

# Evaluation of the thermodynamic parameters for the adsorption of some hydrocarbons on 4A and 13X zeolites by inverse gas chromatography

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Accepted 4 February 2002

## Abstract

Inverse gas chromatography has been used to evaluate the adsorption parameters ( $\Delta H$ ,  $\Delta S$  and  $\Delta G$ ) of some probes, each representing a class of organics (*n*-hexane, cyclohexane and benzene) on 4A and 13X zeolites. The adsorption parameters of the probes on 4A were determined in the finite concentration region, and those on 13X were determined in the infinite dilution region. The interactions between the probes and the surface were discussed in the light of determined thermodynamic parameters of adsorption. It was found that the adsorption isotherms for 4A conform with the Langmuir equation and benzene exhibits more negative  $\Delta H$  than for *n*-hexane and cyclohexane on both 4A and 13X. Also, interactions of the benzene and *n*-hexane with 13X were found to be stronger than that on 4A.

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**Keywords:** Inverse gas chromatography; Heat of adsorption; Adsorption thermodynamic parameters; Molecular sieve 13X; Molecular sieve 4A

## 1. Introduction

The majority of physicochemical adsorption properties studied by gas–solid chromatography (GSC) refers to the stationary phase and its interaction with known probe solutes, and this is known as inverse gas chromatography (IGC), since it has the stationary phase of the system as the main object of investigation.

IGC offers an alternative to the conventional gravimetric or volumetric methods of determining adsorption equilibrium isotherms. This method enables a fast yield of adsorption data with an extended range of temperatures and partial pressures and is even applicable under reaction conditions. Many physicochemical properties such as surface activity, surface area, and adsorption enthalpy, entropy and free energy can be measured by IGC [1–3].

IGC measurements may be carried out both at finite surface coverage (finite concentration region) and zero surface coverage (Henry's law region or infinite dilution region). When adsorption takes place at finite concentration region, the isotherms are non-linear and thus retention volumes are dependent upon the adsorbate concentration in the gas phase.

A requirement for the application of IGC in such cases is that diffuse boundaries of the peaks fall on a common curve.

In the infinite dilution region, the elution peaks are characterized by a good symmetry with the retention volumes independent of the vapor sample size indicating that the Henry's law region is indeed reached.

In this study, the adsorptions of some hydrocarbons (probes), each representing a class of organics (*n*-hexane, cyclohexane and benzene) on two molecular sieves (4A and 13X) were investigated at finite concentration and infinite dilution region by IGC.

This paper is a continuation of our work devoted to the study of the heats of adsorption of some hydrocarbons on some natural and synthetic zeolites [4].

The objectives of this study were:

- to give a brief review about the different methods used to calculate the adsorption parameters in finite concentration and infinite dilution regions;
- to construct the adsorption isotherms of the probes on 4A in the finite concentration region;
- to determine the basic thermodynamic parameters ( $\Delta H$ ,  $\Delta G$ ,  $\Delta S$ ) for the adsorption of the probes on 4A in the finite concentration region;
- to determine these parameters for the adsorption of the probes on 13X in the infinite dilution region.

*Abbreviations:* ECP, elution by characteristic point method; GSC, gas–solid chromatography; IGC, inverse gas chromatography

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### Nomenclature

$b$	adsorption equilibration constant ( $\text{mmHg}^{-1}$ )
$F_a$	volumetric flow rate
$\Delta G$	free energy of adsorption
$\Delta H$	differential enthalpy of adsorption
$\Delta H_{st}$	isosteric enthalpy of adsorption
$j$	James–Martin correction factor
$K$	surface partition coefficient
$n$	amount adsorbed ( $\text{mol g}^{-1}$ )
$n_m$	maximum amount adsorbed ( $\text{mol g}^{-1}$ )
$p$	partial pressure of adsorbate
$p^0$	standard pressure (1 atm)
$P_{s/g}$	standard-state vapor pressure of adsorbate (1 atm)
$q$	amount adsorbed ( $\text{mol m}^{-2}$ ) (see Eq. (9))
$q$	heat of adsorption ( $q = -\Delta H$ )
$q_{st}$	isosteric heat of adsorption ( $q_{st} = -\Delta H_{st}$ )
$R$	universal gas constant
$S$	specific surface area of adsorbent ( $\text{m}^2 \text{g}^{-1}$ )
$\Delta S$	entropy of adsorption
$t_m$	dead time
$t_R$	retention time of the probe
$T$	column temperature (K)
$T_a$	ambient temperature (K)
$T_{av}$	average temperature (K)
$V_N$	net retention volume

### Greek letters

$\theta$	fractional coverage of adsorbent (dimensionless)
$\pi_s$	two-dimensional surface pressure

## 2. Experimental

### 2.1. Materials and columns

Two adsorbents were used: molecular sieve 13X (Alltech) and molecular sieve 4A (Alltech). A 1.5 m long, 5.35 mm ID stainless steel column was used in this work. The characteristics of the column and adsorbents were given in Table 1.

The adsorbates (probes) used were *n*-hexane, cyclohexane, and benzene (Merck, reagent grade) and were employed without further purification.

### 2.2. Instrumentation

The chromatographic experiments were performed with an Unicam 610 gas chromatograph. Thermal conductivity detector was used in the finite concentration region and

flame ionization detector was used in the infinite dilution region. Retention times were recorded on an Unicam 4815 integrator.

High purity nitrogen was used as carrier gas. The flow rate of carrier gas was measured at the detector outlet with a soap bubble flowmeter and was corrected for pressure drop in the column using pressure gradient correction factor ( $j$ ), correction at column temperature was also made.

The adsorbents were conditioned at 523 K in the nitrogen gas flow for 24 h prior to the measurements. Retention times were calculated from a chart recorder trace of the elution chromatograms and were corrected for column “dead time”.

## 3. Calculations

### 3.1. Adsorption isotherms

In order to obtain adsorption isotherms from the shape of a single gas chromatographic peak, “finite concentration” GC techniques were used [1–3]. When adsorption takes place at finite surface coverage, the isotherms are generally non-linear and hence retention volumes are dependent upon the adsorbate concentration in the gas phase. In addition, a non-linear isotherm results in asymmetrical peaks. The shape of which and the retention time being dependent on the volume injected.

If an adsorption isotherm is to be derived from the shape of a single gas chromatographic peak, several conditions have to be met [1]. (1) The isotherm should not have a point of inflection; otherwise, at least two peaks are needed to construct the isotherm. (2) The so-called “coincidence phenomenon” has to occur, namely all diffuse boundaries of the peaks obtained by injecting varying amounts of the probe have to be superimposable.

Each point on the diffuse boundary is related to a point on the isotherm through the net retention volume,  $V_N$ , at this point and the partial pressure of the adsorbate,  $p$ .

$$V_N = wRT \left( \frac{\partial n}{\partial p} \right)_T \quad (1)$$

where  $n$  is the number of moles of probe adsorbed per gram of adsorbent and  $w$  is the mass of adsorbent. After integration, one obtains

$$n = \frac{1}{wRT} \int_0^p V_N dp \quad (2)$$

The  $V_N/wRT$  versus  $p$  values are plotted and the adsorption isotherm is obtained by integrating this curve (Simpson’s approximation).

Table 1  
Description of the columns and adsorbents

Adsorbent	Particle size (mesh)	Packing weight of adsorbent (g)	Column temperature (K)	Carrier gas flow rate (ml/min)
4A	80–100	15.53	373–473	25
13X	80–100	1.48	503–593	30–40

The net retention volume ( $V_N$ ) was calculated from the following relation:

$$V_N = (t_R - t_m)F_a \frac{T}{T_a} j \quad (3)$$

where  $t_R$  is the probe retention time,  $t_m$  the retention time of the mobile phase (holdup time, dead time),  $F_a$  the volumetric flow rate measured at column outlet and at ambient temperature,  $T_a$  the ambient temperature (K),  $T$  the column temperature (K) and  $j$  the James–Martin gas compressibility correction factor.

This method of deriving isotherm data from the profile of the diffuse boundary of an overloaded elution band in GSC is known as elution by characteristic point method (ECP). ECP was introduced by Cremer and Huber [5].

In this study chromatographic peaks recorded for evaluation of adsorption isotherms for 4A in finite concentration region have a sharp front and a diffuse rear boundary and there was good coincidence of diffuse peak boundaries forming a common envelope.

### 3.2. Adsorption parameters

#### 3.2.1. Finite concentration region

Assuming that the moving phase behaves as an ideal gas mixture of carrier gas and adsorbate vapor at a partial pressure  $p$  (atm), chemical potential of the adsorbate in the gas phase ( $\mu_G$ ) can be calculated from the following well known equation [6].

$$\mu_G = \mu^0 + RT \ln \frac{p}{p^0} \quad (4)$$

This equation is the fundamental thermodynamic equation for an ideal gas mixture. In Eq. (4),  $\mu_G$  is the chemical potential of the adsorbate vapor in the gas phase at temperature  $T$ ,  $\mu^0$  the chemical potential of pure ideal adsorbate vapor at temperature  $T$  and at 1 atm pressure (the standard pressure),  $p$  the partial pressure of the adsorbate vapor in the mixture and  $p^0 = 1$  atm. Note that  $\mu^0$  depends only on  $T$  because the pressure fixed at 1 atm for the standard state.

The following equation is a general criterion for adsorption equilibrium:

$$\mu_S = \mu_G \quad (5)$$

where  $\mu_S$  is the chemical potential of the adsorbate in the adsorbed state. Based on Eqs. (4) and (5), Gibbs free energy of adsorption may be defined as:

$$\Delta G = \mu_S - \mu^0 = RT \ln p \quad (6)$$

where  $p$  is in atm. According to Eq. (6),  $\Delta G$  is equal to the difference in the chemical potential between 1 mol of adsorbate on the surface at a given coverage and 1 mol of adsorbate in the “standard” state [1,7].

Isothermic enthalpy of adsorption ( $\Delta H_{st}$ ) and entropy of adsorption ( $\Delta S$ ) may be calculated from the temperature

dependence of the free energy of adsorption ( $\Delta G$ ) at a given coverage according to Eq. (7) (Gibbs–Helmholtz equation):

$$\left[ \frac{\partial(\Delta G/T)}{\partial(1/T)} \right]_{\theta} = \Delta H_{st} \quad (7)$$

where the subscript  $\theta$  indicates quantities measured at a given value  $\theta$  (= fractional coverage).

If we assume as an approximation that over the small temperature range examined  $\Delta H_{st}$  remains essentially constant and therefore a plot of  $\Delta G/T$  versus  $1/T$  at constant coverage gives a straight line, the slope of which is  $\Delta H_{st}$  and the intercept is  $(-\Delta S)$  [8].

Free energies of adsorption ( $\Delta G$ ) were calculated from the classical equation:

$$\Delta G = \Delta H_{st} - T_{av} \Delta S$$

where  $T_{av}$  is the average temperature.

In finite concentration region, isosteric enthalpy of adsorption also can be calculated using isosteres obtained from adsorption data (i.e. using plots of partial pressures ( $\ln p$ ) versus temperatures ( $1/T$ ) at constant coverages) according to the following equation (in IGC studies this equation is so-called as Clausius–Clapeyron equation) [9,10].

$$\left[ \frac{\partial \ln p}{\partial(1/T)} \right]_{\theta} = \frac{\Delta H_{st}}{R} \quad (8)$$

Eq. (8) may be derived from Langmuir equation and van't Hoff equation [11].

#### 3.2.2. Infinite dilution region

IGC may be performed either under finite concentration conditions or under infinite dilution conditions. In the infinite dilution region injection of minor amounts of adsorbates to approach zero surface coverage, permitting neglect of lateral interactions between adsorbed molecules. Chromatographic peaks recorded in this region were symmetrical, with retention times and thus retention volumes being essentially independent of injection sample size. This result indicates that, under the experimental conditions employed, adsorption data obeyed Henry's law.

Based on Eq. (6) free energy of adsorption is

$$\Delta G = RT \ln p = RT \ln(cRT) = RT \ln \left( \frac{qRT}{K} \right) \quad (9)$$

where  $c$  is the concentration of the adsorbate in the gas phase,  $q$  the amount of adsorbate adsorbed per unit area of adsorbent and  $K$  the surface partition coefficient of the given probe between adsorbed and gaseous state.  $K$  is also called as Henry's constant which is the slope of the isotherm at infinite dilution ( $K = q/c$ ).

In the infinite dilution region,  $K$  is defined as the net retention volume per unit area of the adsorbent inside the column:

$$K = \frac{V_N}{mS} \quad (10)$$

where  $S$  is the specific surface area of adsorbent,  $m$  the mass of adsorbent in the column [1,12–14]. Substituting  $V_N/mS$  for  $K$  in Eq. (9) and solving for  $V_N$  one obtains

$$V_N = RTmSq \exp\left(-\frac{\Delta G}{RT}\right),$$

$$V_N = RTn_s \exp\left(\frac{\Delta S}{R} - \frac{\Delta H}{RT}\right) \quad (11)$$

where  $n_s$  (mol) is the total amount of adsorbate in the adsorbed state.

By taking logarithms on both sides, Eq. (11) can be transformed into a convenient linear form:

$$\ln V_N = \ln(RTn_s) + \frac{\Delta S}{R} - \frac{\Delta H}{R} \frac{1}{T} \quad (12)$$

Thus, by determining  $V_N$  at various temperatures, one can calculate  $\Delta H$  from the slope and  $\Delta S$  from the intercept of the plot of  $\ln V_N$  versus  $1/T$ , provided that the range of  $T$  is narrow enough for  $\Delta H$  and  $\Delta S$  to be regarded as temperature independent. The intercept is equal to  $\ln(RTn_s) + \Delta S/R$ , but in ordinary gas chromatography the first term is negligible and can be ignored [7,15].  $\Delta H$  which is calculated by Eq. (12) is the “differential” enthalpy of adsorption (it is not the “isosteric”) [7]. An analogous way for calculating differential enthalpy of adsorption by GSC has been described by Milonjic and Kopečni [16].

It is known for a long time [2,16] that the differential enthalpy of adsorption ( $\Delta H$ ) is related to the isosteric enthalpy of adsorption ( $\Delta H_{st}$ ) by the equation:

$$|\Delta H_{st}| = |\Delta H| + RT_{av} \quad (13)$$

where  $T_{av}$  is the average temperature for the interval studied.

The isosteric enthalpy of adsorption in the infinite dilution region may be calculated from a plot  $\ln(V_N/T)$  or  $\ln(K/T)$  against  $1/T$  where the slope is  $(-\Delta H_{st}/R)$  [1,2,9,16].

It should be noted here that many authors use the dependence  $\ln V_N$  against  $1/T$  to evaluate the isosteric enthalpy of adsorption. The calculated value from this relation is

smaller than the actual value for the  $RT$  product [1,16]. This difference, being only a few kilojoules per mole, is insufficient to influence the linearity of the plots and is usually within the expected experimental error on  $\Delta H$ . This fact was clearly pointed out by Habgood and Hanlan [17].

Some authors have calculated the free energy of adsorption at infinite dilution from the relation:

$$\Delta G = -RT \ln \left( \frac{KP_{s/g}}{\pi_s} \right) \quad (14)$$

or

$$\Delta G = -RT \ln V_N + c \quad (15)$$

where  $K$  is the surface partition coefficient,  $P_{s/g}$  the adsorbate standard-state vapor pressure, and  $\pi_s$  the two-dimensional spreading or surface pressure of the adsorbed gas in the standard adsorption state [14,16,18]. The standard reference states are taken [19] as  $P_{s/g} = 101 \text{ kN m}^{-2}$  (1 atm) and  $\pi_s = 0.338 \text{ mN m}^{-1}$ . Constant  $c$  takes into account the mass and the specific surface area of the adsorbent in the column and the standard states of adsorbates in the mobile and adsorbed states [20].

## 4. Results

### 4.1. Finite concentration region

In this study, the adsorption isotherms of *n*-hexane, cyclohexane and benzene on 4A were determined in the finite concentration region and thermodynamic parameters in this region were calculated from the plots of  $\Delta G/T$  versus  $1/T$  at constant coverages according to Eq. (7).

The isotherms are drawn in Figs. 1–3. The plots of  $\Delta G/T$  versus  $1/T$  are given in Figs. 4–6 and thermodynamic parameters (average values) are tabulated in Table 2.

Elution peaks with a sharp front and a tailing (diffuse rear boundary) give Langmuir type isotherms (type I according to

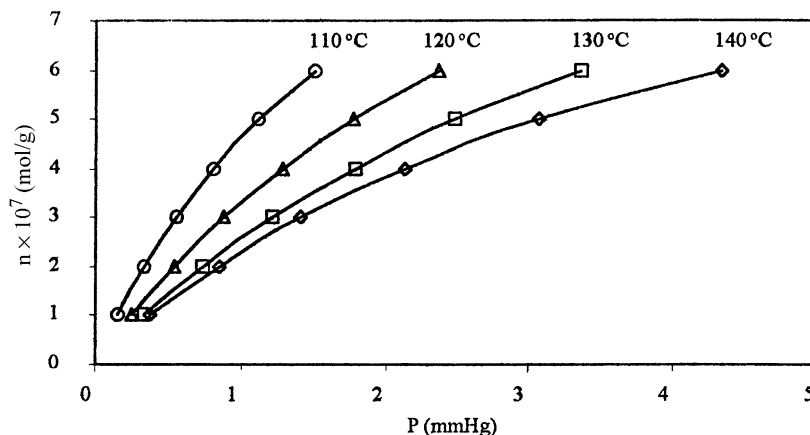


Fig. 1. Adsorption isotherms of *n*-hexane on 4A at various temperatures.

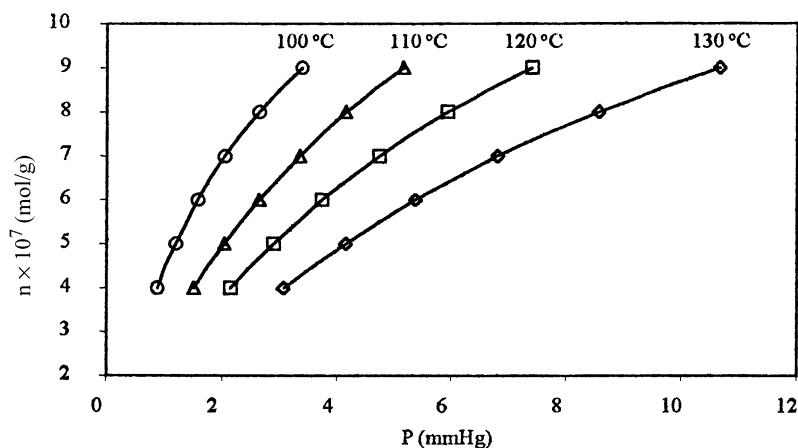


Fig. 2. Adsorption isotherms of cyclohexane on 4A at various temperatures.

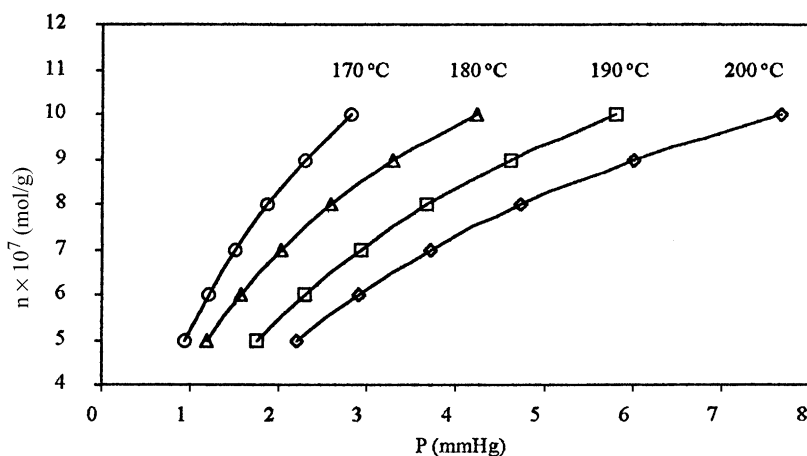


Fig. 3. Adsorption isotherms of benzene on 4A at various temperatures.

Brunauer’s classification) [1]. The same result was observed in this study and the adsorption data were analyzed according to the Langmuir equation [6].

$$\frac{p}{n} = \frac{p}{n_m} + \frac{1}{n_m b} \tag{16}$$

where  $p$  is the partial pressure of probe in mmHg,  $n$  the amount of probe adsorbed per unit weight of adsorbent at  $p$  in  $\text{mol g}^{-1}$ ,  $n_m$  the amount adsorbed in the high pressure limit when monolayer covers the entire surface in  $\text{mol g}^{-1}$  and  $b$  the adsorption equilibration constant in  $\text{mmHg}^{-1}$  ( $n_m$  and  $b$  are called as Langmuir constants).

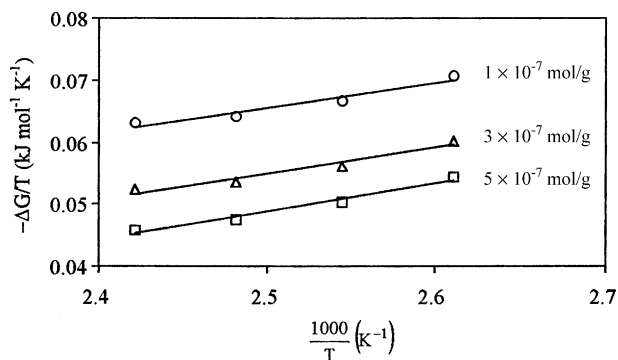


Fig. 4. The plot of  $\Delta G/T$  versus  $1/T$  for  $n$ -hexane adsorption on 4A at various coverages.

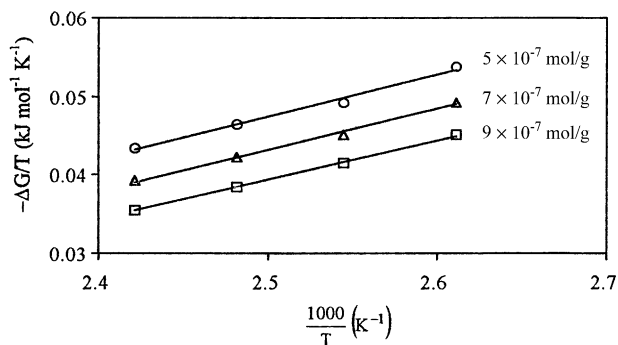


Fig. 5. The plot of  $\Delta G/T$  versus  $1/T$  for cyclohexane adsorption on 4A at various coverages.

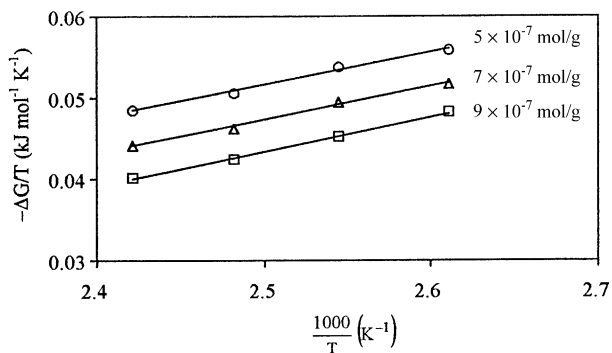


Fig. 6. The plot of  $\Delta G/T$  versus  $1/T$  for benzene adsorption on 4A at various coverages.

Table 2  
Thermodynamic parameters for the adsorption of the probes on 4A

Probe	$-\Delta H_{st}$ (kJ mol $^{-1}$ )	$-\Delta S$ (kJ mol $^{-1}$ K $^{-1}$ )	$-\Delta G$ (kJ mol $^{-1}$ )
<i>n</i> -Hexane	42.564	$52.015 \times 10^{-3}$	21.862
Cyclohexane	49.791	$83.276 \times 10^{-3}$	17.480
Benzene	54.711	$72.503 \times 10^{-3}$	21.505

Table 3  
Langmuir constants and correlation coefficients for the adsorption of the probes on 4A

Probe	$T$ (K)	$n_m$ ( $\times 10^6$ mol g $^{-1}$ )	$b$ ( $\times 10^2$ mmHg $^{-1}$ )	Correlation coefficient
<i>n</i> -Hexane	383	1.403	49.608	0.9999
	393	1.451	29.819	0.9997
	403	1.375	23.069	0.9998
	413	1.277	20.876	0.9974
Cyclohexane	373	1.567	39.679	0.9996
	383	1.683	21.385	0.9946
	393	1.971	15.217	0.9945
	403	1.677	10.479	0.9926
Benzene	443	2.075	33.347	0.9986
	453	1.786	31.414	0.9979
	463	1.804	21.657	0.9998
	473	1.727	18.224	0.9997

The plot of  $p/n$  against  $p$  should give a straight line of slope  $1/n_m$  and the intercept  $1/n_m b$ . Straight lines were fitted to the points by the method of least squares which had highly significant correlation coefficients ( $r$ ), indicating a good fit to the Langmuir equation. The Langmuir constants and correlation coefficients are tabulated in Table 3.

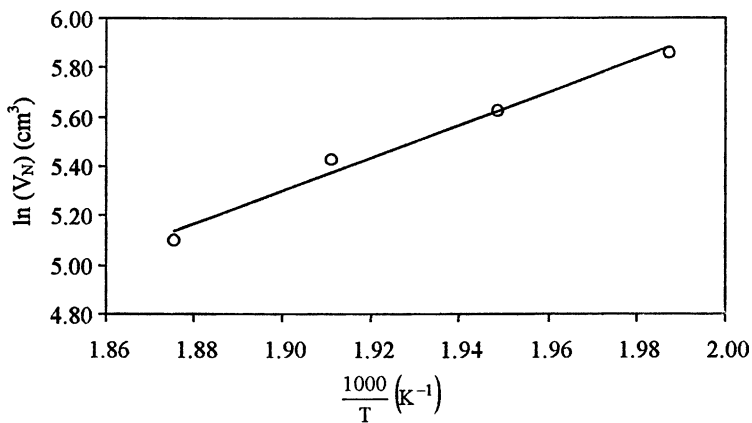


Fig. 7. The plot of  $\ln V_N$  versus  $1/T$  for *n*-hexane adsorption on 13X.

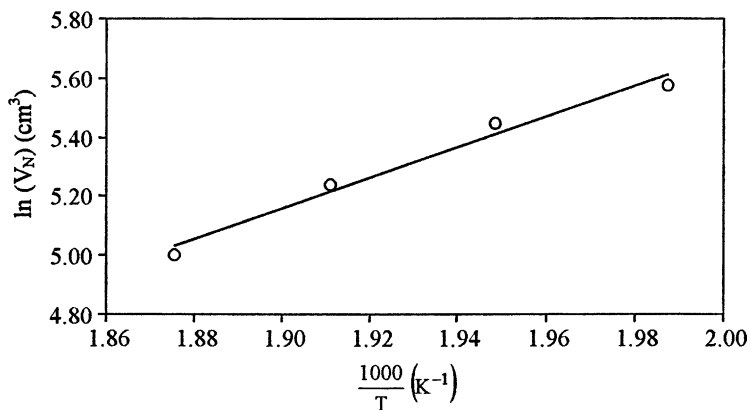


Fig. 8. The plot of  $\ln V_N$  versus  $1/T$  for cyclohexane adsorption on 13X.

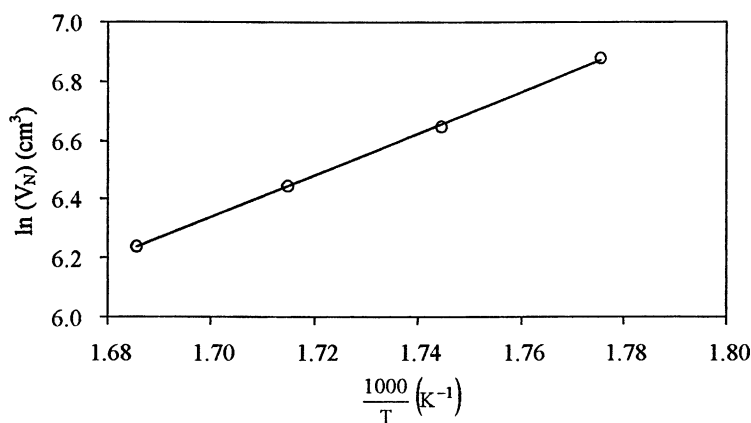


Fig. 9. The plot of  $\ln V_N$  versus  $1/T$  for benzene adsorption on 13X.

Table 4  
Thermodynamic parameters for the adsorption of the probes on 13X

Probe	$-\Delta H_{st}$ (kJ mol <sup>-1</sup> )	$-\Delta S$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$-\Delta G$ (kJ mol <sup>-1</sup> )
<i>n</i> -Hexane	59.676	$61.149 \times 10^{-3}$	27.988
Cyclohexane	47.283	$38.777 \times 10^{-3}$	27.189
Benzene	63.787	$47.578 \times 10^{-3}$	36.278

#### 4.2. Infinite dilution region

In this study, thermodynamic parameters for adsorption of *n*-hexane, cyclohexane and benzene on 13X were determined in the infinite dilution region.

Differential enthalpy of adsorption ( $\Delta H$ ) and entropy of adsorption ( $\Delta S$ ) were calculated from the slopes and intercepts of the plots of  $\ln V_N$  versus  $1/T$  according to Eq. (12). These plots were given in Figs. 7–9.

Isosteric enthalpies of adsorption ( $\Delta H_{st}$ ) were calculated by Eq. (13) and checked by the values found from the plots of  $\ln(V_N/T)$  against  $1/T$ . Free energies of adsorption ( $\Delta G$ ) were calculated from the following equation:

$$\Delta G = \Delta H_{st} - T_{av} \Delta S$$

Thermodynamic parameters in the infinite dilution region are tabulated in Table 4.

### 5. Discussion

It is evident from the data that benzene exhibits more negative  $\Delta H$  than the corresponding values for aliphatic and alicyclic hydrocarbons with the same carbon number (i.e., *n*-hexane and cyclohexane). The more negative the  $\Delta H$ , the greater the interaction between the adsorbate and the adsorbent. This stronger adsorption of benzene on 4A and 13X was attributed to the contribution of the special interaction between the Na<sup>+</sup> adsorption sites and the  $\pi$  electrons of the benzene ring.

Kiselev [21] has found more negative  $\Delta H$  for benzene than for *n*-hexane on 13X (infinite dilution). Papaioannou et al. [22] have studied the adsorption of the benzene, cyclohexane, cyclohexene and methylcyclopentane on X and Y zeolites by GC and they have found that the adsorption strength on NaX and NaY decreases according to the following sequence: benzene > cyclohexene > cyclohexane  $\approx$  methylcyclopentane. Milonjic and Kopečni [16] have investigated the adsorption properties of thermally treated silicas by GC method and have found that benzene exhibits more negative  $\Delta H$  than the corresponding values for hexane and cyclohexane due to the specific interaction between the benzene ring and the SiO<sub>2</sub> surface.

According to the classification of Kiselev and Yashin [2] silica is an adsorbent of the second type due to the free hydroxyl groups on the surface, OH groups linked to silicon acts as a weak acid, with the H partly protonized. So, silica can interact specifically with the molecules containing  $\pi$  electrons (group B adsorbates). Due to its three  $\pi$  bonds, benzene is strongly attached to the surface of the silica.

The walls in the channels of porous zeolites consist of Si–O and Al–O tetrahedra. The coordination number of Al (four) exceeds the valency (three), so the Al–O tetrahedra have excess negative charge, which is distributed over the numerous Al–O–Si bonds within the framework, whereas the compensating positive charge is localized on exchangeable cations, usually of small radius. This charge distribution is somewhat similar to that on a hydroxylated acidic oxide, e.g., silica, so we expect generally similar behavior and zeolites are adsorbents of the second type.

If the surface of adsorbent bears no functional groups or exchangeable ions, these adsorbents interact largely non-specifically with the adsorbate molecules. These adsorbents are classified as type I adsorbents by Kiselev, and graphitized carbon black is a typical example.

The “heats” of adsorption of benzene and cyclohexane are less than that of *n*-hexane on graphitized carbon black [2]. (The heat of adsorption is written as “*q*” and is defined as  $q = -\Delta H$ .) This sequence of heats of adsorption

corresponds to the sequence of nonspecific (mainly dispersion) interactions. The order of release of these six-membered compounds is mainly due to differences in spatial structure. There is only nonspecific interaction with the adsorbent, which is almost independent of the dipole or quadrupole moment and of the local charge distribution in the bonds or links.

Similar results were obtained for active carbons. Grajek et al. [23] have measured the heats of adsorption of some hydrocarbons including *n*-hexane, cyclohexane and benzene on some active carbons and heats of adsorption sequence has been found to be; *n*-hexane > cyclohexane > benzene.

The studies on the heats of adsorption of the studied probes on the zeolites in the literature generally belong to 13X. Some of the  $q_{st}$  data available are as follows: 13X—*n*-hexane: 45.19 kJ mol<sup>-1</sup> [24], 58.4 kJ mol<sup>-1</sup> [25], 61.51 kJ mol<sup>-1</sup> [21], 63.60 kJ mol<sup>-1</sup> [26]; 13X—benzene: 64.85 kJ mol<sup>-1</sup> [24], 75.31 kJ mol<sup>-1</sup> [21].

4A presents pores of free diameter 4 Å, therefore 4A pores cannot be invaded by the studied probes. These molecules may still be adsorbed on the external surface. The external surface of 4A corresponds to the zone of meso-porosity, characterized by extra-crystalline pores of larger dimensions than the micro-pores. Zeolite 13X presents pores of free diameter 7.5 Å, so that the probe molecules can be sorbed into the cavity. The heats of adsorption of *n*-hexane and benzene on 13X were found to be higher than those on 4A.

The contribution of the interaction between the  $\pi$  electrons of the benzene ring and zeolite surface can be evaluated considering  $\Delta(\Delta G)$  values. For the pair benzene–cyclohexane,  $\Delta(\Delta G) = \Delta G_{\text{benzene}} - \Delta G_{\text{cyclohexane}}$ . This value represents the difference in the interaction ability between benzene and cyclohexane with zeolite surface. The values of  $\Delta(\Delta G)$  for 13X and 4A are -9.09 and -4.03, respectively. Interaction of the benzene ring with 13X was found to be stronger in comparison to the interaction with 4A. Comparison of the pair benzene–*n*-hexane leads to the same conclusion.

$q_{st}$  and  $(-\Delta G)$  sequences for 13X have been found to be benzene > *n*-hexane > cyclohexane, but the same sequence for  $q_{st}$  and  $(-\Delta G)$  was not obtained for 4A. The sequence obtained for 13X is similar to that obtained for silica surfaces [16].

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