mole fraction of the ith component on the lth type of adsorption site. Combining eqns. 6 and 7 we have

$$k'_{(1,2,\ldots,n)s} = \sum_{i=1}^{n} k'_{(i)s} \sum_{l=1}^{L} (k'_{(i)s,l}/k'_{(i)s}) f_l y_{i,l}$$ (8)

where $k'_{(i)s}$ is an averaged capacity ratio for the sth compound and ith pure solvent, referring to the whole adsorbent surface. Eqn. 8 is a general expression describing the

capacity ratio for the sth compound in an n-component mobile phase on heterogeneous surfaces of l types of adsorption sites. Evaluation of the capacity ratio $k'_{(1,2,....,n)s}$ by means of eqn. 8 for real chromatographic systems is very difficult. For this purpose the exact theoretical expressions, defining the dependences of $k'_{(i)s,l}$ and $y_{i,l}$ on the adsorption energy of the lth type of adsorption sites, and the parameters $f_1, f_2,..., f_L$, characterizing the energetic heterogeneity of the adsorbent surface, should be known. However, using the suitable approximation in eqn. 8, we shall transform this equation to a considerably simpler form, which may be used to describe the real chromatographic systems.

It has been demonstrated[6] that summations of the type appearing in eqn. 8 can be well represented by a simpler function

$$\sum_{l=1}^{L} (k'_{(i)s,l}/k'_{(i)s})f_l y_{i,l} = G_i(y_i) \text{ for } i = 1,2,...,n \tag{9}$$

It can be shown from physical considerations that for a large number of homotactic patches the functions $G_i(y_i)$ are monotonic, increasing from zero to unity. Simulations, similar to that used previously[6], have shown that the function $G_i(y_i)$ is well represented by

$$G_i(y_i) = (y_i)^{1/m_i} \text{ where } m_i > 0 \tag{10}$$

The parameter m_i characterizes the energetic heterogeneity of the adsorbent surface with respect to the ith component. For $m_i = 1$ the surface is energetically homogeneous; however, for m_i decreasing from unity to zero the energetic heterogeneity of the adsorbent surface increases. The adsorbent heterogeneity is usually characterized by a distribution function of the adsorption energy[7], which for many adsorption systems is of a quasi-gaussian type; the parameter m_i determines the shape of this distribution. Thus, for m_i close to unity this distribution is similar to the sharp chromatographic peak (the adsorption sites appearing on the surface have similar adsorption energies); however, for m_i close to zero this distribution is similar to the broad peak (the range of adsorption energies is large).

Substitution of eqn. 10 in eqn. 8 gives

$$k'_{(1,2,...,n)s} = \sum_{i=1}^{n} k'_{(i)s} \cdot (y_i)^{1/m_i} \tag{11}$$

If the shapes of the distribution functions for all components of the mobile phase are similar, the parameters $m_1, m_2,...,m_n$ are also similar, i.e.

$$m_1 \approx m_2 \approx m_3 \approx ... \approx m_n = m \tag{12}$$

Then, eqn. 11 becomes

$$k'_{(1\,2,...,n)s} = \sum_{i=1}^{n} k'_{(i)s} \cdot (y_i)^{1/m} \tag{13}$$

Eqn. 13 defines the capacity ratio $k'_{(1,2,....,n)s}$ for the sth compound in an n-component

mobile phase on heterogeneous surfaces by means of the capacity ratios $k'_{(i)s}$, mole fractions y_i and the parameter m. The values of $k'_{(i)s}$ and y_i are characteristic for the ith solvent and whole adsorbent surface. The parameter m characterizes the effects of adsorbent heterogeneity with respect to all adsorbing molecules, *i.e.*, m is characteristic for the whole chromatographic system. Since the concentration of the chromatographed compound is infinitely small, the parameter m depends mainly on the type of the adsorbent and mobile phase.

In eqn. 13 the mole fraction of the ith component in the surface phase, y_i, may be calculated according to a suitable expression derived for adsorption on heterogeneous surfaces. The theory of adsorption kinetics from multicomponent liquid mixtures on heterogeneous solid surfaces, based on the approach expressed in eqn. 10, leads[7] to

$$y_i = (x_i/k'_{(i)s})^m / \sum_{j=1}^{n} (x_j/k'_{(j)s})^m \tag{14}$$

Combining eqns. 14 and 11, we obtain the direct dependence of $k'_{(1,2,\ldots,n)s}$ on the mole fractions of components in the mobile phase

$$(k'_{(1,2,\ldots,n)s})^{-m} = \sum_{i=1}^{n} (x_i/k'_{(i)s})^m \tag{15}$$

Eqn. 15 for $m = 1$ becomes eqn. 2, which was derived for homogeneous adsorbents.

Now, we shall discuss LC with a two-component mobile phase. In this case, eqn. 15 assumes the form

$$(k'_{(1,2)s})^{-m} = (x_1/k'_{(1)s})^m + (x_2/k'_{(2)s})^m \tag{16}$$

Let us assume that the second component is a more efficient eluting solvent in the binary mobile phase. Then $k'_{(2)s} < k'_{(1)s}$. Eqn. 16 predicts the correct values of $k'_{(1,2)s}$ at $x_2 = 0$ and $x_2 = 1$, *i.e.*

$$k'_{(1,2)s}(x_2 = 0) = k'_{(1)s} \text{ and } k'_{(1,2)s}(x_2 = 1) = k'_{(2)s} \tag{17}$$

Dividing eqn. 16 by the second term appearing at the left side of this equation, we obtain

$$\left[\frac{k'_{(2)s}}{k'_{(1,2)s} x_2} \right]^m = 1 + \left[\frac{k'_{(2)s} x_1}{k'_{(1)s} x_2} \right]^m \tag{18}$$

Since

$$\left[\frac{k'_{(2)s} x_1}{k'_{(1)s} x_2} \right]^m > 0 \text{ for } 0 < x_2 < 1 \tag{19}$$

the left side of eqn. 18 is still greater than unity. Thus, the right side of eqn. 18 must be greater than unity

$$(k'_{(1,2)s} x_2)^m < (k'_{(2)s})^m \tag{20}$$

It follows from the inequality 20 that eqns. 16 and 4 may be used for analysis of experimental data, for which the values of $k'_{(1,2)s}$ satisfy the relationship 20. Analogous limitations apply to eqns. 2 and 15.

Considering a simplification of eqn. 18, it may be rewritten in a slightly different form

$$\log\left[\frac{k'_{(2)s}}{k'_{(1,2)s}x_2}\right] = (1/m)\log\left[1 + \left(\frac{k'_{(2)s}\,x_1}{k'_{(1)s}x_2}\right)^m\right] \tag{21}$$

Eqn. 21 generates the expression

$$\log\left[\frac{k'_{(2)s}}{k'_{(1,2)s}x_2}\right] \approx (1/m)\left[\frac{k'_{(2)s}\,x_1}{k'_{(1)s}x_2}\right]^m \tag{22}$$

If the relationship 20 is valid, eqn. 22 may be rewritten as

$$\log\left\{\log\left[\frac{k'_{(2)s}}{k'_{(1,2)s}x_2}\right]\right\} = \beta + m\log(x_1/x_2) \tag{23}$$

where:

$$\beta = -\log m + m\log(k'_{(2)s}/k'_{(1)s}) \tag{24}$$

Finally, we transform eqn. 16 to the linear form, which may be convenient for the approximation of experimental data

$$(k'_{(1,2)s}\,x_1)^{-m} = a_1 + b_1(x_2/x_1)^m \text{ for } x_1 \neq 0 \tag{25}$$

where:

$$a_1 = (k'_{(1)s})^{-m} \text{ and } b_1 = (k'_{(2)s})^{-m} \tag{26}$$

Eqn. 16 or its linear form, eqn. 25, may be used for analysis of experimental data in two ways:

(i) using the experimental values $k'_{(1)s}$ and $k'_{(2)s}$ in eqn. 16, the average value of the parameter m is calculated for all experimental values of $k'_{(1,2)s}$.

(ii) the experimental points $k'_{(1,2)s}$ vs. x_2 are approximated by eqn. 25, and the constants a_1, b_1 and m are treated as best-fit parameters.

The second method is analogous to that which is used in eqn. 5.

EXPERIMENTAL

The LC measurements were carried out on a liquid chromatograph utilizing a pneumatic pump having PTFE antidiffusion membranes from Varian Aerograph (Series 4000 liquid chromatograph). A Model Spekol spectrocolorimeter (Carl Zeiss Jena, Jena, G.D.R.) equipped with a flow cuvette (10 × 1 mm) was used as the detector[8]. Stainless-steel columns (10 cm × 3.5 mm I.D.) were slurry packed with LiChrosorb SI 60 of 10 μm particle size (E. Merck, Darmstadt, G.F.R.). The samples were intro-

duced with a 10 mm³ Hamilton syringe in 0.2% (v/v) benzene solutions. The column was conditioned in each run by passing through *ca.* 50 cm³ of the mobile phase at 1.0 cm³ min⁻¹. The solvents were dried over a 5 Å molecular sieve.

All measurements were carried out at 24° for nine substances in two mobile phases: benzene(1)–diisopropyl ether(2) and benzene(1)–diisopropyl ether(2)–dichloromethane(3): the numbers in parentheses denote codes for component of the mobile phase.

RESULTS AND DISCUSSION

Figs. 1 and 2 show the theoretical curves $k'_{(1,2)s}$ *vs.* x_2, calculated according to

$$k'_{(1,2)s} = \left[\left(\frac{1-x_2}{k'_{(1)s}}\right)^m + \left(\frac{x_2}{k'_{(2)s}}\right)^m\right]^{-1/m} \tag{27}$$

These model calculations were performed for $k'_{(1)s} = 5$ and $k'_{(2)s} = 3$ (Fig. 1) and $k'_{(1)s} = 5$ and $k'_{(2)s} = 0.5$ (Fig. 2), and for different values of m. Eqn. 27 is another form of eqn. 16. The function $k'_{(1,2)s}(x_2)$ for $k'_{(1)s} > k'_{(2)s}$ and $m = 1$ is a decreasing one. However, for $m \neq 1$ this function reaches its extreme value at the point

$$x_2 = [1 \div (k'_{(2)s}/k'_{(1)s})^{m/(1-m)}]^{-1} \tag{28}$$

In the case $-\infty < m < 1$ the curve $k'_{(1,2)s}(x_2)$ reaches a minimum, whereas for
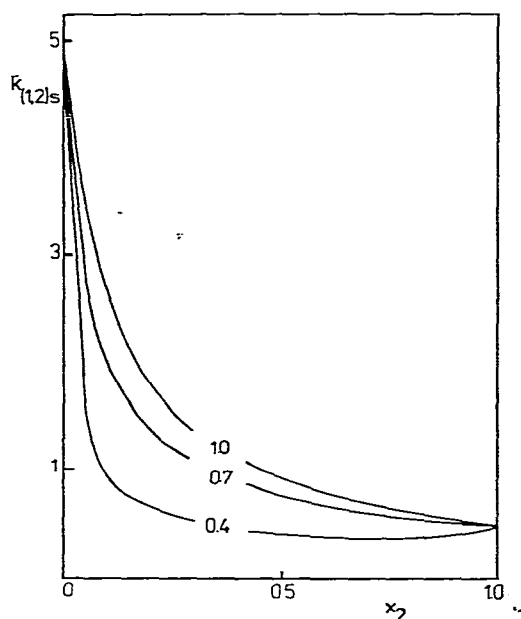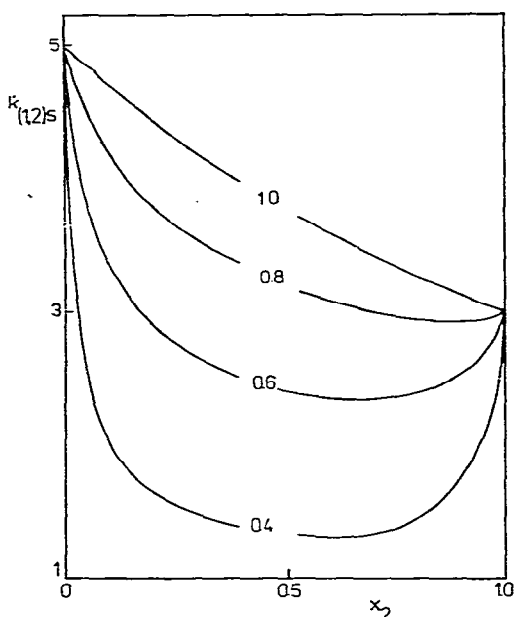

Fig. 1. Functions $k'_{(1,2)s}(x_2)$ calculated according to eqn. 27 for $k'_{(1)s} = 5$ and $k'_{(2)s} = 3$ and for different values of m.

Fig. 2. Functions $k'_{(1,2)s}(x_2)$ calculated according to eqn. 27 for $k'_{(1)s} = 5$ and $k'_{(2)s} = 0.5$ and for different values of m.

$1 < m < \infty$ it reaches a maximum. The values of x_2, calculated according to eqn. 28 for $m = \infty$ and $m = -\infty$, are identical:

$$x_2 = [1 + (k'_{(1)s}/k'_{(2)s})]^{-1} = \hat{s} \tag{29}$$

Using the constant $\hat{s}$, we can define the regions in which the function 27 reaches a point of inflection:

$$\hat{s} \quad < x_2^{min.} < 0.5 \text{ for } -\infty < m < 0$$

$$0.5 < x_2^{min.} < 1 \quad \text{for} \quad 0 < m < 1 \tag{30}$$

$$0 \quad < x_2^{max.} < \hat{s} \quad \text{for} \quad 1 < m < \infty$$

The symbols $x_2^{min.}$ and $x_2^{max.}$ refer to minimum and maximum points, respectively. Thus, for m changing from minus infinity to unity, $x_2^{min.}$ changes from $\hat{s}$ to unity; however, for m changing from plus infinity to unity $x_2^{max.}$ changes from $\hat{s}$ to zero.

The value of $k'_{(1,2)s}$ at the turning point is

$$k'_{(1,2)s} = k'_{(2)s} [1 + (k'_{(2)s}/k'_{(1)s})^{m/(1-m)}]^{-(1-m)/m} \tag{31}$$

Eqn. 31 for $m = \infty$ and $m = -\infty$ may be written in the form

$$k'_{(1,2)s} = k'_{(1)s} + k'_{(2)s} = w \tag{32}$$

Analogous relationships to those for $x_2^{min.}$ and $x_2^{max.}$ (see eqn. 30) can be written for $k'^{min.}_{(1,2)s}$ and $k'^{max.}_{(1,2)s}$:

$$w \quad > k'^{min.}_{(1,2)s} > 0 \text{ for } -\infty < m < 0$$

$$0 \quad < k'^{min.}_{(1,2)s} < k'_{(2)s} \text{ for } 0 < m < 1 \tag{33}$$

$$k'_{(1)s} < k'_{(1,2)s} < w \text{ for } 1 < m < \infty$$

An interesting case is that of $k'_{(1)s} = k'_{(2)s}$. Then, for $m < 1$ the function 27 has a minimum at $x_2 = 0.5$; however, for $m > 1$ this function reaches a maximum at $x_2 = 0.5$. The value of $k'_{(1,2)s}$ at the turning point is

$$k'_{(1,2)s} = k'_{(2)s} \cdot 2^{(m-1)/m} \tag{34}$$

A more thorough explanation of the connection between surface heterogeneity and the extreme of function 27 is given in the Appendix.

Figs. 1 and 2 show the functions 27, calculated only for $0 < m < 1$. This region of m results from theoretical considerations concerning the derivation of eqn. 27. Some authors[9] assume also for m, appearing in eqn. 10, values greater than unity. Since the experimenal data $k'_{(1,2)s}$ *vs.* x_2 often yield minima[10-14], and in some cases show maxima[14], eqn. 27 may be treated as an empirical one, where m is a best-fit

TABLE I

PARAMETERS $k'_{(1)s}$, $k'_{(2)s}$ AND m FOR DIFFERENT SUBSTANCES IN BENZENE(1)–DIISOPROPYL ETHER(2) SOLVENT MIXTURE

Code	Substance	$k'_{(1)s}$	$k'_{(2)s}$	m	S.D.
A	N,N–Diethyl-p-aminoazobenzene	1.04	0.45	0.36	0.10
B	p-Hydroxyazobenzene	5.08	0.46	0.38	0.07
C	p-Aminoazobenzene	7.51	1.26	0.38	0.15
D	2,6-Dinitroaniline	1.02	0.34	0.34	0.03
E	o-Nitroaniline	1.09	0.75	0.44	0.06
F	m-Nitroaniline	5.50	1.34	0.46	0.06
G	p-Nitroaniline	6.34	2.34	0.50	0.09
H	2-Methyl-4-nitroaniline	4.95	3.20	0.50	0.27
J	2,4-Dinitroaniline	9.00	4.26	0.42	0.29

parameter. Therefore, we have discussed the behaviour of function 27 for all values of m. Consequently the course of function 27 explains all experimental dependences $k'_{(1,2)s}$ *vs.* x_2. Evidently, the present theoretical considerations give clear physical meaning to m varying from zero to unity.

Table I presents the parameters $k'_{(1)s}$, $k'_{(2)s}$ and m, appearing in eqn. 27, for different chromatographed substances. The values $k'_{(1)s}$, $k'_{(2)s}$ refer to pure solvents. They were determined experimentally. In Table I the standard deviations S.D. of the experimental points from the theoretical curves 27 are also summarized. Fig. 3 shows the dependence of S.D. on the parameter m for substances D and E in Table I. These dependences show distinct minima. Thus, the expression 27 predicts exactly the best-fit value of m. Figs. 4a–6a demonstrate the good agreement between the theoretical curves 27, calculated for the parameters from Table I, and the experimental points. Figs. 4b–6b show the linear functions, plotted according to eqn. 25.

Eqn. 25 is very convenient for the approximation of experimental data and
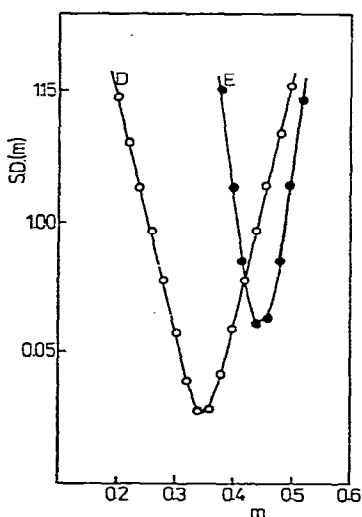

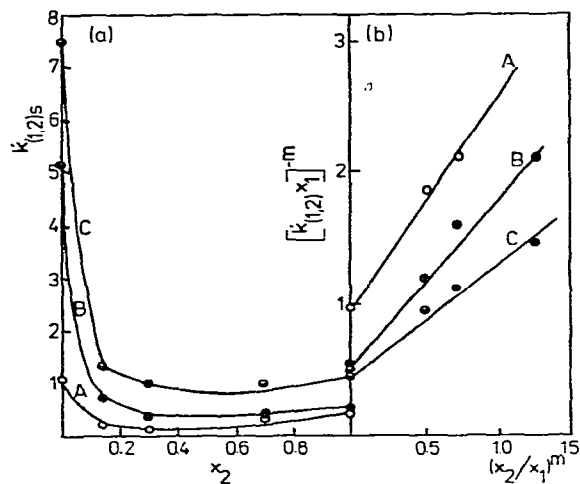Fig. 3. Dependence of S.D. on m for substances D and E in benzene(1)–diisopropyl ether(2) solvent mixture.

Fig. 4. a, Comparison of theoretical curves 27 and experimental points (part a) for substances A, B and C in benzene(1)–diisopropyl ether(2) solvent mixture. b, the linear dependence 25 for these substances.
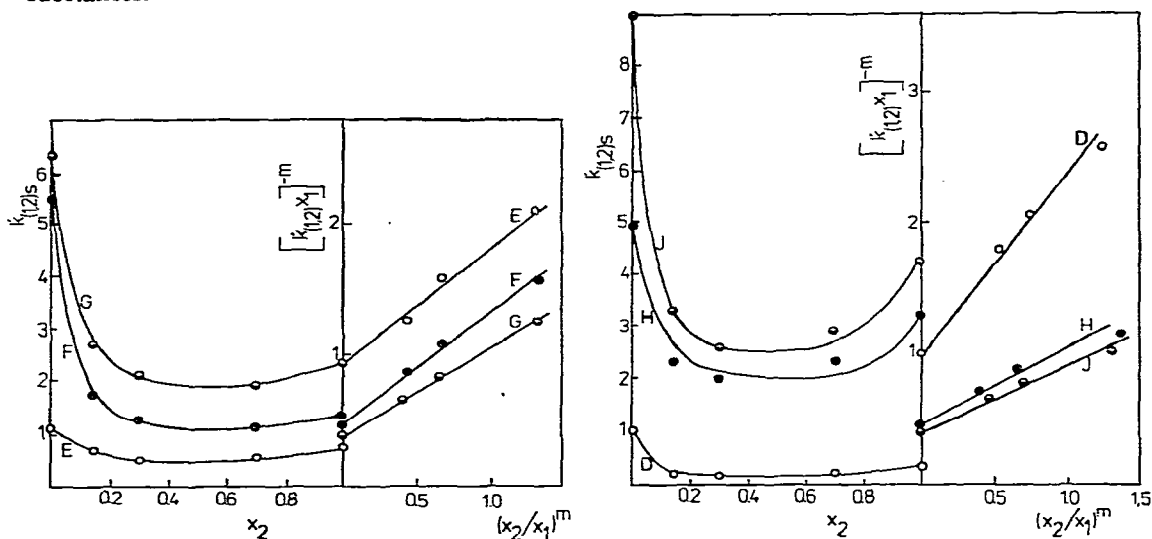

Fig. 5. Comparison of theoretical curves and experimental points for substances E, F and G. Labelled as Fig. 4.

Fig. 6. Comparison of theoretical curves and experimental points for substances D, H and J. Labelled as Fig. 4.

evaluation of the parameters a_1, b_1 and m. The capacity ratios $k'_{(1)s}$ and $k'_{(2)s}$ are related to the constants a_1 and b_1

$$k'_{(1)s} = a_1^{-1/m} \tag{35}$$

and

$$k'_{(2)s} = b_1^{-1/m} \tag{36}$$

All parameters m, summarized in Table I, oscillate around the mean value of m, i.e., $\bar{m} = 0.4$. Thus, m depends somewhat on the kind of chromatographed

substance. A more exact analysis of the parameters m, summarized in Table I, shows that for azobenzene derivatives $\bar{m} = 0.37$, slightly less than $\bar{m} = 0.44$ for aniline derivatives.

The next calculations concern the analysis of experimental data measured in benzene(1)–diisopropyl ether(2)–dichloromethane(3). All chromatographic measurements for the three-component mobile phase were carried out at identical volume percentages of components 2 and 3. Then, the ratio of x_2/x_3 is approximately constant. For $x_2/x_3 = $ constant, eqn. 15 for $n = 3$ may be transformed to the following linear form

$$(k'_{(1,2,3)s} \, x_2)^{-m} = p + q \, (x_1/x_2)^m \tag{37}$$

where

$$q = (k'_{(1)s})^{-m} \text{ and } p = (k'_{(2)s})^{-m} + (k'_{(3)s})^{-m}(x_3/x_2)^m \tag{38}$$

Figs. 7–9 show the linear plots of eqn. 37 for the substances investigated. Table II summarizes the parameters $k'_{(3)s}$, m and S.D. As in the case of the two-component mobile phase, $\bar{m} = 0.59$ for azobenzene derivatives is smaller than $\bar{m} = 0.77$ for aniline derivatives. It follows from a comparison of the values of $\bar{m}$ that addition of dichloromethane to a benzene–diisopropyl ether mixture causes an increase in the values of $\bar{m}$ (see Table III). The higher values of $\bar{m}$ indicate that the heterogeneity of the adsorbent surface is less. Thus, the elution strength of the three-component solvent mixture, after addition of dichloromethane, is greater than that of the two-component mobile phase and the adsorbent heterogeneity of the three-component mixture is less than that measured for the two-component mobile phase.

It can be seen from our discussion that the parameter m is only slightly dependent on the kind of chromatographed substance, and mainly characterizes the adsorbent–mobile phase system.
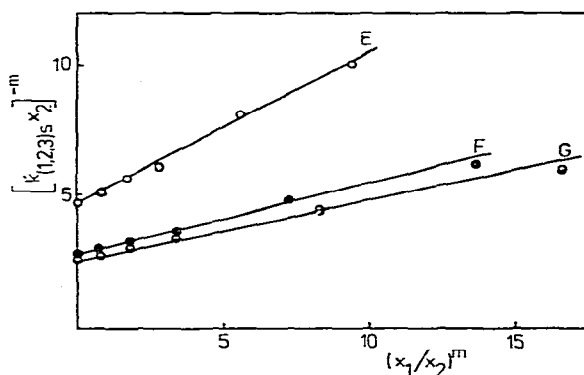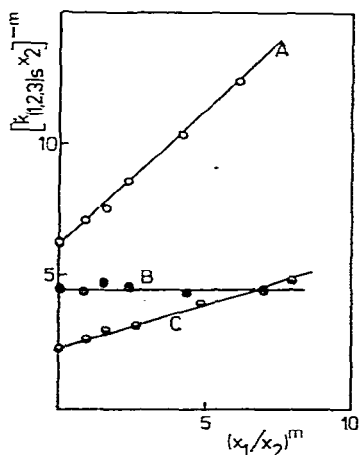

Fig. 7. Linear dependence 37 for substances A, B and C in benzene(1)–diisopropyl ether(2)–dichloromethane(3). ·

Fig. 8. Linear dependence 37 for substances E, F and G in the same solvent mixture as in Fig. 7.
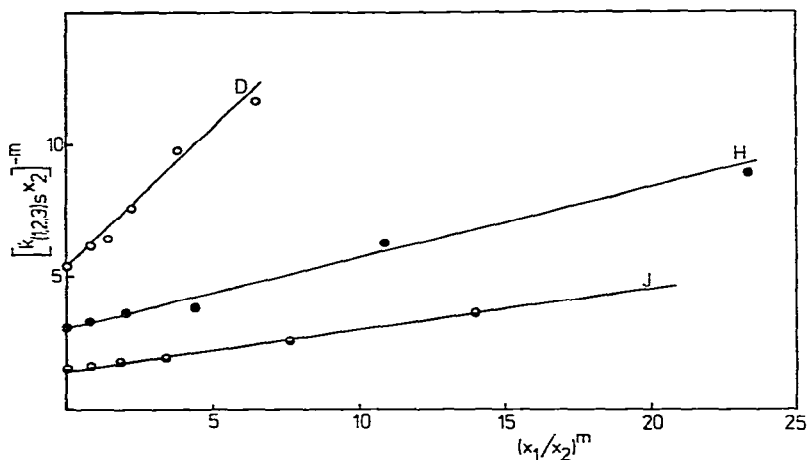
Fig. 9. Linear dependence 37 for compounds D, H and J in the same solvent mixture as in Fig. 7.

TABLE II

PARAMETERS $k'_{(3)s}$ AND m FOR DIFFERENT SUBSTANCES IN BENZENE(1)–DI-ISOPROPYL ETHER(2)–DICHLOROMETHANE(3) SOLVENT MIXTURE

Code	Substance	$k'_{(3)s}$	m	S.D.
A	N,N-Diethyl-p-aminoazobenzene	0.15	0.56	0.006
B	p-Hydroxyazobenzene	2.62	0.58	0.366
C	p-Aminoazobenzene	0.98	0.62	0.065
D	2,6-Dinitroaniline	0.22	0.56	0.013
E	o-Nitroaniline	0.43	0.68	0.034
F	m-Nitroaniline	0.97	0.78	0.084
G	p-Nitroaniline	0.86	0.84	0.116
H	2-Methyl-4-nitroaniline	0.64	0.94	0.169
J	2,4-Dinitroaniline	1.01	0.80	0.144

TABLE III

VALUES OF THE PARAMETER m FOR SYSTEMS INVESTIGATED

Mobile phase	Group of substances	$\bar{m}$
Benzene(1)–diisopropyl ether(2)	azobenzene derivatives	0.37
	aniline derivatives	0.44
	all substances	0.40
Benzene(1)–diisopropyl ether(2)–dichloromethane(3)	azobenzene derivatives	0.59
	aniline derivatives	0.77
	all substances	0.68

APPENDIX

According to the theory of adsorption on heterogeneous solid surfaces the term "surface heterogeneity" refers to the energetic heterogeneity of the adsorbent surface with respect to the given adsorbate[7]. It is characterized by the distribution function of adsorption energy. For example, the difference between the adsorption

energies of the sth compound and ith solvent, ΔE_{si}, characterizes the adsorption sites. This concept of the surface heterogeneity differs from Snyder's[2]. Snyder assumes that ΔE_{si} is a simple product of the adsorbent activity α and the solute–solvent strength parameters $S^0 - A\varepsilon^0$, i.e., $\Delta E_{si} = \alpha(S^0 - A\varepsilon^0)$. The first factor in Snyder's expression is characteristic of the adsorbent surface only. However, the second factor depends on the properties of solute and solvent only. Following Snyder[2], the surface is heterogeneous if the adsorption sites are characterized by different values of α. Thus, the distribution function of α is a measure of the "absolute" surface heterogeneity. However, the distribution function of ΔE_{si} is a measure of the "relative" surface heterogeneity[7]; it also depends on the type of adsorbing molecules.

Now, we consider LC with the binary mobile phase $1 + 2$ on an adsorbent having two types of adsorption site. Let f_1 and f_2 denote fractions of adsorption sites of the first and second types; $f_1 + f_2 = 1$. Then

$$k'_{(1)s} = f_1 k'_{(1)s,1} + f_2 k'_{(1)s,2} \tag{A1}$$

and

$$k'_{(2)s} = f_1 k'_{(2)s,1} + f_2 k'_{(2)s,2} \tag{A2}$$

where $k'_{(1)s}$ and $k'_{(2)s}$ are the capacity ratios for the sth substance on the whole adsorbent surface in pure solvents 1 and 2, respectively. These capacity ratios may be obtained from experimental measurements. The symbol $k'_{(i)s,l}$ denotes the capacity ratio for the sth compound and ith pure solvent on the lth type of adsorption sites. The combined capacity ratio $k'_{(1,2)s}$ may be calculated according to eqn. 8 for $L = 2$ and $n = 2$. The curve $k'_{(1,2)s}$ vs. x_2 should occur between the curves $k'_{(1,2)s,1}$ vs. x_2 and $k'_{(1,2)s,2}$ vs. x_2 (the dashed lines in Fig. 10), which refer to the homogeneous surfaces having adsorption sites of types 1 or 2 only. Evidently, the dashed lines from Fig. 10 are decreasing functions. However, the curve $k'_{(1,2)s}$ vs. x_2, calculated for a heterogeneous surface, may have an extreme (minimum or maximum). The shape of this curve depends on many quantities: f_1, $y_{i,l}$ and $k'_{(i)s,l}$. For x_2 close to zero the capacity ratio $k'_{(1,2)s}$ approaches $k'_{(1)s}$, whereas for x_2 close to unity the capacity ratio $k'_{(1,2)s}$
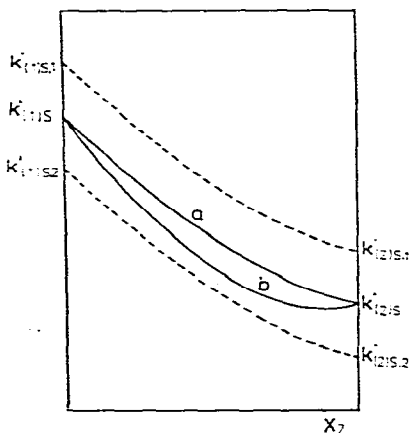

Fig. 10. Schematic diagram illustrating the types of the curve $k'_{(1,2)s}$ vs. x_2 for heterogeneous solid surfaces.

approaches $k'_{(2)s}$. However, the values of $y_{i,l}$ depend strongly on values of $\Delta E_{sl,l}$. For example, at higher concentrations of the more efficient eluting solvent 2, the mole fraction of this solvent in the surface phase, y_2, is considerably greater than y_1. If the adsorption occurs mainly on the second type of adsorption site, the values of $k'_{(1,2)s}$ may be smaller than the value of $k'_{(2)s}$ observed experimentally, but they are always greater than the value $k'_{(2)s,2}$. Such behaviour of $k'_{(1,2)s}$ vs. x_2 is observed for strongly heterogeneous surfaces and for chromatographic systems having similar values of $k'_{(1)s}$ and $k'_{(2)s}$ (see curve b in Fig. 10). However, for many chromatographic systems the function $k_{(1,2)s}$ vs. x_2 is a decreasing one (see curve a in Fig. 10).

LIST OF SYMBOLS

a	initial ordinate of the straight line 5
a_1	initial ordinate of the straight line 25
b	slope of the straight line 5
b_1	slope of the straight line 25
f_l	ratio of the number of adsorption sites of lth type to the total number of adsorption sites
i	ith solvent
j	jth solvent
$k'_{(i)s}$	capacity ratio for sth compound in ith pure solvent
$k'_{(i)s,l}$	capacity ratio $k'_{(i)s}$ for lth type of adsorption site
$k'_{(1,2,\ldots,n)s}$	capacity ratio for sth substance in n-component mobile phase
$k'_{(1,2,\ldots,n)s,l}$	capacity ratio $k'_{(1,2,\ldots,n)s}$ for lth type of adsorption site
L	number of types of adsorption site
l	lth type of adsorption site
m	heterogeneity parameter defined by eqn. 12
m_i	heterogeneity parameter introduced in eqn. 10
n	number of components in the mobile phase
p	initial ordinate of the straight line 37
q	slope of the straight line 37
s	sth chromatographed substance
$\hat{s}$	constant defined by eqn. 29
w	constant defined by eqn. 32
x_i	mole fraction of ith solvent in the mobile phase
y_i	mole fraction of ith solvent in the surface phase
$y_{i,l}$	mole fraction y_i referring to lth type of adsorption site
β	constant defined by eqn. 24

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