

Adsorption of 1-Olefin/*n*-Paraffin Liquid Mixtures on NaX and NaY Zeolites

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Abstract. The isotherm equation for adsorption of binary liquid mixtures of nonelectrolytes, involving differences in molecular sizes of components and quasi-Gaussian energy distribution of adsorption sites, is used to describe the excess adsorption data for 1-olefin/*n*-paraffin liquid mixtures on NaX and NaY zeolites at 293 K. This equation gives a good representation of the above adsorption data. Analysis of these data showed that the heterogeneity parameter is slightly dependent on the difference in molecular sizes of both components.

Key words: Adsorption, liquid hydrocarbons, zeolites.

1. Introduction

Adsorption from gaseous and liquid phases on zeolites underlies a number of extremely important processes of utilitarian significance, e.g., catalytic processes, separation processes, etc. Therefore, the theoretical and experimental studies concerning the kinetics of molecular transport phenomena and adsorption equilibria at the systems' gaseous phase (zeolite and solution) zeolite, are very important from the viewpoint of their practical applications. Recently, a great interest in adsorption from solutions on zeolites has been observed because of its industrial applications. It induced some authors to experimentally study liquid adsorption on zeolites. Systematic experimental studies of adsorption from liquid hydrocarbon mixtures on zeolites have been undertaken by Schöllner's group [1].

In the paper [1], the experimental data concerning the adsorption of different liquid *n*-olefins from *n*-hexane on NaX zeolites are presented and interpreted by using the Everett equation for describing the mole fractions of components in the surface phase. The extensive experimental data on 1-tetradecene/dodecene adsorption on different types of NaX zeolites, modified by ions of the alkali and calcium groups, are discussed by using the isotherm equations derived for energetically heterogeneous solids [2]. It follows from this paper that the isotherm equations, derived for quasi-Gaussian energy distributions, give good representation of the data in question.

The aim of this paper is to discuss the excess adsorption data for 1-olefin/*n*-paraffin liquid mixtures on NaX and NaY zeolites by means of an equation involving energetic heterogeneity of the zeolites and the differences in molecular sizes of the hydrocarbons forming the liquid mixture.

2. Theoretical

The averaged equilibrium constant \bar{K}_{12}^* describing adsorption from binary liquid mixtures on energetically heterogeneous solids, characterized by quasi-Gaussian energy distribution, may be expressed as follows [3]:

$$\bar{K}_{12}^* = \frac{(\phi_1^s)^{1/m}}{\phi_1^l} \left[\frac{\phi_2^l}{(\phi_2^s)^{1/m}} \right]^{1/r} \quad (1)$$

where ϕ_i^s and ϕ_i^l for $i = 1, 2$ are the volume fractions of the i th component in the surface and bulk phases, respectively, r is the ratio of the molecular sizes of second and first components and m is the heterogeneity parameter varying from zero to unity and characterizing the width of the quasi-Gaussian energy distribution. A quite analogous expression for Equation (1) was proposed by Jaroniec [4]; it is written by means of the mole fractions of the components in the surface and bulk phases, respectively.

For $m = 1$ (energetically homogeneous adsorbent) Equation (1) becomes

$$K_{12}^* = \frac{\phi_1^s}{\phi_1^l} \left(\frac{\phi_2^l}{\phi_2^s} \right)^{1/r} \quad (2)$$

where K_{12}^* may be approximated as follows:

$$K_{12}^* = \exp\left(\frac{E_1 - E_2/r}{RT}\right) \quad (3)$$

and E_i is the adsorption energy of the i th component.

Equation (2) was used by some authors [1, 5, 6] for analysing the excess adsorption data. For $r = 1$ (identical molecular sizes of both components) Equation (1) reduces to the expression:

$$\bar{K}_{12} = \left(\frac{x_1^s}{x_2^s} \right)^{1/m} \left(\frac{x_2^l}{x_1^l} \right) \quad (4)$$

where x_i^s and x_i^l are the mole fractions of the i th component in the surface and bulk phases, respectively. However, the constant

$$\bar{K}_{12} = \langle K_{12} \rangle; \quad K_{12} = \exp\left(\frac{E_1 - E_2}{RT}\right) \quad (5)$$

is obtained by averaging the equilibrium constants K_{12} referring to different types of adsorption sites. Equation (4) was applied to determine the heterogeneity effects of liquid adsorption on solids [7, 8] and the surface-phase capacity [9]. Thus, the constant \bar{K}_{12}^* appearing in Equation (1) is obtained by averaging the equilibrium constants K_{12}^* referring to different types of adsorption sites, i.e.,

$$\bar{K}_{12}^* = \langle K_{12}^* \rangle \quad (6)$$

where K_{12}^* is given by Equation (3).

The theoretical foundations of Equation (1) are described in [3] and [10] and deal with the adsorption from solutions of nonelectrolytes on solid surfaces. However, its application in describing the solute adsorption data from dilute solutions on solids is reviewed by Jaroniec [11].

Now we shall discuss the theoretical excess adsorption isotherms generated by Equation (1). These isotherms were calculated as follows: at first, the mole fraction x_1^l was recalculated from the volume fraction ϕ_1^l for a given value of r by using the following equation:

$$\phi_1^l = \frac{x_1^l}{x_1^l + r(1 - x_1^l)} \quad (7)$$

Assuming the values m and $A_{12} = (\overline{K}_{12}^*)^r$, we calculated the volume fraction ϕ_1^s by solving the following equation:

$$A_{12} = \left[\frac{(\phi_1^s)^{1/m}}{\phi_1^l} \right]^r \frac{(1 - \phi_1^l)}{(1 - \phi_1^s)^{1/m}} \quad (8)$$

with respect to ϕ_1^s for the different values of ϕ_1^l evaluated by means of Equation (7).

Next, the volume fraction ϕ_1^s was recalculated from the mole fraction x_1^s according to the expression

$$x_1^s = \frac{r\phi_1^s}{r\phi_1^s + (1 - \phi_1^s)} \quad (9)$$

The mole and volume fractions in the surface phase were recalculated by assuming the same value of r as that used in the bulk solution. Having the mole fraction x_1^s corresponding to a given value of x_1^l , we can calculate the adsorption excess of the first component as follows [3,6]:

$$n_1^e = \frac{n_{m1}^s (x_1^s - x_1^l)}{(1 - r)x_1^s + r} \quad (10)$$

where n_{m1}^s is the total number of moles of the first component in the surface phase containing only the molecules of the first component.

Figures 1–4 show the excess adsorption isotherms calculated according to Equation (9) by assuming $A_{12} = 3.5$, $n_{m1}^s = 1$ and different values of r and m . Figure 1 presents the curves n_1^e vs. x_1^l for $r = 1$ (identical molecular sizes of both components) and different values of m . Then, the constant \overline{K}_{12} is expressed by means of Equation (4) and the adsorption excess n_1^e is defined as follows:

$$n_1^e = n^s (x_1^s - x_1^l) \quad (11)$$

where

$$n^s = n_{m1}^s = n_{m2}^s \quad (12)$$

The isotherm curves presented in Figure 1 change from type II ($m = 1$) to type IV (m smaller than unity) in the Schay and Nagy classification [12]. The influence of the heterogeneity parameter m on the course of the excess adsorption isotherm was discussed in [2, 7]. Figures 2–4 present the isotherm curves n_1^e vs. x_1^l for different values of r and selected values of the heterogeneity parameter $m = 1$ (Figure 2), $m = 0.8$ (Figure 3) and $m = 0.6$ (Figure 4).

The parameter r is frequently approximated by the ratio n_{m1}^s/n_{m2}^s [13]; then, performing the model calculations for the selected value of $n_{m1}^s = 1$ and different values of r , we change the value of n_{m2}^s . Thus, Figure 2 presents the excess isotherms for $m = 1$ and different values of n_{m2}^s . The excess adsorption isotherms calculated for $n_{m1}^s = 1$ and $n_{m2}^s = 1/r > 1$ (see Figure 2) lie above the excess isotherm plotted for $n_{m1}^s = n_{m2}^s = 1$ ($r = 1$). It follows from this figure and

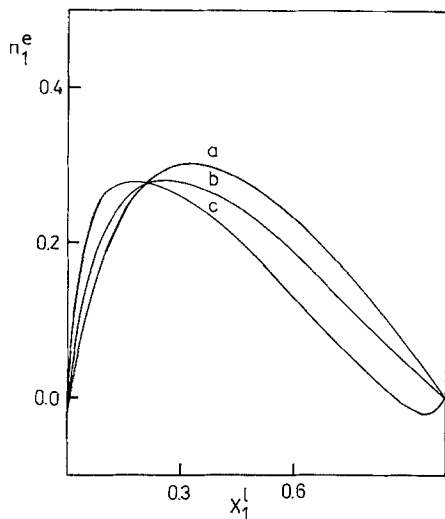


Fig. 1. Theoretical excess adsorption isotherms calculated for $A_{12} = 3.5$, $r = 1$ and $m = 1.0$ (curve a), 0.8 (curve b) and 0.6 (curve c).

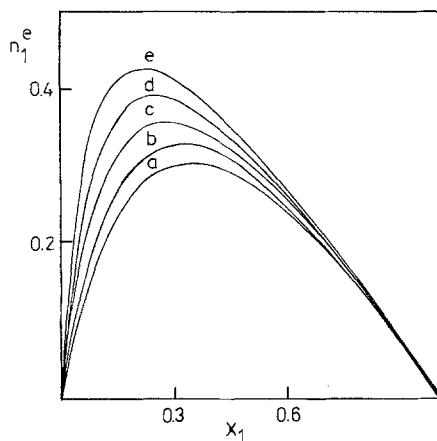


Fig. 2. Theoretical excess adsorption isotherms calculated for $A_{12} = 3.5$, $m = 1$ and $r = 1.0$ (curve a), 0.9 (curve b), 0.8 (curve c), 0.7 (curve d) and 0.6 (curve e).

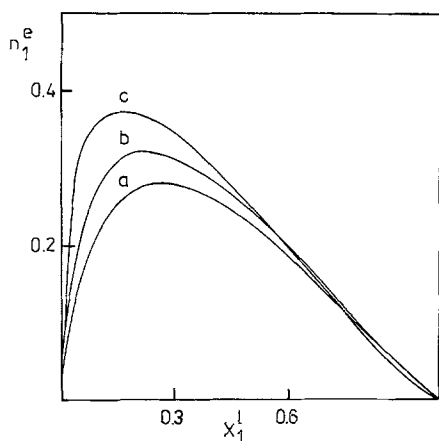


Fig. 3. Theoretical excess adsorption isotherms calculated for $A_{12} = 3.5$, $m = 0.8$ and $r = 1.0$ (curve a), 0.8 (curve b) and 0.6 (curve c).

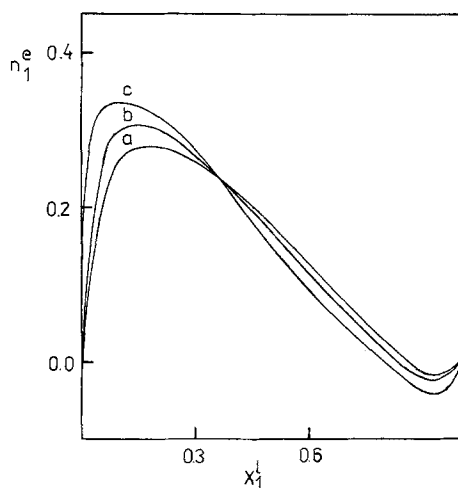


Fig. 4. Theoretical excess adsorption isotherms calculated for $A_{12} = 3.5$, $m = 0.6$ and $r = 1.0$ (curve a), 0.8 (curve b), and 0.6 (curve c).

Figures 3 and 4 that the parameter r does not change its type of excess adsorption isotherm. The type of excess isotherm is mainly determined by the heterogeneity parameter m ; however, parameter r mainly causes an increase or decrease in the adsorption excess.

3. Experimental

The chemical composition and some other adsorption properties of the zeolites used are summarized in Table I. The samples were activated for 20 h at 673 K and at a pressure less

Table I. Chemical composition of the unit cell and the adsorption properties of the zeolites used

Zeolite	Unit cell composition	Micropore volume ^a [ml/g]	Nitrogen capacity ^b [mmole/g]
NaX	Na _{80.0} Al _{80.0} Si _{112.0} O ₃₄₈	0.30	10.428
NaY	Na _{50.5} Al _{50.5} Si _{141.5} O ₃₈₄	0.28	0.143

^a Determined by *n*-hexane adsorption capacity by using the density of liquid *n*-hexane at 293 K.

^b At 77 K.

than 10 m Pa in a special tube diameter 25 mm, height 10 mm. The specific surface excess amount n_1^e of the preferentially adsorbed component '1' (the olefin) was calculated from the change in its concentration, $x_1^0 - x_1^l$, before and after the adsorption

$$n_1^e = \frac{n^0}{m_a} (x_1^0 - x_1^l), \tag{13}$$

where m_a is the mass of the adsorbent in equilibrium with n^0 moles of the solution. After equilibrium the concentration x_1^l was determined by a calibrated refractometer. The absolute error of the surface excess was ± 0.03 mmole/g. The hydrocarbons were distilled and dried with 3A molecular sieve very carefully before use. The excess adsorption isotherms were measured for nonene, decene, undecene, dodecene, and tridecene from *n*-octane solutions on NaX and NaY zeolites at 293 K. These measurements were carried out in Schollner's Laboratory (Leipzig). For the purpose of illustration, Figures 5 and 6 presents the excess adsorption isotherms for 1-decene and 1-tridecene from *n*-octane solutions on NaX (Figure 5) and NaY (Figure 6) zeolites.

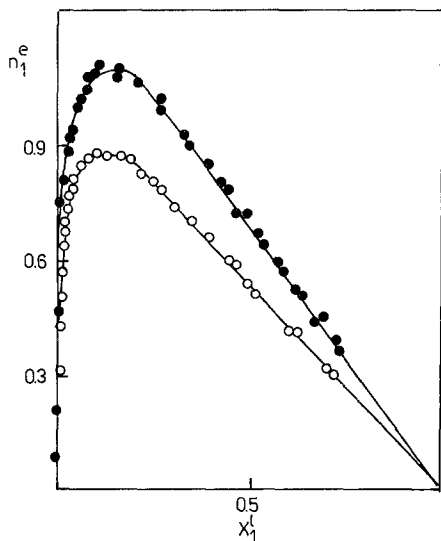


Fig. 5. Excess adsorption isotherms for 1-decene/*n*-octane (●) and 1-tridecene/*n*-octane (○) liquid mixtures on NaX zeolites at 293 K.

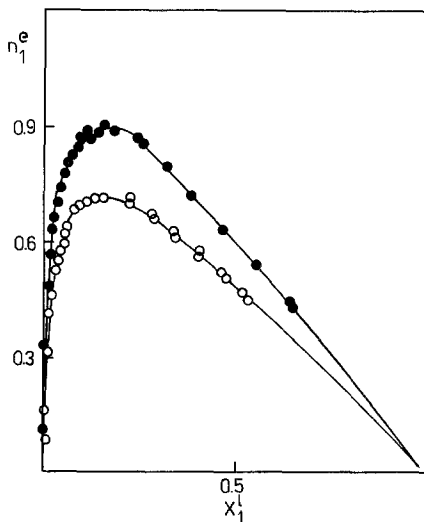


Fig. 6. Excess adsorption isotherms for 1-decene/*n*-octane (●) and 1-tridecene/*n*-octane (○) liquid mixtures on NaY zeolites at 293 K.

4. Results and Discussion

The excess adsorption data n_1^e vs. x_1^l for olefins from *n*-octane solutions on NaX and NaY zeolites were analysed by using Equation (1). This equation contains four parameters: n_{m1}^s , r , m , \bar{K}_{12}^* . To reduce the number of parameters which should be evaluated from the excess adsorption data, the limiting adsorption values of the olefins, n_{m1}^s , and *n*-octane, n_{m2}^s , were determined by a pycnometric method described by Dubinin *et al.* [14]. These values make possible the calculation of the parameter r by means of the limiting values of adsorption; it may be evaluated as the ratio of n_{m1}^s to n_{m2}^s [13]. Table II contains the quantities n_{m1}^s and

Table II. Parameters of Equation (1) characterizing adsorption of different olefins from *n*-octane on NaX and NaY zeolites at 293 K

I-Olefin	Zeolite	n_{m1}^s [mmol/g]	r	$\ln \bar{K}_{12}^*$	m
nonene	NaX	1.67	0.92	3.89	0.90
decene		1.51	0.83	3.75	0.93
undecene		1.38	0.76	3.84	0.95
dodecene		1.25	0.69	3.70	0.97
tridecene		1.16	0.64	3.62	0.99
nonene	NaY	1.47	0.92	3.68	0.92
decene		1.32	0.83	3.48	0.93
undecene		1.20	0.76	3.56	0.94
dodecene		1.10	0.69	3.36	0.95
tridecene		1.01	0.64	3.28	0.96

r evaluated by using the independent method in question. Thus, the number of unknown parameters in Equation (1) has been reduced; the parameters m and \bar{K}_{12}^* may be easily evaluated from the excess adsorption data by means of Equation (1). Application of this equation for analysing these data only requires the calculation of the volume fractions ϕ_1^l and ϕ_1^s , because $\phi_2^l = 1 - \phi_1^l$ and $\phi_2^s = 1 - \phi_1^s$. Volume fraction ϕ_1^l may be calculated according to Equation (7), whereas, ϕ_1^s may be evaluated by means of the analogous expression to Equation (7):

$$\phi_1^s = \frac{x_1^s}{x_1^s + r(1 - x_1^s)} \quad (14)$$

The mole fractions x_1^s appearing in Equation (14) may be evaluated according to Equation (10) by using the quantities n_{m1}^s and r summarized in Table II. After calculating the volume fractions ϕ_i^s and ϕ_i^l , for $i = 1, 2$, we plotted the experimental data according to the linear form to Equation (1); it is

$$\ln \frac{\phi_1^s}{(\phi_2^s)^{1/r}} = m \ln \bar{K}_{12}^* + m \ln \frac{\phi_1^l}{(\phi_2^l)^{1/r}} \quad (15)$$

These linear plots are presented in Figures 7 and 8. It follows from these figures that Equation (15) gives a good representation of the adsorption data studied in a large concentrated region. Deviations of the experimental points from the straight line given by Equation (15) appear at the low and high concentrations of the first component. These deviations are greater in the

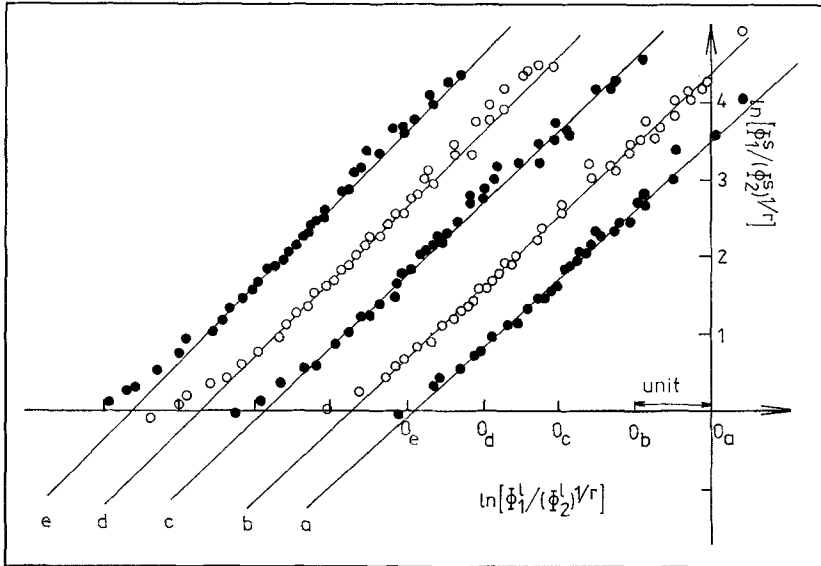


Fig. 7. Linear dependence $\ln[\phi_1^s/(\phi_2^s)^{1/r}]$ vs. $\ln[\phi_1^l/(\phi_2^l)^{1/r}]$ for adsorption systems with NaX zeolites at 293 K: 1-nonene/*n*-octane (a), 1-decene/*n*-octane (b), 1-undecene/*n*-octane (c), 1-dodecene/*n*-octane (d), 1-tridecene/*n*-octane (e). The symbol 0_a denotes zero on the axis $\ln[\phi_1^l/(\phi_2^l)^{1/r}]$ referring to the system a, b, etc.

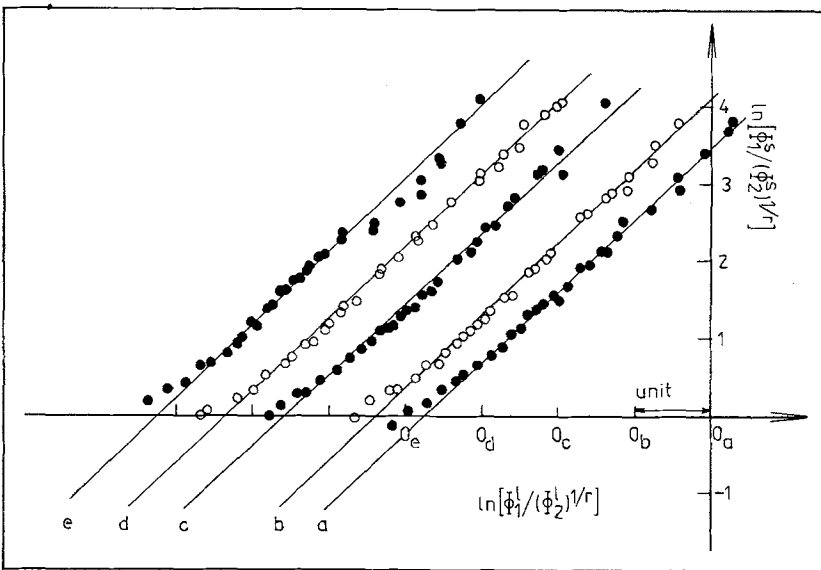


Fig. 8. Linear dependence $\ln[\phi_1^s/(\phi_2^s)^{1/r}]$ vs. $\ln[\phi_1^l/(\phi_2^l)^{1/r}]$ for adsorption systems with NaY zeolite at 293 K. The symbols a, b, c, d, e denote the same liquid mixtures as in Figure 3.

case of adsorption data on NaY zeolite. The parameters m and \bar{K}_{12}^* , evaluated from the linear plots presented in Figures 7 and 8, are summarized in Table II. The values of m for the adsorption of different olefin/*n*-octane mixtures on NaX and NaY zeolites lie between 0.9 and

1.0. They increase when the number of carbon atoms increases in the olefin chain, which is in good agreement with the numerical simulation results performed for Equation (1) [15].

The values of the constant \bar{K}_{12}^* for adsorption on NaX zeolites are larger than those obtained for NaY zeolites. This may be due to the presence of cations in the S III-position in the large cage of the X zeolites. The constant \bar{K}_{12}^* , given by Equation (6), should be somewhat sensitive to changes in the value of r . This is illustrated by using Equation (3).

Let us assume that the energy E_2 for a given n -paraffin is proportional to the number of CH_2 groups appearing in the paraffin chain; then E_2 may be approximated as follows:

$$E_2 = n_C E_0 \quad (16)$$

where n_C is the number of carbon atoms in the paraffin chain and E_0 is the energy contribution from the CH_2 groups. Similarly, the energy of a given olefin may be approximated by

$$E_1 = E^* + n_C E_0 \quad (17)$$

where E^* is the energy contribution from the group containing the double bond. According to Equation (16) and (17), the expression $(E_1 - E_2/r)$ for a 1-nonene/ n -octane mixture ($r = 0.92$ is close to unity) may be approximated by E^* because the terms $8E_0$ and $8E_0/r$ compensate. Similarly, the values of $(E_1 - E_2/r)$ for other 1-olefin/ n -octane mixtures oscillate about E^* , e.g., for 1-tridecene/ n -octane mixture the term $12E_0$ is compensated by the term $8E_0/r$, which is close to $12E_0$, because $1/r = 1.56$. The above approximate calculations show that the constant K_{12}^* is nearly independent of r for hydrocarbon mixtures, which suggests that the constant \bar{K}_{12}^* should also show the same behaviour as the constant K_{12}^* .

Of course, in the case of \bar{K}_{12}^* , its dependence on r may be stronger than in the case of K_{12}^* because the heterogeneity parameter m is dependent on the type of hydrocarbon mixture (see Table II). The values of \bar{K}_{12}^* summarized in Table II confirm the above suggestion. Moreover, the dependence of the constant \bar{K}_{12}^* on the carbon number of the olefins shows irregularities for odd numbered olefins (see Figure 9).

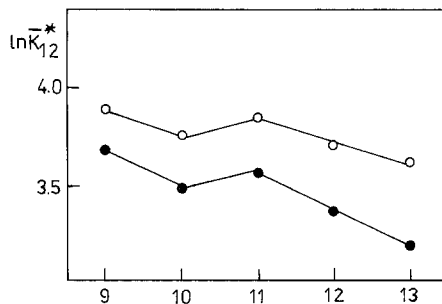


Fig. 9. Dependence of $\ln \bar{K}_{12}^*$ vs. n_C for adsorption systems summarized in Table I; the white circles refer to the systems with NaX zeolites, whereas the black circles refer to the systems with NaY zeolites.

A quite similar behaviour is found for the immersion heating of these hydrocarbons on NaX and NaY zeolites [16] caused by alternating dipole moments.

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