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Adsorption of 1-Tetradecene/Dodecane Mixtures on Different Types of Zeolites

M. Jaroniec[a, *], **A. W. Marczewski**[a], **W. D. Einicke**[b], **H. Herden**[b], and **R. Schöllner**[b]

[a] Institute of Chemistry, M. Curie-Skłodowska University,
PL-20031 Lublin, Poland

[b] Department of Chemistry, Karl-Marx-University,
DDR-7010 Leipzig, German Democratic Republic

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The influence of heterogeneity parameters on the shape of excess adsorption isotherms has been discussed. These isotherms have been calculated according to the equations corresponding to different energy distributions. Next, the isotherm equations have been applied to examine the experimental excess isotherms for 1-tetradecene/dodecane mixture adsorption on different types of X-zeolites at 293 K, 313 K and 333 K. The zeolite samples have been prepared from NaX-zeolite by exchanging the sodium ions for ions of alkalines and calcium group. Analysis of the above adsorption data by means of different isotherm equations showed that the parameters of a *Dubinin-Radushkevich*-type equation change correctly with temperature and the contents of alkalines in the zeolite samples.

(Keywords: Adsorption from solutions on zeolites; Adsorption of 1-tetradecene/dodecane; Adsorption on heterogeneous solids; Dubinin-Radushkevich equation for liquid adsorption)

Die Adsorption von 1-Tetradecen/Dodecan-Gemischen an verschiedenen X-Zeolithen

Es wird der Einfluß der Heterogenitätsparameter auf die Form der Excessadsorptionsisothermen diskutiert. Diese Isothermen werden nach Gleichungen berechnet, die unterschiedlichen Energieverteilungen entsprechen. Die Isothermengleichungen werden auf experimentelle Excessisothermen für die Adsorption von 1-Tetradecen/Dodecan-Gemischen an verschiedenen X-Zeolithen bei 293 K, 313 K und 333 K angewendet. Die Zeolithe wurden durch Ionenaustausch der Natriumionen gegen Ionen der Alkali- und Erdalkaligruppe hergestellt. Die Analyse der Daten mit Hilfe der unterschiedlichen Isothermengleichungen zeigt, daß sich die Parameter einer *Dubinin-Radushkevich*-Gleichung korrekt mit der Temperatur und dem Gehalt an Alkalikationen in den Zeolithen ändern.

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Introduction

Deviations from ideal behaviour of the liquid/solid adsorption systems are frequently interpreted by non-ideality of the bulk and surface phases[1–4] and energetic heterogeneity of the adsorbent surface[5–11]. The problem of the energetic heterogeneity in liquid adsorption was intensively studied in the recent seven years. During that time several new isotherm equations for liquid adsorption on heterogeneous surfaces have been derived[5–11] and applied for describing the excess adsorption data[12–15]. These studies showed that in many cases the isotherm equations, involving energetic heterogeneity, satisfactorily explain deviations of the liquid/solid adsorption systems from ideal behaviour. Although many papers have been devoted to the theory of liquid adsorption on heterogeneous solids, only a few of them show the influence of heterogeneity parameters on the shape of the excess adsorption isotherms[7]. Many isotherm equations were not analysed graphically.

In this paper we shall present the dependence of shape of the excess adsorption isotherms upon values of the heterogeneity parameter. It will be done for different isotherm equations. These model studies are very helpful in interpretation of the excess adsorption data by means of the isotherm equations. The main purpose of this paper is to interpret the excess isotherms for adsorption of 1-tetradecene/dodecane mixtures on different types of zeolites at 293 K, 313 K and 333 K by means of isotherms equations involving the adsorbent heterogeneity.

Theory

One of the fundamental equations in the theory of adsorption from binary liquid mixtures on energetically homogeneous solids is the relationship[1]:

$$x^s_{1,l} = \frac{K_{12}\, x^l_1/x^l_2}{1 + K_{12}\, x^l_1/x^l_2} \tag{1}$$

where x^s_i and x^l_i are the mole fractions of the i-th component in the surface and bulk phases, respectively, and K_{12} is the equilibrium constant describing the phase exchange of molecules. The subscript "l" at $x^s_{1,l}$ refers to a homogeneous surface. Eq. (1) has been derived by assuming ideality of both the phases and equality of molecular sizes of components. Many authors[7,10,11] generalized Eq. (1) to the case of adsorption on heterogeneous surfaces. Extension of Eq. (1) for exponential decreasing energy distribution function gives[11]:

$$x_1^s = \left[\frac{K_{12}\, x_1^l/x_2^l}{1 + K_{12}\, x_1^l/x_2^l}\right]^m \tag{2}$$

where m is the heterogeneity parameter varying from zero to unity. Eq. (2) for $m = 1$ (homogeneous surface) becomes the adsorption isotherm given by Eq. (1). The excess adsorption isotherm may be calculated by means of the following relationship[1–3]:

$$n_1^e = n^s (x_1^s - x_1^l) \tag{3}$$

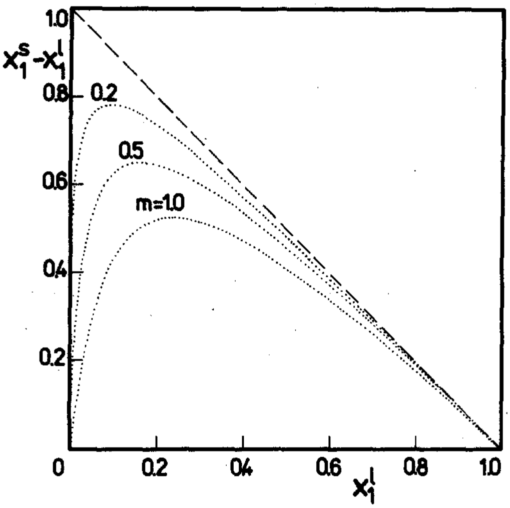

Fig. 1. Excess adsorption isotherms calculated according to Eqs. (2) and (3) for $K_{12} = 10$ and different values of m

where n^s is the total number of moles in the surface phase. Fig. 1 presents the adsorption excess $(x_1^s - x_1^l)$ vs. x_1^l corresponding to Eq. (2) for $m = 0.2$, 0.5 and 1.0. It follows from this figure that an increase in the adsorption excess is caused by a decrease of the heterogeneity parameter. The excess adsorption isotherms produced by Eqs. (2) and (3) show type II according to the *Schay* and *Nagy* classification[16].

One of the most popular equations, which for $m = 1$ reduces to Eq. (1), is so-called *Langmuir-Freundlich* (*LF*) isotherm:

$$x_1^s = \frac{(K_{12}\, x_1^l/x_2^l)^m}{1 + (K_{12}\, x_1^l/x_2^l)^m} \tag{4}$$

Eq. (4) has been discussed theoretically by *Jaroniec*[8] and *Dąbrowski* et al.[7]. Moreover, this equation associated with Eq. (3) has been used for determining the surface phase capacity[15] and for interpreting the experimental adsorption data[12,17].

It has been shown in the paper[7] that Eq. (4) corresponds to the symmetrical quasi-*Gauss*ian energy distribution. Fig. 2 shows the excess adsorption isotherms relating to Eq. (4) for different values of the heterogeneity parameter m. The isotherm curves change from type II ($m = 1$), through type III to type IV (m close to zero) in the *Nagy* and *Schay* classification[16]. Moreover, these curves intersect at the point $x_1^l = 1/(1 + K_{12})$. The behaviour of the excess adsorption isotherms before the intersection point is analogous as in Fig. 1, i.e., an increase in the adsorption excess is caused by a decrease in the heterogeneity parameter. However, after intersection point the position of the excess adsorption isotherms is inverse.

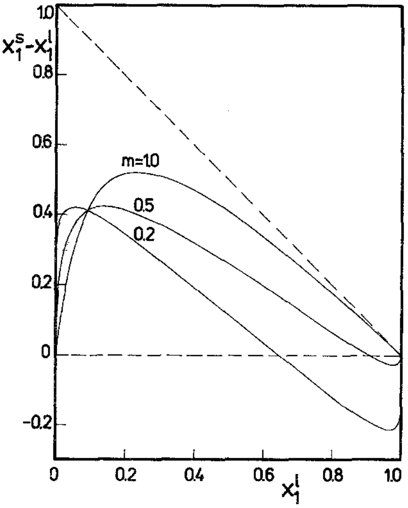

Fig. 2. Excess adsorption isotherms calculated according to Eqs. (3) and (4) for $K_{12} = 10$ and different values of m

An analogous behaviour of the excess adsorption isotherms to that presented in Fig. 2 in the region from the intersection point to $x_1^l = 1$ gives the *Tóth*-type equation:

$$x_1^s = \frac{K_{12}\, x_1^l/x_2^l}{[1 + (K_{12}\, x_1^l/x_2^l)^m]^{1/m}} \tag{5}$$

Eq. (5) has been introduced by *Patrykiejew* et al.[18] and it is analogous to the gas adsorption isotherm proposed by *Tóth*[19]. Fig. 3 presents the excess adsorption isotherms calculated according to Eqs. (5) and (3) for $K_{12} = 10$ and different values of m. The isotherms change from type II ($m = 1$), through types III and IV to type II with contrary sign of the adsorption excess (m close to zero). An increase in the adsorption excess is caused by an increase of the heterogeneity parameter. Such a behaviour of the excess adsorption isotherms is caused by the special shape of the energy distribution corresponding to Eq. (5), which is asymmetrical quasi-*Gauss*ian function with a widened left-hand side[20]. The functions of energy distribution corresponding to Eqs. (2) and (5) are extended in the opposite directions. Therefore, the behaviour of the

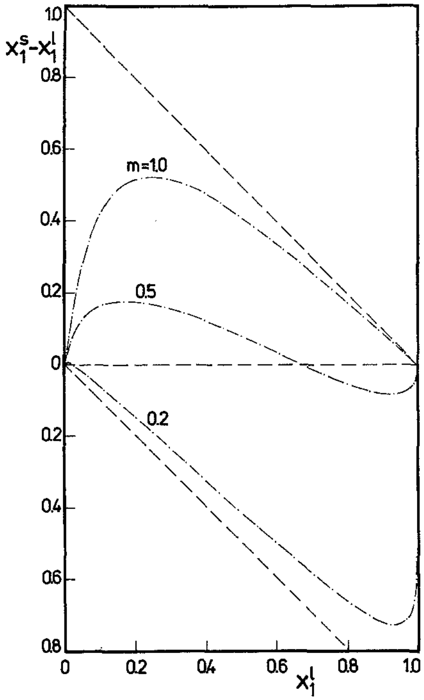

Fig. 3. Excess adsorption isotherms calculated according to Eqs. (3) and (5) for $K_{12} = 10$ and different values of m

excess adsorption isotherms presented in Figs. 1 and 3 for $m = 0.2$, 0.5 and 1.0 is different. The dependence of the excess adsorption isotherms upon the heterogeneity parameter m is clearly presented in Fig. 4, which shows the excess adsorption isotherms for $K_{12} = 1$ and different values of m. The excess adsorption isotherms calculated according to

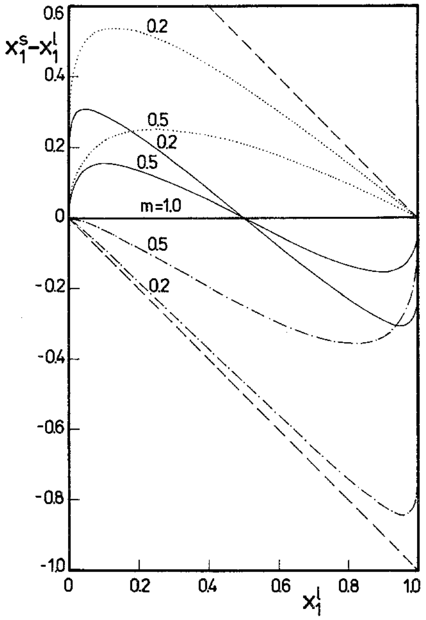

Fig. 4. Excess adsorption isotherms calculated according to Eqs. (2) and (3) (dotted lines), Eqs. (3) and (4) (solid lines) and Eqs. (3) and (5) (dotted-dashed lines) for $K_{12} = 1$ and different values of m

Eqs. (2), (4), (5) and (3) for $m = 1$ become Eq. (1), which for $K_{12} = 1$ predicts a zero value for the adsorption excess in the whole concentration region. It is known that for homogeneous solid surfaces and $K_{12} = 1$ Eq. (1) predicts a zero value for $(x_1^s - x_1^l)$. However, for energetically heterogeneous surfaces (m varies from unity to zero) the adsorption excess is different from zero even for $K_{12} = 1$. For exponential decreasing distribution the excess adsorption isotherms of type II are obtained [the dotted lines calculated according to Eqs. (2) and (3)]. The same type of the adsorption isotherms is obtained for Eq. (5) but they are negative (the dotted-dashed lines). However, the excess isotherms corresponding to Eq. (4) intersect the axis x_1^l at the point 0.5

(the solid lines). Thus, the type of the energy distribution function influences strongly the behaviour of the excess adsorption isotherms.

Now, we will consider the *Dubinin-Radushkevich* (*DR*)-type equation[10,13,14]:

$$x_1^s = \exp\left[-B_0\left(RT\ln\frac{x_{12}^l}{x_{12}^0}\right)^2\right] \text{ for } x_{12}^l \leq x_{12}^0 \tag{6}$$

where

$$x_{12}^l = x_1^l/x_2^l \tag{7}$$

The parameter x_{12}^0 is analogous to the constant K_{12}, however, B_0 is the heterogeneity parameter analogous to m. Eq. (6) corresponds to the asymmetrical quasi-*Gauss*ian energy distribution with widened right-hand side. This function becomes sharper and sharper when the parameter B_0 increases. It means that the width of this function is greater and greater (strong surface heterogeneity) when B_0 decreases.

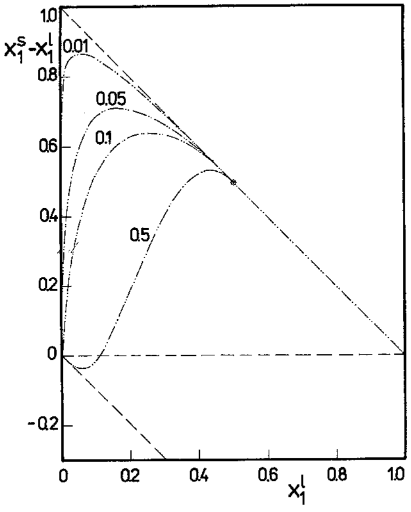

Fig. 5. Excess adsorption isotherms calculated according to Eqs. (3) and (6) for $x_{12}^0 = 1$ and different values of $A = B_0\,(RT)^2$

From the equations considered above Eq. (2) shows most similar behaviour to Eq. (6) (cf. Fig. 5). Similarily as in Fig. 1, for strongly heterogeneous surfaces (smallest values of B_0) the excess isotherms are highest. It means that for energy distribution functions widened left-hand side an increase in the adsorption excess is caused by an increase in energetic heterogeneity of the adsorbent surface, i.e., decrease in values of the heterogeneity parameters m and B_0. However, for energy distribution widened right-hand side a opposite behaviour is observed.

The above discussed adsorption isotherms will be applied to interpret the adsorption data of 1-tetradecene/dodecane mixtures on different types of zeolites.

Experimental

The used zeolite samples were prepared from NaX-zeolite (VEB Chemiekombinat Bitterfeld, Wolfen, DDR) by using the ion exchange in aqueous solution. The degree of ion exchange was determined by analysis of the exchange solution and of the solids by means of the standard chemical methods. The formula $Na_{0.35}Rb_{0.65}X$ denotes a zeolite sample in which 65% of the sodium ions were exchanged by rubidium ions. For all zeolites the silicon/aluminium ratio was equal to 1.4.

The zeolite samples were activated for 20 h at 673 K and a pressure less than 10 m Pa in a special tube (diameter 25 mm, height 10 mm) under so-called "deep bed" conditions. 3 ml of a 1-tetradecene/dodecane mixture of well known composition were added to about 1 g activated zeolite. The system was stirred at 293 K, 313 K, and 333 K and after two days the equilibrium was reached. The composition of the bulk phase was analysed by means of gas chromatography and refractometry. The second method is only applicable if no chemical reactions (i.e. isomerization) occures. In the case of zeolites containing Na, K, Rb, Cs, and Ba we could show that these conditions are accomplished. For zeolites containing Li, Ca and Sr the adsorption data are related to the sum of the olefins.

The surface excess was calculated according to:

$$n_1^e = \frac{n^0}{m}(x_1^0 - x_1^l) \tag{8}$$

where n^0 is the total number of moles in the original solution brought into contact with m grams of adsorbent, x_1^0 and x_1^l are the mole fractions of component 1 (olefin) in the bulk phase before and after contact with the solid, respectively. The hydrocarbons were obtained from Fluka AG, Buchs Switzerland (purum quality) and were dryed with a 3 Å molecular sieve very carefully before used.

Results and Discussion

The excess adsorption isotherms of 1-tetradecene/dodecane mixtures on sixteen different samples of zeolites at temperatures 293 K, 313 K and 333 K were described by means of Eq. (3), in which the mole fraction x_1^s was replaced successively by Eqs. (1), (2), (4), (5) and (6). In the case of Eqs. (1) and (3) two parameters—n^s and K_{12}—were evaluated by using a best-fit procedure. However, in the case of other equations, except the parameters n^s and K_{12}, the heterogeneity parameter was also evaluated. Of course all isotherm equations involving energetic heterogeneity of the adsorbent surface gave the smaller standard deviations of the experimental data from the theoretical excess adsorption isotherm in comparison to that evaluated for Eqs. (1) and (3) (homogeneity of the adsorbent surface).

However, the *DR*-Eq. (6) and *LF*-Eq. (4) better fit the experimental isotherms studied than Eqs. (2) and (5). The *DR* and *LF* equations correspond to quasi-*Gauss*ian energy distributions[11] but the energy distribution relating to the *DR* equation is asymmetrical with a widened right-hand side[13,14]. In the case of the *DR*-type equation, the adsorption parameters show correct dependence upon the temperature. However, for several systems the dependence of adsorption parameters obtained by means of the *LF* Eq. (4) upon temperature is not correct. Therefore, the *DR*-type equation was selected to describe the adsorption systems studied. This equation gives the smallest standard deviations between theoretical and experimental values of the adsorption excess in comparison with the other equations and it produces the adsorption parameters showing correct dependence upon temperature.

In Table 1 the parameters n^s, B_0 and $\ln x_{12}^0$ calculated from the excess adsorption isotherms by means of Eqs. (3) and (6) are summarized. For the purpose to comparing, we have evaluated the parameters n^s and $\ln K_{12}$ by means of Eqs. (1) and (3). All adsorption parameters were calculated from the excess adsorption isotherms at 293 K, 313 K and 333 K. Moreover, Table 1 contains the standard deviations (SD) and the determination coefficients (DC) for the *DR*-type equation. These quantities were calculated according to the following relationships:

$$\mathrm{SD} = \left\{ \sum_{i=1}^{k} [n_{1,i}^e(\exp) - n_{1,i}^e(\mathrm{calc})]^2/(k-1) \right\}^{1/2} \tag{9}$$

$$\mathrm{DC} = 1 - \frac{\sum_{i=1}^{k} [n_{1,i}^e(\exp) - n_{1,i}^e(\mathrm{calc})]^2}{\sum_{i=1}^{k} \left[n_{1,i}^e(\exp) - \frac{1}{k} \sum_{i=1}^{k} n_{1,i}^e(\exp) \right]^2} \tag{10}$$

where $n_{1,i}^e$ (exp) and $n_{1,i}^e$ (calc) are the experimental and theoretical values of the adsorption excess in the i-th experimental point and k is the total number of experimental points. The theoretical values of the adsorption excess were calculated according to Eqs. (3) and (6) by means of the best fit parameters summarized in Table 1.

Table 1. *Adsorption parameters for 1-tetradecene(1)/dodecane(2) mixtures on different types of zeolites*

Zeolite	Code	T [K]	Eqs. (1) and (3) n^s [mmol/g]	Eqs. (1) and (3) $\ln K_{12}$	Eqs. (3) and (6) n^s [mmol/g]	Eqs. (3) and (6) $B_0 \cdot 10^9$ [(mol/J)^2]	$\ln x_{12}^0$	DC	SD
$Na_{0.17}Li_{0.83}X$	a	293	1.09	4.51	1.62	1.99	3.91	0.998	0.011
		313	0.92	4.33	1.69	2.51	3.88	0.990	0.021
		333	0.76	4.13	1.49	2.60	3.79	0.989	0.018
			0.92	4.32	1.60	2.37	3.86		
NaX	b	293	1.05	4.62	1.76	2.36	4.01	0.990	0.024
		313	0.89	4.43	1.59	2.44	3.89	0.990	0.020
		333	0.73	4.19	1.45	2.55	3.81	0.988	0.018
			0.89	4.41	1.60	2.45	3.90		
$Na_{0.83}K_{0.17}X$	c	293	1.04	4.61	1.89	2.67	3.96	0.987	0.028
		313	0.89	4.43	1.62	2.49	3.90	0.988	0.023
		333	0.73	4.19	1.46	2.64	3.79	0.986	0.019
			0.89	4.41	1.66	2.60	3.88		
$Na_{0.74}K_{0.26}X$	d	293	0.90	4.51	1.55	2.69	3.78	0.994	0.016
		313	0.80	4.32	1.49	2.61	3.88	0.986	0.022
		333	0.70	4.09	1.43	2.75	3.77	0.987	0.018
			0.80	4.31	1.49	2.68^1	3.81		
$Na_{0.41}K_{0.59}X$	e	293	0.73	4.41	1.31	2.83	3.86	0.993	0.014
		313	0.65	4.23	1.25	2.79	3.82	0.990	0.015
		333	0.58	4.03	1.25	2.93	3.72	0.988	0.014
			0.65	4.22	1.27	2.85	3.80		
$Na_{0.35}Rb_{0.65}X$	f	293	0.67	4.28	1.26	3.06	3.85	0.992	0.014
		313	0.61	4.13	1.21	3.00	3.76	0.990	0.013
		333	0.55	3.95	1.15	2.93	3.72	0.988	0.013
			0.61	4.12	1.21	3.00	3.78		
$Na_{0.50}Cs_{0.50}X$	g	293	0.63	4.17	1.23	3.33	3.77	0.985	0.018
		313	0.57	4.04	1.15	3.11	3.77	0.989	0.014
		333	0.51	3.89	1.15	3.22	3.67	0.985	0.014
			0.57	[illegible]	[illegible]	[illegible]	[illegible]		

K X	h	293	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		
		313	0.65	4.23	1.22	2.69	3.84	0.992	0.014
		333	0.58	4.03	1.26	2.93	3.73	0.984	0.017
			0.65	4.22	1.26	2.80	3.81		
K Y	i	293	0.73	4.39	1.29	2.74	3.89	0.994	0.013
		313	0.65	4.23	1.28	2.87	3.83	0.987	0.017
		333	0.58	4.03	1.24	2.89	3.73	0.987	0.015
			0.65	4.22	1.27	2.83	3.82		
$Na_{0.80}Ca_{0.20}X$	j	293	1.03	4.91	1.87	2.45	4.13	0.979	0.038
		313	0.95	4.70	1.80	2.41	4.03	0.979	0.034
		333	0.87	4.44	1.83	2.57	3.91	0.980	0.030
			0.95	4.68	1.83	2.48	4.02		
$Na_{0.41}Ca_{0.59}X$	k	293	1.05	6.13	1.38	0.98	4.55	0.994	0.023
		313	0.97	5.91	1.33	0.99	4.55	0.991	0.025
		333	0.89	5.66	1.32	1.12	4.44	0.988	0.026
			0.97	5.90	1.34	1.03	4.51		
$Na_{0.80}Ba_{0.20}X$	l	293	0.89	5.50	1.34	1.56	4.35	0.987	0.026
		313	0.81	5.23	1.33	1.68	4.29	0.985	0.026
		333	0.73	4.83	1.37	2.01	4.11	0.977	0.028
			0.81	5.19	1.35	1.75	4.25		
$Na_{0.41}Ba_{0.59}X$	m	293	0.86	5.80	1.27	1.35	4.50	0.985	0.028
		313	0.79	5.55	1.18	1.32	4.41	0.987	0.023
		333	0.72	5.23	1.18	1.50	4.28	0.982	0.025
			0.79	5.53	1.21	1.39	4.40		
CaX	n	293	1.00	6.15	1.25	0.81	4.58	0.994	0.016
		313	0.91	5.92	1.24	0.94	4.61	0.986	0.022
		333	0.83	5.66	1.20	1.05	4.42	0.987	0.018
			0.91	5.91	1.23	0.93	4.54		
SrX	o	293	0.93	5.95	1.22	0.98	4.52	0.995	0.018
		313	0.85	5.75	1.19	1.08	4.49	0.991	0.021
		333	0.77	5.46	1.19	1.26	4.36	0.986	0.024
			0.85	5.72	1.20	1.11	4.46		
BaX	p	293	0.83	5.81	1.11	1.16	4.40	0.986	0.025
		313	0.77	5.59	1.12	1.26	4.38	0.988	0.022
		333	0.71	5.24	1.17	1.51	4.28	0.984	0.023

Now, we shall discuss the adsorption parameters summarized in Table 1. The dependence of the values of n^s obtained by means of Eqs. (1), (3) and (6), is analogous in both cases. The values of n^s predicted by the *DR*-type equation are higher than those obtained by means of Eqs. (1) and (3). The values of n^s evaluated by means of the *DR*-type equation seem to be too high[21]; this is caused by the mathematical properties of Eq. (6). Nevertheless, these values decrease slightly when temperature increases; the values of n^s obtained by means of Eqs. (1) and (3) show similar temperature dependence.

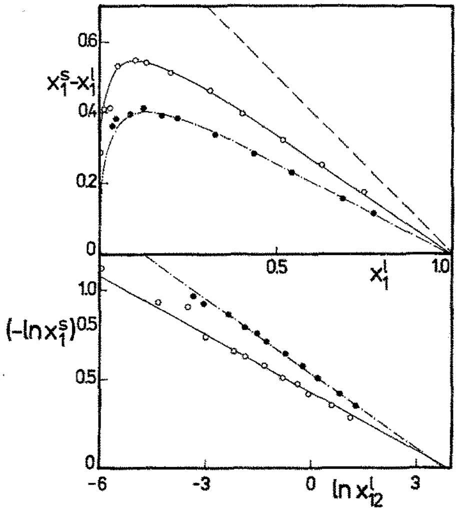

Fig. 6. Excess adsorption isotherms $(x_1^s - x_1^l)$ vs. x_1^l and *DR* linear plots $(-\ln x_1^s)^{0.5}$ vs. $\ln x_{12}^l$ for 1-tetradecene/dodecane mixtures on $Na_{0.17}Li_{0.83}X$ (white circles) and $Na_{0.50}Cs_{0.50}X$ (black circles) at 293 K

Figs. 6 and 7 show the dependence of the relative adsorption excess $n_1^e/n^s = (x_1^s - x_1^l)$ upon x_1^l for four selected systems. The relative adsorption excess was calculated by using the values of n^s obtained from a *DR*-type equation. Fig. 6 presents the dependence $(x_1^s - x_1^l)$ vs. x_1^l for adsorption of 1-tetradecene/dodecane mixtures on $Na_{0.17}Li_{0.83}X$ (the white circles) and on $Na_{0.50}Cs_{0.50}X$ (the black circles) at 293 K. However, Fig. 7 shows this dependence for Ca*X* (the white circles) and Ba*X* (the black circles) at 293 K. The relative excess adsorption isotherms for zeolite samples containing cations of the smaller radius lie above the isotherms for samples containing cations of the greater radius and belonging to the same periodic group. Comparing this sequence of the relative excess adsorption isotherms with the theoretical *DR* isotherms (cf. Fig. 5), we can conclude that the B_0-value for Na-$_{0.17}$Li$_{0.83}X$ should be smaller than that for Na$_{0.50}$Cs$_{0.50}X$, and similarily the B_0-value for CaX should be smaller than that for BaX.

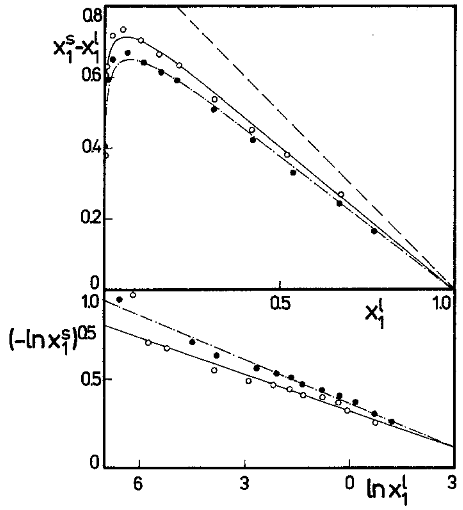

Fig. 7. Excess adsorption isotherms $(x_1^s - x_1^l)$ vs. x_1^l and *DR* linear plots $(-\ln x_1^s)^{0.5}$ vs. $\ln x_{12}^l$ for 1-tetradecene/dodecane mixtures on CaX (white circles) and BaX (black circles) at 293 K

In Figs. 6 and 7 the *DR* linear dependences are also shown. They were plotted according to the linear form of Eq. (6):

$$(-\ln x_1^s)^{1/2} = B_0^{1/2} RT \ln x_{12}^0 - B_0^{1/2} RT \ln x_{12}^l \tag{11}$$

It follows from these figures that experimental points show small deviations from the straight lines.

Fig. 8 illustrates the temperature dependence of $\ln x_{12}^0$. This dependence is analogous to that of $\ln K_{12}$. The values of x_{12}^0 and K_{12} decrease when temperature increases. Therefore, the dependence of $\ln x_{12}^0$ and $\ln K_{12}$ upon $1/T$ is an increasing function in the majority cases. In many cases this dependence may be linearized. From the theoretical point of view the dependences of $\ln x_{12}^0$ and $\ln K_{12}$ upon $1/T$ should be linear with the slopes proportional to the difference of adsorption energies of 1-tetradecene and dodecane. Because these parameters were evaluated

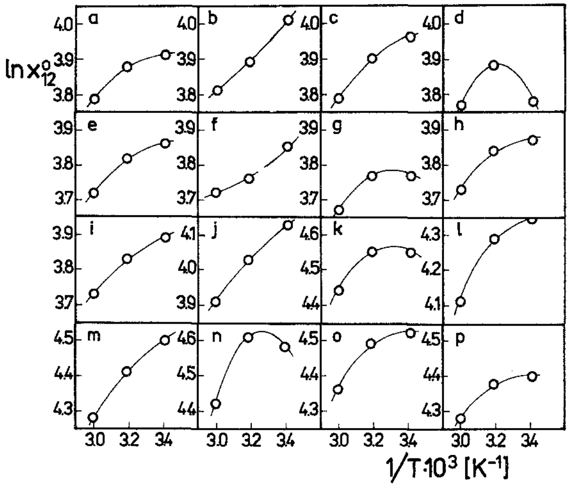

Fig. 8. Dependences $\ln x_{12}^0$ vs. $1/T$ for adsorption systems studied; letters at curves denote adsorption systems summarized in Table 1

from each experimental isotherm by using the best-fit procedure, their temperature dependence is insufficiently precisely found for some systems. Nevertheless, the changes of $\ln K_{12}$ and $\ln x_{12}^0$ with temperature are rather small and their values can be averaged. In Table 1 the average values of $\ln x_{12}^0$ and $\ln K_{12}$ are summarized. Similarily, we averaged the values of parameters n^s and B_0; their average values are given in Table 1 also.

Fig. 9 presents the dependence of the average values of $\overline{B}_0$, $\overline{n^s}$ and $\overline{\ln x_{12}^0}$ upon the percentage contents of cations of K, Ca and Ba in zeolite $Na_{1-p}Me_pX$, where p denotes the fraction of a metal cation in the zeolite sample. The dependence of $\overline{B}_0$ upon % K in the zeolite $Na_{1-p}K_pX$ is slowly increasing; it is connected with the smaller $\overline{B}_0$-value for NaX than that for KX.

Thus, the energetic heterogeneity of $Na_{1-p}K_pX$ with respect to a 1-tetradecene/dodecane mixture decreases slowly when % K in the zeolite increases. If the zeolite $Na_{1-p}Me_pX$ contains Ca or Ba cations its energetic heterogeneity increases with the increase of % *Me* in the sample, because the dependence of $\overline{B}_0$ upon % *Me* in the zeolite is decreasing.

The dependence of $\overline{\ln x_{12}^0}$ upon % *Me* in the zeolite correlates with changes of $\overline{B}_0$ upon % *Me*. If the dependence of $\overline{B}_0$ vs. % *Me* is a decreasing function, then the curve $\overline{\ln x_{12}^0}$ vs. % *Me* is an increasing

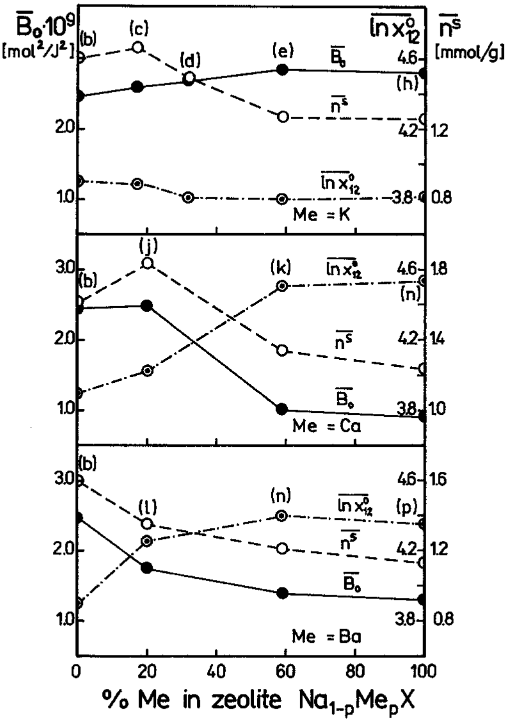

Fig. 9. Dependences of $\bar{B}_0$ (solid lines), $\overline{\ln x^0_{12}}$ (dotted-dashed lines) and $\overline{n^s}$ (dashed lines) upon % *Me* in the zeolites $Na_{1-p}Me_pX$, where *Me* denotes potassium, calcium or barium; letters at the experimental points refer to the systems shown in Table 1

function. The average difference of the adsorption energies of 1-tetradecene and dodecane is proportional to $\overline{\ln x^0_{12}}$; this means that the average difference of adsorption energies is greater for greater values of $\overline{\ln x^0_{12}}$. However, an increase in the average difference of adsorption energies can be caused by an increase in the energetic heterogeneity, i.e., a decrease in $\bar{B}_0$.

Fig. 10 illustrates the dependence of adsorption parameters upon the ratio of formal charge to ion radius, *e*/*r*. It is shown for cations of alkalines (systems a, b, h, f and g) and the calcium group (systems n, o and p). The correlation between dependences $\bar{B}_0$ vs. *e*/*r* and $\overline{\ln x^0_{12}}$ vs. *e*/*r* is analogous as in Fig. 9, i.e., because the first dependence is a decreasing function, the second one is an increasing function. The decrease in $\bar{B}_0$ with the increase of *e*/*r* indicates that for zeolites containing cations of alkalines the energetic heterogeneity increases

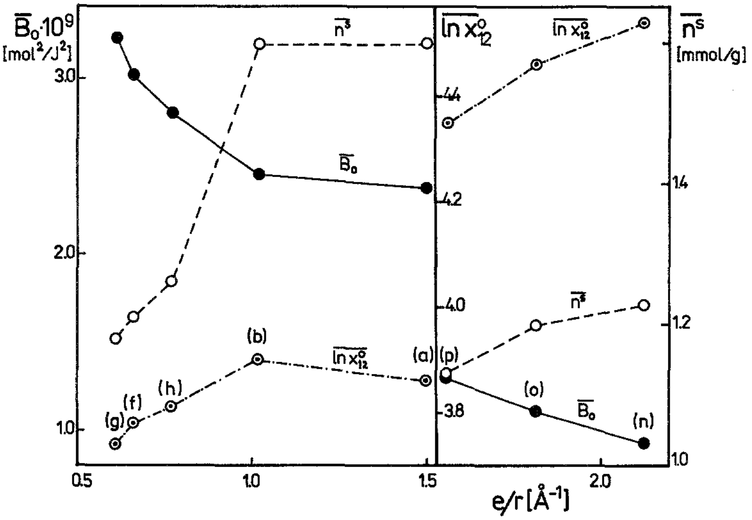

Fig. 10. Dependences of $\bar{B}_0$ (solid lines), $\overline{\ln x_{12}^0}$ (dotted-dashed lines) and $\overline{n^s}$ (dashed lines) upon e/r for different samples of zeolites; letters at the experimental points refer to the systems summarized in Table 1

beginning from Cs, through Rb, K and Na to Li. Perhaps it is due to the smaller mobility of the smaller cations[21]. An analogous behaviour to the above is observed for zeolites containing cations of the calcium group.

The strongest energetic heterogeneity is observed for CaX, however, the smallest one is observed for BaX. In general the $\bar{B}_0$ values are lower for $\mathrm{Na}_{1-p}Me_p^{+2}X$. Also the mobility of Me^{+2} in the zeolite is lower than that for Me^+. It means that the energetic heterogeneity of the zeolite samples containing cations of the calcium group is stronger in comparison with the zeolites with alkalines cations. This fact corresponds with the average difference of adsorption energies, which is greater for $\mathrm{Na}_{1-p}Me_p^{+2}X$ as for $\mathrm{Na}_{1-p}Me_p^{+}X$. It is due to stronger interactions of 1-tetradecene molecules with the cations Me^{+2} in comparison to Me^+.

The dependences of $\bar{B}_0$ vs. e/r and $\overline{\ln x_{12}^0}$ vs. e/r are nearly linear for the cations of calcium group and for the cations of alkalines except Li. An exception of the zeolites containing Li-cations was discussed in the previous paper[21].

The above discussion shows that the exchange in the zeolite of a given cation for the cation of higher value of e/r causes an increase in the average adsorption energy of 1-tetradecene with respect to the adsorption energy of dodecane. It is caused by an increase in the electrostatic potential of the cation and the energetic heterogeneity of the zeolite. In other words, a strong energetic heterogeneity is observed for the samples containing cations strongly interacting with 1-tetradecene molecules and showing smaller mobility in the zeolite. However, an increase in the mobility of cations in the zeolite leads to averaging of the adsorbent potential field in the whole adsorption space resulting in a greater energetic homogeneity of the adsorbent.

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