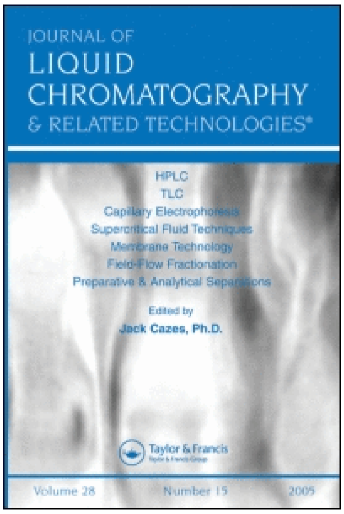

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M. Jaroniec[a]; B. Ościk-Mendyk[a]; A. Dabrowski[a]; H. Kołodziejczyk[a]
[a] Institute of Chemistry, Maria Curie-Skłodowska University, Lublin, Poland

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DEPENDENCE OF THE CAPACITY RATIO UPON TYPE OF THE EXCESS ADSORPTION ISOTHERM

M.Jaroniec, B.Ościk-Mendyk,
A.Dąbrowski and H.Kołodziejczyk
Institute of Chemistry,
Maria Curie-Skłodowska University
20-031 Lublin, Poland

ABSTRACT

Model calculations of the capacity ratio for binary mobile phase "1+2" and the excess adsorption isotherm of 1-st solvent have been made by assuming nonideality of mobile and surface phases and energetic heterogeneity of the adsorbent surface. These calculations make posible the study of correlation between shapes of the folloving functions: the capacity ratio and the excess adsorption isotherm as functions of the mobile phase composition.

INTRODUCTION AND THEORETICAL

According to the theoretical results of Jaroniec and al. (1-2) the capacity ratio of the r-th substance in binary mobile phase "1+2" can be evaluated as follows:

$$k_r = k_{1r}\, y_1^{1/m} + k_{2r}(1-y_1)^{1/m} + A_{12}(y_1 - x_1) \qquad (1)$$

where k_{1r} and k_{2r} are the capacity ratios of the r-th substance in 1-st and 2-nd solvent, respectively;

y_1 and x_1 are the mole fractions of 1-st solvent in the surface and mobile phases; m is the constant characterizing energetic heterogeneity of the adsorbent surface; A_{12} is the parameter describing the solute-solvent interactions. The mole fraction of 1-st solvent in the surface phase y_1 may be calculated according to the following equation(3):

$$y_1 = \left\{ 1 + \left[K_{12} x_1 / (1 - x_1) \right]^{-m} \exp \left[m q^{l} (M - 1)(1 - 2x_1) + m L q^{s} (1 - 2y_1) \right] \right\}^{-1} \qquad (2)$$

where the parameters L, M, q^l and q^s have their usual meaning, i.e., q^l and q^s are the parameters characterizing the interactions in the bulk and surface phases, respectively; L and M are the parameters describing the lattice model of solution; K_{12} is the equilibrium constant for exchange reaction between molecules of 1-st and 2-nd solvents in both phases.

However, the excess adsorption isotherm of 1-st solvent $n^e_{1,t}$ is equal to:

$$n^e_{1,t} = n^s \, (y_1 - x_1) \qquad (3)$$

where n^s is the total number of moles in the surface phase.

Basing on equations 1,2 and 3, the following factors determining the liquid adsorption chromatography, can be studied:

(a) energetic heterogeneity of solid surface of random distribution of adsorption sites - the parameter m ,

(b) nonideality of the surface phase - the parameter q^s,

(c) nonideality of the bulk phase - the parameter q^l

(d) lattice model of the solution - the parameters L and M ,

(e) solute - solvent interactions - the parameter A_{12}.

Parameters q^s and q^l characterize the surface and bulk regular solution, respectively.

Now, we shall discuss the correlation between the excess adsorption isotherm of 1-st solvent equations 3 and 2 and the capacity ratio of the r-th solute in the binary mobile phase "1+2" equations 1 and 2 . This discussion gives answer on the following question: in such degree type of the excess adsorption isotherm determines shape of the curve k_r vs.x_1.

RESULTS AND DISCUSSION

Studies of Dąbrowski and al.(3) and Roe (4) showed that influence of lattice model of solution on the shape of the theoretical adsorption isotherms is small. Thus, a change of the parameters L and M i.e., change of the lattice model of solution, changes slightly the values of k_r. In Figures 1 - 3 the comparative model calculations of the excess adsorption isotherms $n^e_{1,t}(x_1)$ (equations 2 and 3) and capacity ratios $k_r(x_1)$ (equations 1 and 2) with A_{12} = 0 are presented. All model calculations have been made for the close-packed hexagonal lattice, i.e., L = 0.5 and M = 0.25. For k_{1r} and k_{2r} the values 1.0 and 3.0 were assumed, respectively. The other parameters, characterizing the curves k_r vs. x_1 presented in Figures 1-3 have been summarized in Table 1. The excess adsorption isotherms $n^e_{1,t}(x_1)$ have been evaluated according to equations 3 and 2, whereas, the capacity ratios $k_r(x_1)$ were calculated according to equations 1 and 2 . For n^s the value 1.0 was assumed.

Table 1

PARAMETERS m, q^l AND q^s USED IN CALCULATIONS OF THE FUNCTIONS $n^e_{1,t}(x_1)$ AND $k_r(x_1)$ PRESENTED IN FIGURES 1-3

The other parameters are equal to: K_{12}= 2.718 , k_{1r} =1.0 , k_{2r}=3.0 , L= 0.5, M=0.25, A_{12}=0, n^s=1.0

Figure	Code of the curve	m	q^l	q^s
1A, 1B	a	0.3	0	0
	b	0.6	0	0
	c	0.9	0	0
2A, 2B	a	0.9	-1	0
	b	0.9	0	0
	c	0.9	1	0
2C, 2D	a	0.9	-1	0
	b	0.9	-1	-1
3C, 3D	a	0.9	1	0
	b	0.9	1	1
3A, 3B	a	0.6	-1	-1
	b	0.6	0	0
	c	0.6	1	1

Now, we will describe succesively Figures 1-3. In Figure 1 the dependence of k_r and $n^e_{1,t}$ upon the heterogeneity parameter m is showed. It follows from this figure that for homogeneous surfaces, i.e., m = 1, the excess adsorption isotherm $n^e_{1,t}(x_1)$ is the U-shape isotherm according to Schay and Nagy clasification(5). However, for heterogeneous surfaces. i.e., for m belonging to the interval $(0,1)$, the S-shape excess adsorption isotherm may be obtained. The relationship k_r vs.x_1, corresponding to the U-shape excess adsorption isotherms are a decreasing functions. In the case of the S-shape adsorption isotherms, they show a minimum (see Figure 1).

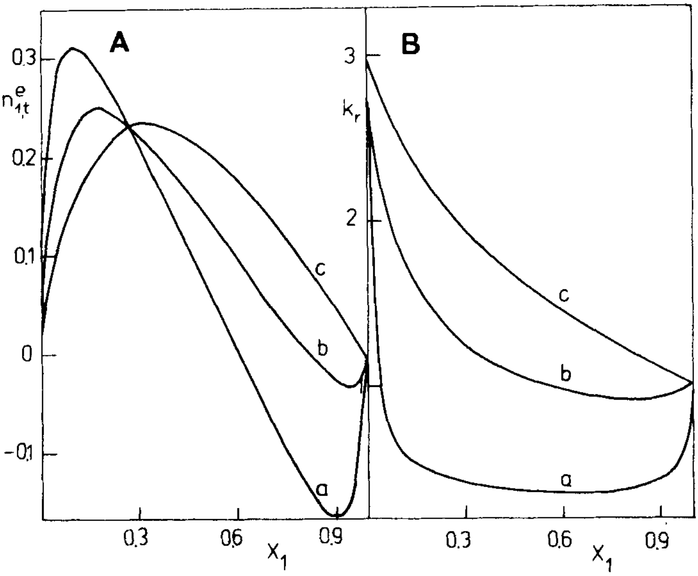

Figure 1
The functions $n^e_{1,t}(x_1)$ (part A) and $k_r(x_1)$ (part B) for different values of m . Parameters used in calculations are summarized in Table 1.

Thus, energetic heterogeneity of the adsorbent surface may be one of the reasons of minimum on the curves k_r vs.x_1.

Figures 2A and 2B shows the influence of the parameter q^l, characterizing the regular mobile phase, on the excess adsorption isotherm and the relationship k_r vs.x_1. It follows from these Figures that for different values of q^l the curves $n^e_{1,t}(x_1)$ and $k_r(x_1)$ intersect at the same value of x_1. For negative values of q^l the U-shape excess adsorption isotherms are observed, wereas, the positive values of q^l can give the S-shape isotherms. For values of q^l belonging to the interval $(-1,1)$ the curves $k_r(x_1)$ are a decreasing functions. For low concentrations of x_1 $k_r(q^l<0)>k_r(q^l = 0)$, whereas, after the inflection point high values of x_1 this inequality is reversed. In the case of $q^l>0$, $k_r<k_r(q^l = 0)$ at low concentrations of x_1 and $k_r>k_r(q^l = 0)$ after the inflection point.

Figures 2C, 2D, 3C, 3D show the influence of the parameter q^s on the curves $k_r(x_1)$. The calculations were made for two cases: (a) the parameters q^l and q^s are identical, (b) the parameter $|q^l|$ is grater than $|q^s|$. Such model is usually used in adsorption from solutions. The curves $k_r(x_1)$, presented in Figures 2C, 2D, 3C, 3D have similar shape as those showed in Figures 2A and 2B.

Figures 3A and 3B show the model calculations for heterogeneous solid surface m=0.6 and regular both phase $q^l = q^s = (-1,0.1)$. It follows from these figures that effects of energetic heterogeneity of adsorbent surface are more significant that those connected with regularity of both phases (6,7).

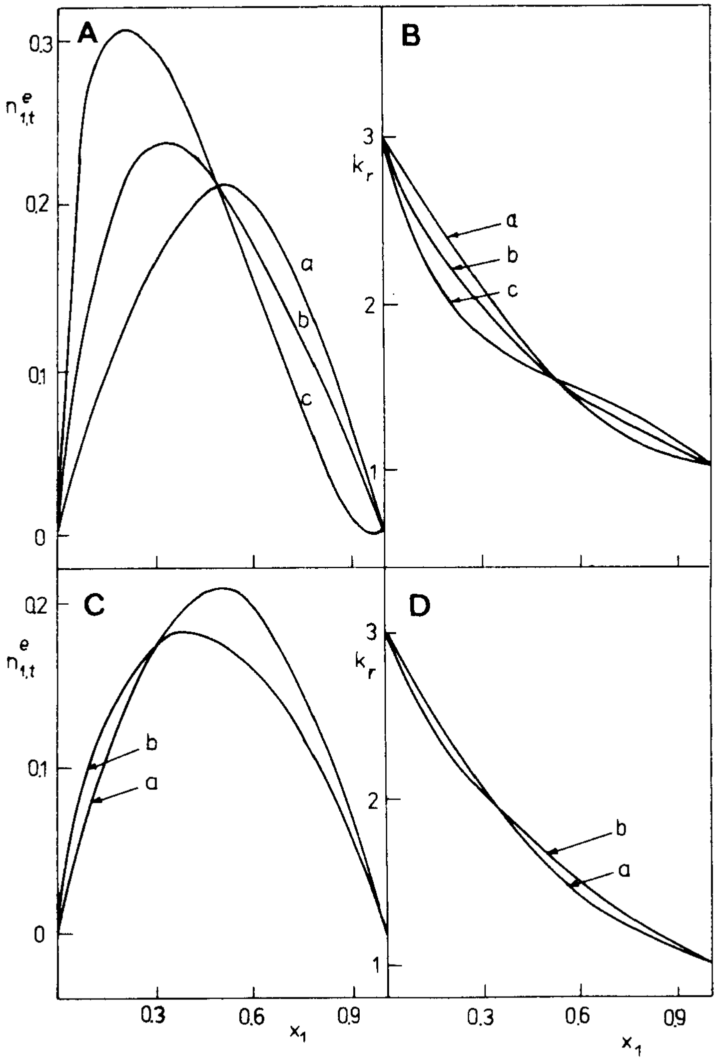

Figure 2

The functions $n^e_{1,t}(x_1)$ (parts A, C) and $k_r(x_1)$ (parts B, D). The parameters are summarized in Table 1.

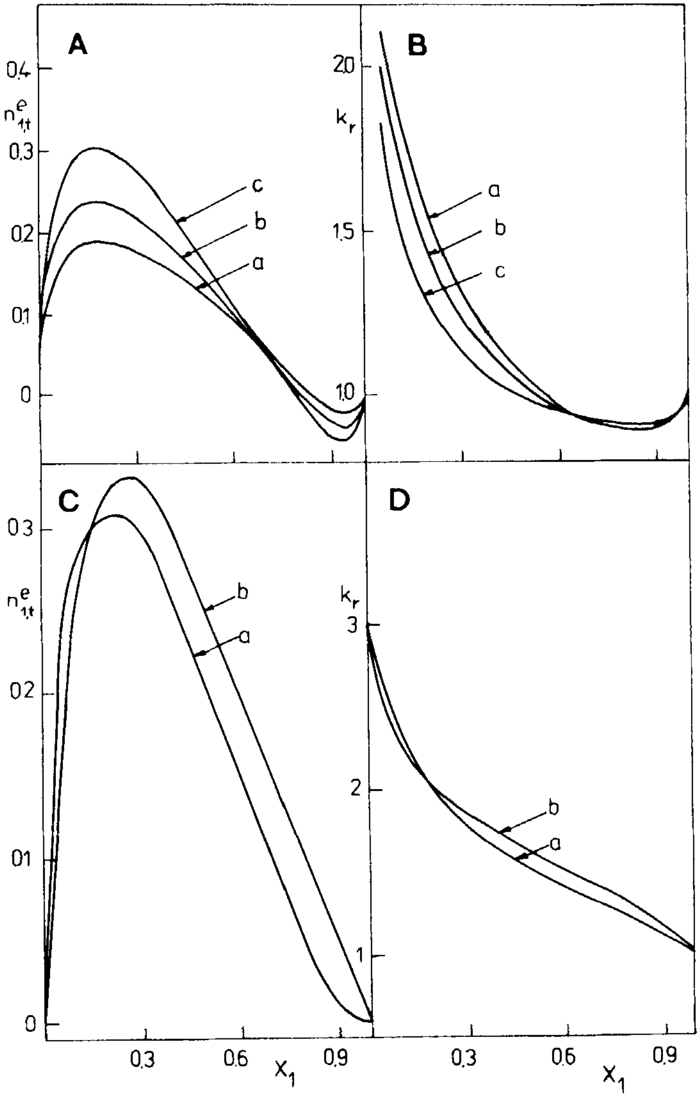

Figure 3

The function $n^{e}_{1,t}(x_1)$ (parts A, C) and $k_r(x_1)$ (parts B, D). The parameters are summarized in Table 1.

The conclusions resulting from presented model calculations are following:

(a) a correlation exists between the excess adsorption isotherm of 1-st solvent and the function $k_r(x_1)$: U-shape isotherms correspond to a decreasing k_r - functions without inflection point, whereas, S-shape isotherms relate to k_r- functions with inflectionpoint.

(b) k_r- curves with inflection point are most frequently obtained for strongly heterogeneous surfaces and regular solutions of positive deviations from Raoult's law.

(c) k_r- curves without inflection point are obtained for homogeneous adsorbent and regular solutions of negative deviations from Raoult's law.

The knowledge of excess adsorption isotherm, characterizing the system: mobile phase-adsorbent, is very important in liquid adsorption chromatography. The experimental values of $n^e_{1,t}$ may be directly used to determine the parameters m and A_{12}, according to the following equation :

$$k_r = k_{1r}\left(n^e_{1,t}/n^s + x_1\right)^{1/m} + k_{2r}\left(1 - n^e_{1,t}/n^s - x_1\right)^{1/m} + A_{12}/n^s \; n^e_{1,t} \qquad (4)$$

which is obtained from equations 1 and 3 . Application of equation 4 creates a new possibilities for characterization of chromatographic systems. Such investigations have been intiated in the paper (8) .

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