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Evaluation of the thermodynamic parameters for the adsorption of some *n*-alkanes on A type zeolite crystals by inverse gas chromatography

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Abstract

Inverse gas chromatography (IGC) has been used to evaluate the adsorption parameters (ΔH, ΔS and ΔG) of some *n*-alkanes (n-C_5 to n-C_8) on 3A, 4A and 5A zeolites. The adsorption parameters of the probes on 4A were determined in the finite concentration region, and those on 3A and 5A were determined in the infinite dilution region. It was found that the adsorption isotherms for 4A conform with the Langmuir equation and the adsorption parameters increase linearly with increasing carbon number of the probes for 3A, 4A and 5A. Thermodynamic compensation effect between the adsorption enthalpy and entropy was observed. Also, heats of adsorption for 3A were found to be higher than those for 5A.

Keywords: Inverse gas chromatography; Heat of adsorption; Adsorption thermodynamic parameters; A type molecular sieve

1. Introduction

Zeolites offer excellent opportunities for separations which are otherwise difficult to achieve. Particularly, the isolation of normal alkanes—a classical problem in petroleum chemistry—can be very efficiently carried out by Molecular Sieves Type 5A. The understanding of the adsorption phenomena at temperatures relevant to zeolite catalysis is essential in the comprehension and the modeling of reaction kinetics on zeolites. For obvious reasons, the adsorption of *n*-alkanes on zeolites has received a lot of interest [1].

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, adsorption enthalpy, entropy and free energy can be measured by IGC [2–4].

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). In the finite concentration region, retention volumes are dependent upon the adsorbate concentration in the gas phase. In the infinite dilution region injection of minor amounts of adsorbates to approach zero surface coverage, permitting neglect of lateral interactions between adsorbed molecules and retention volumes are independent of injection sample size.

The experimental data published in the literature from methane to *n*-decane on 5A zeolites were compiled by Silva and Rodrigues [5]. However, little information is available in the literature on the adsorptive properties of 3A and 4A.

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 [6,7]. The objectives of this study were

(a) to construct the adsorption isotherms (adsorption isotherms were constructed for the adsorption of *n*-alkanes on 4A);
(b) to determine the basic thermodynamic parameters (ΔH, ΔG, ΔS) in the finite concentration region (4A was studied in the finite concentration 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 (mmHg^{-1})
F_a	volumetric flow rate
ΔG	free energy of adsorption
ΔH_d	differential enthalpy of adsorption
ΔH_{st}	isosteric enthalpy of adsorption
j	James–Martin correction factor
k	retention factor
K_s	surface partition coefficient (m)
n	amount adsorbed ($\mathrm{mol\,g^{-1}}$)
n_m	maximum amount adsorbed ($\mathrm{mol\,g^{-1}}$)
p	partial pressure of adsorbate
p^0	standard pressure (1 atm)
$p_{s/g}$	standard state vapor pressure of adsorbate
q_{st}	isosteric heat of adsorption ($q_{st} = -\Delta H_{st}$)
R	universal gas constant
S	specific surface area of adsorbent ($\mathrm{m^2\,g^{-1}}$)
ΔS	entropy of adsorption
t_m	dead time
t_R	retention time of the probe
T	column temperature (K)
T_a	ambient temperature (K)
V_N	net retention volume
w	mass of adsorbent (g)

Greek letters

θ	fractional coverage of adsorbent
π_s	two-dimensional surface pressure

(c) to determine these parameters in the infinite dilution region (3A and 5A were studied in the infinite dilution region to investigate the effect of the pore size of the zeolite on the adsorption).

2. Experimental

2.1. Materials and columns

Three adsorbents were used: molecular sieve 3A (Greyhound), molecular sieve 4A (Alltech), and molecular sieve 5A (Greyhound). The surface area of adsorbents was determined by the nitrogen adsorption (BET method) with Micromeritics-Flowsorb II 2300. The measurements were performed in the laboratories of the TÜBİTAK (Scientific and Technical Research Council of Turkey) Research Institute.

A 1.5 m long, 5.35 mm i.d. stainless steel column was used in this work. The characteristics of the column and adsorbents are given in Table 1.

The adsorbates (probes) used were *n*-pentane, *n*-hexane, *n*-heptane and *n*-octane (Merck, reagent grade) and were employed without further purification. Linear alkanes have a molecular diameter of 0.42 nm [8].

Table 1
Description of the column and adsorbents

Adsorbent	Particle size (μm)	Packing weight of adsorbent (g)	Specific surface area ($\mathrm{m^2\,g^{-1}}$)	Column temperature (K)	Carrier gas flow rate ($\mathrm{ml\,min^{-1}}$)
3A	147–175	10.622	21.7	483–513	30
4A	147–175	14.004	22.0	383–413	10–30
5A	147–175	5.000	39.0	593–623	10

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 in the finite concentration region and helium was used in the infinite dilution region 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 carrier 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 [2–4]. 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 [2]: (a) The isotherm should not have a point of inflection; otherwise, at least two peaks are needed to construct the isotherm. (b) 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:

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

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

$$n = \frac{1}{wRT}\int_0^p V_N \,\mathrm{d}p \tag{2}$$

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

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

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

where t_R is the probe retention time, t_m the retention time of the mobile phase (hold-up 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 is 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 [9], and Huber and Keulemans [10].

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

The thermodynamic parameters in this region can be calculated from the following equations [11–13]:

$$\Delta H_{st} = R\left[\frac{\partial \ln p}{\partial(1/T)}\right]_\theta \tag{4}$$

$$\Delta G = RT \ln \frac{p}{p^0} \tag{5}$$

$$\Delta S = \frac{\Delta H_{st} - \Delta G}{T} \tag{6}$$

where ΔH_{st} is the "isosteric" enthalpy of adsorption, the subscript θ indicates quantities measured at a given value θ (i.e. fractional coverage) and p^0 is the standard pressure (1 atm).

Eq. (4) is the so-called as Clausius–Clapeyron equation in IGC studies and according to Eq. (5), ΔG 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 [2,12].

3.2.2. Infinite dilution region

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.

The thermodynamic parameters in this region can be calculated according to the following equations [14–16]:

$$\Delta H_d = -R\frac{\mathrm{d}\ln K_s}{\mathrm{d}(1/T)} \tag{7}$$

$$\Delta G = -RT \ln\left(\frac{K_s p_{s/g}}{\pi_s}\right) \tag{8}$$

$$\Delta S = \frac{\Delta H_d - \Delta G}{T} \tag{9}$$

where ΔH_d is the "differential" enthalpy of adsorption, K_s the partition coefficient and $p_{s/g}$ the adsorbate vapor pressure in the gaseous standard state having a value of 101.3 kN/m^2 (1 atm), π_s is the reference two-dimensional surface pressure whose standard state is arbitrary. The standard reference state was taken as π_s equal to 0.338 mJ/m^2 proposed by de Boer [17].

Eq. (7) is analogue to the van't Hoff equation and the partition coefficient K_s is related to the retention volume V_N by

$$K_s = \frac{V_N}{wS} \tag{10}$$

where w is the mass of adsorbent in the column and S is the specific surface area of adsorbent.

4. Results and discussion

4.1. Finite concentration region

In this study, elution peaks were asymmetrical (one example is given in Fig. 1), hence the adsorption isotherms of n-pentane, n-hexane, n-heptane and n-octane on 4A were determined in the finite concentration region and thermodynamic parameters in this region were calculated according to Eqs. (4)–(6).

The isotherms are drawn in Figs. 2–5. The plots of $\ln p$ versus $1/T$ (adsorption isosteres) are given in Figs. 6–9 and thermodynamic parameters (average values) are tabulated in Table 2 (these parameters are average values for the temperature range studied).

Elution peaks with a sharp front and a tailing (diffuse rear boundary) give Langmuir type isotherms (type I according to Brunauer's classification) [2]. The same result was observed in this study and the adsorption data were analyzed according to the Langmuir equation [18]:

$$\frac{p}{n} = \frac{p}{n_m} + \frac{1}{n_m b} \tag{11}$$

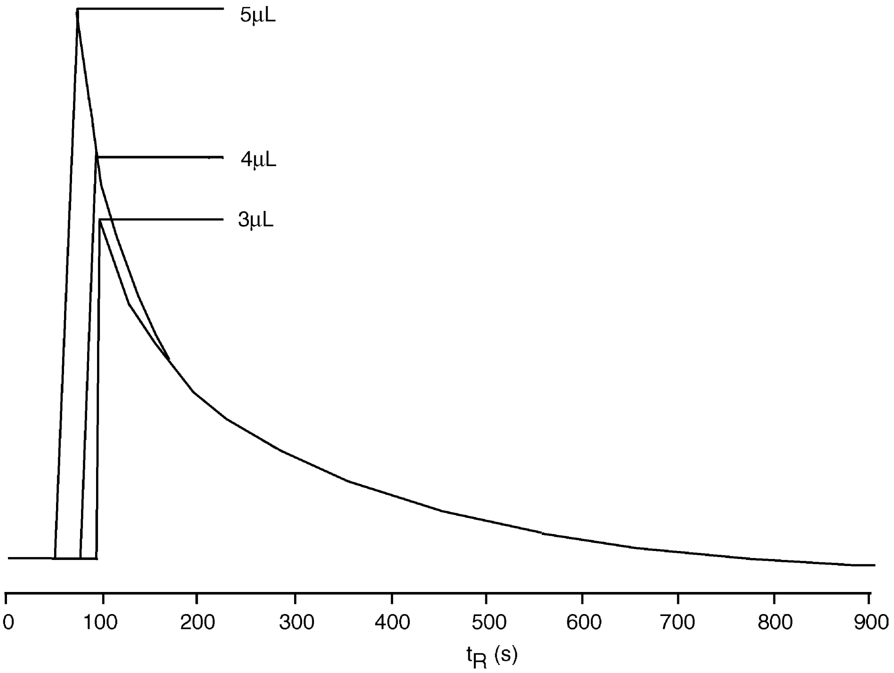

Fig. 1. Elution peaks obtained for different amounts of *n*-hexane on 4A at 110 °C.

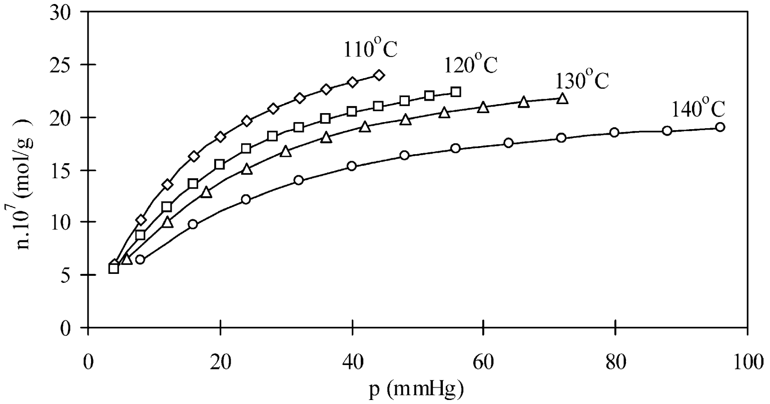

Fig. 2. Adsorption isotherms of *n*-pentane on 4A at various temperatures.

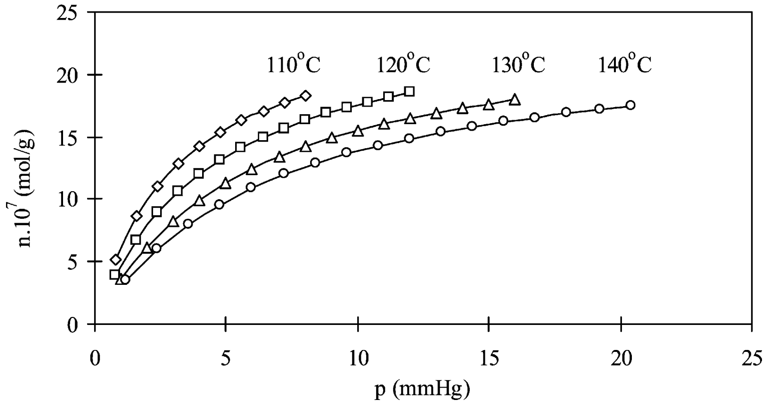

Fig. 3. Adsorption isotherms of *n*-hexane on 4A at various temperatures.

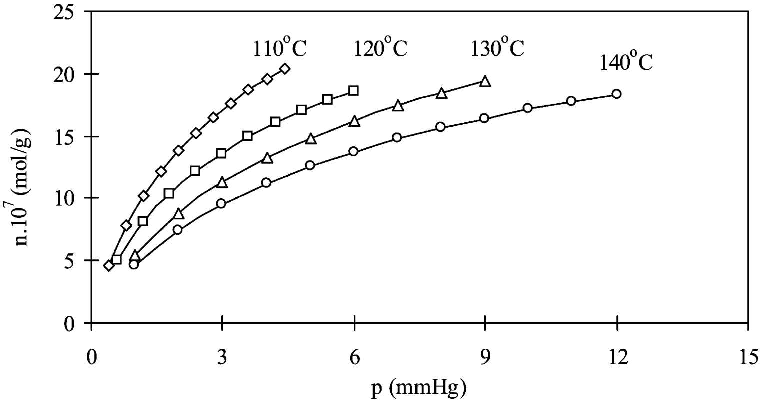

Fig. 4. Adsorption isotherms of *n*-heptane on 4A at various temperatures.

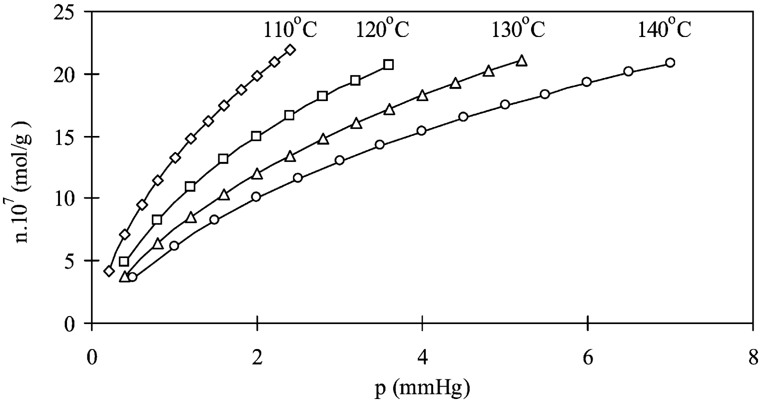

Fig. 5. Adsorption isotherms of *n*-octane on 4A at various temperatures.

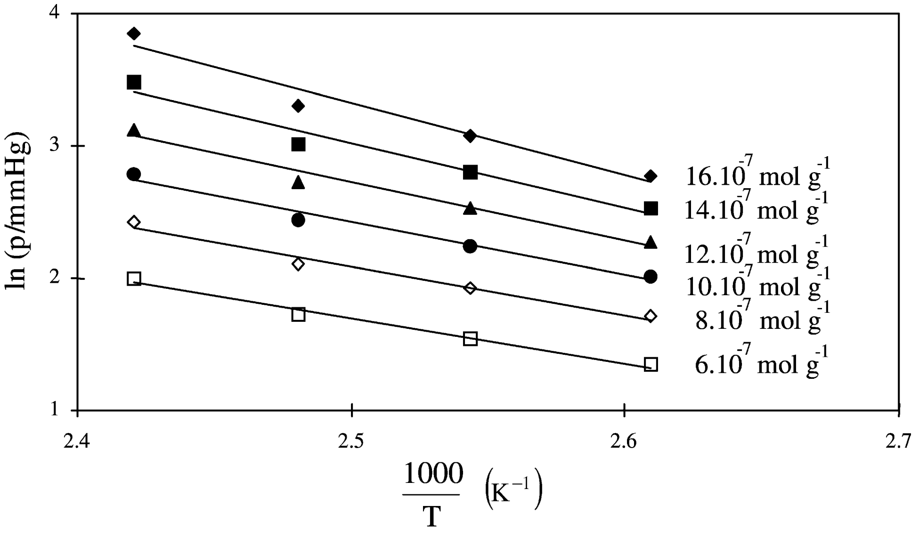

Fig. 6. Adsorption isosteres of *n*-pentane on 4A at various coverages.

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

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

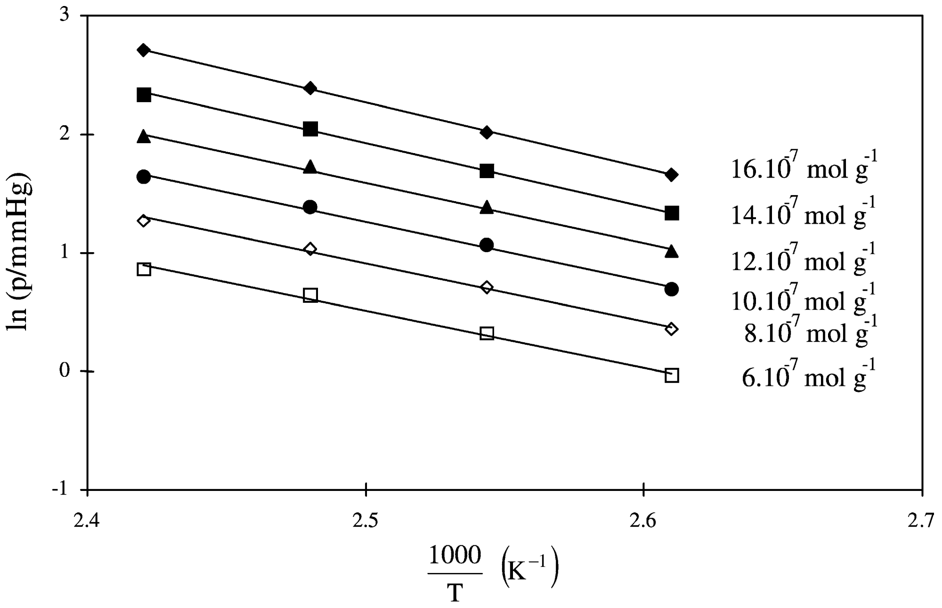

Fig. 7. Adsorption isosteres of *n*-hexane on 4A at various coverages.

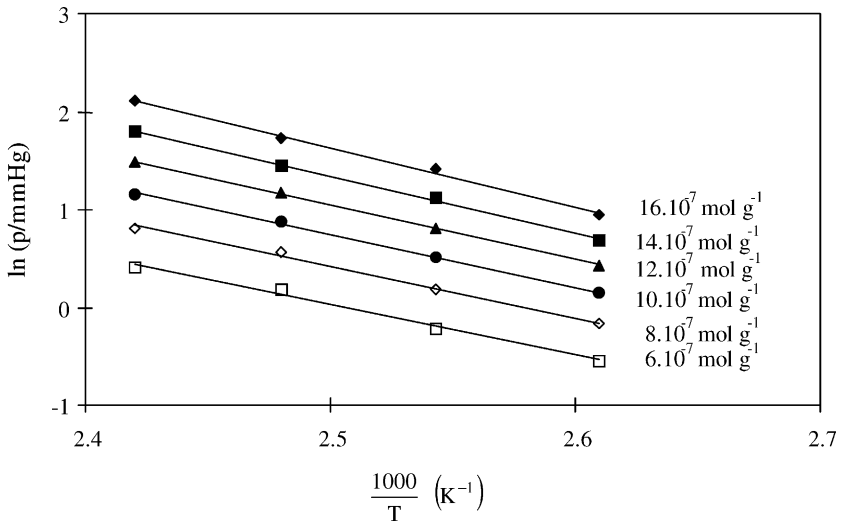

Fig. 8. Adsorption isosteres of *n*-heptane on 4A at various coverages.

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.

The thermodynamic parameters for adsorption on 4A are plotted against the carbon number of probes in Fig. 10. The values of $-\Delta H$, $-\Delta S$ and $-\Delta G$ values increase with increasing carbon number and that the linear increase was obtained. This study confirms the linear increase of $-\Delta H$, $-\Delta S$ and $-\Delta G$ with carbon number as reported in other studies [1,5,8,11,19–21].

Fig. 11 shows the existence of so-called "thermodynamic compensation effect", i.e. a linear dependence of ΔS on ΔH. Thermodynamic compensation effect between the adsorption enthalpy and entropy of *n*-alkanes was observed in different studies, indicating that the stronger adsorption of longer *n*-alkanes is accompanied by a higher loss of degrees of freedom [1,22–25]. A molecular interpretation of the linear dependence of ΔS on ΔH was given by Katsanos et al. [22] by assuming a heterogeneous surface and exponential distribution of adsorption sites with respect to the energy.

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})
n-Pentane	35.61	55.07×10^{-3}	13.69
n-Hexane	42.50	62.90×10^{-3}	17.46
n-Heptane	46.22	67.68×10^{-3}	19.28
n-Octane	48.95	70.03×10^{-3}	21.08

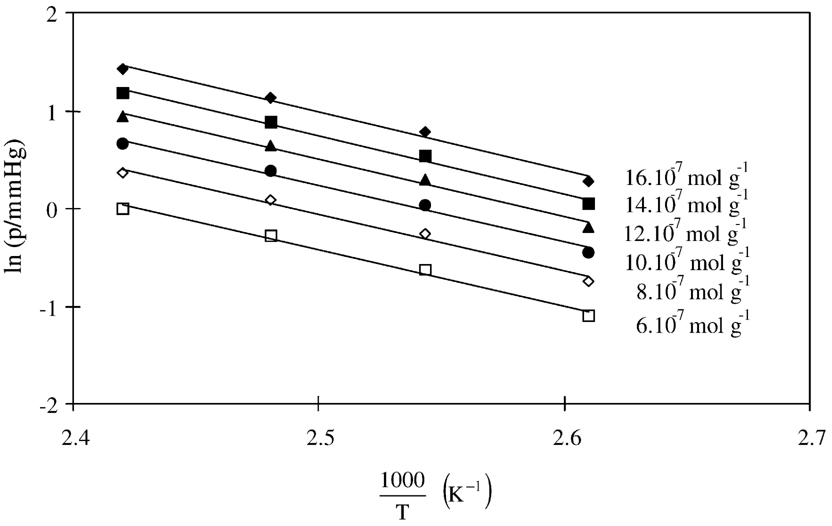

Fig. 9. Adsorption isosteres of *n*-octane on 4A at various coverages.

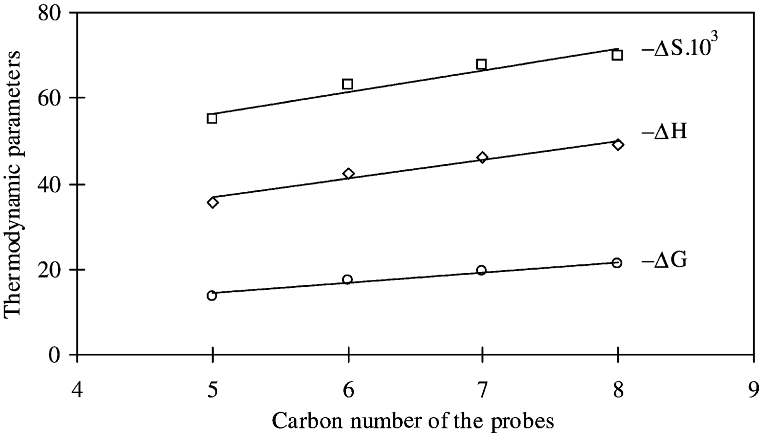

Fig. 10. Relationship between thermodynamic parameters and carbon number of the probes for 4A.

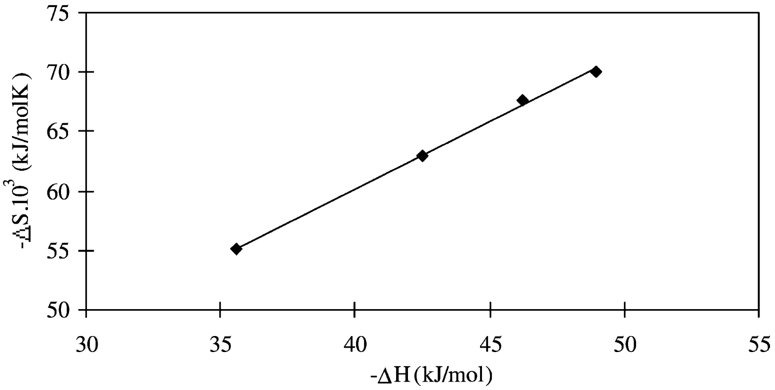

Fig. 11. The dependence of ΔS on ΔH for 4A.

It was found that the "*b*"-values (adsorption equilibrium constant) increase with increasing carbon number of the probes at the same temperatures for 4A. Because of the adsorption equilibrium constant depends on the strength of the adsorbate–adsorbent interaction, this result is in agreement with the dependency of isosteric heats of adsorption with carbon number of the probes for 4A (isosteric "heat" of adsorption $= -\Delta H_{\mathrm{st}}$).

Isosteric heat of adsorption depends on the extent of surface coverage, mainly because of the adsorbate–adsorbate

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

Probe	T (K)	$n_m \times 10^7$ (mol g^{-1})	$b \times 10^2$ (mmHg^{-1})	Correlation coefficient
n-Pentane	383	33.821	5.629	0.9992
	393	29.805	5.371	0.9994
	403	28.338	4.775	0.9995
	413	23.233	4.684	0.9996
n-Hexane	383	25.414	32.212	0.9999
	393	25.426	22.413	0.9999
	403	24.478	17.176	0.9999
	413	23.260	14.633	0.9999
n-Heptane	383	31.340	40.636	0.9966
	393	27.007	35.327	0.9955
	403	28.930	21.832	0.9968
	413	25.451	20.329	0.9973
n-Octane	383	36.396	59.493	0.9907
	393	34.857	38.853	0.9940
	403	35.293	26.901	0.9881
	413	33.731	21.709	0.9895

interaction. Isosteric heat of adsorption generally decreases steadily with increasing coverage, asymptotically approaching the heat of liquefaction. In this paper, a slight increase was found in isosteric heat of adsorption with surface coverage (Table 4). Analogue results have been reported in the literature [3,11,26–29]. This discrepancy has been attributed to surface heterogeneity [4], attractive adsorbate–adsorbate interactions [30], or changing of the structure of the adsorbed phase [31]. Some authors claimed that such results can usually be seen in adsorbate–adsorbent systems where chemisorption appears [26].

4.2. Infinite dilution region

In this study, thermodynamic parameters for adsorption of n-hexane, n-heptane and n-octane on 3A and 5A were determined in the infinite dilution region and thermodynamic parameters in this region were calculated according to Eqs. (7)–(9).

At high elution temperatures, major portion of the retention is due to the gas hold-up and carrier gas viscosity may increase with temperature. Therefore, the retention factor (k) decreases with temperature. Retention factor is the ratio of the time a compound spends in the stationary phase to the time spent in the mobile phase as the column is traversed and is defined as

$$k = \frac{t_R - t_m}{t_m} \tag{12}$$

Practically at high temperatures GC analysis should not be performed when $k \ll 1$ [21], because the adsorption model loses its validity. Retention factors of the probes decrease with decreasing carbon number in a homologous series. In this study, $k \ll 1$ was found for n-pentane and adsorption data for n-pentane were not included into the evaluation.

Table 4
Isosteric heat of adsorption of the probes on 4A

$n \times 10^7$ (mol g^{-1})	q_{st} (kJ mol^{-1})			
	n-Pentane	n-Hexane	n-Heptane	n-Octane
6	28.50	40.00	42.98	48.15
8	30.46	40.64	43.90	48.40
10	32.91	41.46	45.03	48.70
12	36.02	42.55	46.44	49.04
14	40.08	44.05	48.26	49.45
16	45.67	46.28	50.69	49.95
Average	35.61	42.50	46.22	48.95

Table 5
Thermodynamic parameters for the adsorption of the probes on 3A

Probe	$-\Delta H_d$ (kJ mol^{-1})	$-\Delta S$ (kJ mol^{-1} K^{-1})	$-\Delta G$ (kJ mol^{-1})
n-Hexane	29.84	40.40×10^{-3}	9.71
n-Heptane	42.81	55.40×10^{-3}	15.22
n-Octane	56.15	71.08×10^{-3}	20.74

The plots of $\ln K_s$ versus $1/T$ (van't Hoff plots) are given in Fig. 12 and thermodynamic parameters (average values) are tabulated in Tables 5 and 6 (these parameters are average values for the temperature range studied).

The thermodynamic parameters for adsorption on 3A and 5A are plotted against the carbon number of the probes in Fig. 13. The values of $-\Delta H$, $-\Delta S$ and $-\Delta G$ values increase linearly with increasing carbon number of the probes, and also thermodynamic compensation effect between the adsorption enthalpy and entropy was observed for 3A and 5A as in the finite concentration region for 4A (Fig. 14).

One of the objectives of this study were to investigate the dependency of the adsorption enthalpy to the pore size of the zeolite, and it was found that the heats of adsorption of the probes increase with decreasing pore size of the zeolite (i.e. heats of adsorption for 3A were found to be higher than those for 5A).

There are similar results for this dependence in the literature. Stach et al. [32] showed that the isosteric adsorption heat of n-decane on zeolites increases exponentially with decreasing pore size for diameters below 100 Å. It was shown by McCullen et al. [33] that the adsorption heat of n-butane increases linearly with decreasing pore size of aluminophosphates. Kiselev et al. [34] investigated the effect of the geometrical structure of silicagels and found that the narrowing of pores increases the heats of adsorption, particularly for

Table 6
Thermodynamic parameters for the adsorption of the probes on 5A

Probe	$-\Delta H_d$ (kJ mol^{-1})	$-\Delta S$ (kJ mol^{-1} K^{-1})	$-\Delta G$ (kJ mol^{-1})
n-Hexane	27.54	30.56×10^{-3}	8.95
n-Heptane	39.12	41.64×10^{-3}	13.79
n-Octane	51.79	54.51×10^{-3}	18.64

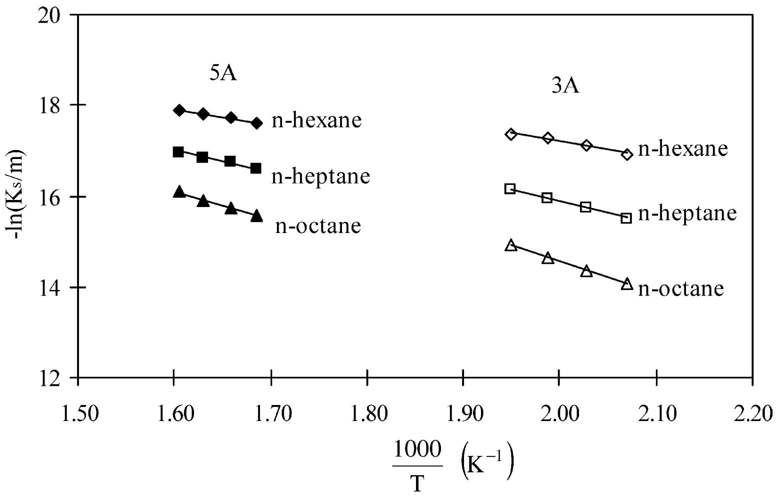

Fig. 12. The plots of $\ln K_s$ vs. $1/T$ for the adsorption of the probes on 3A and 5A.

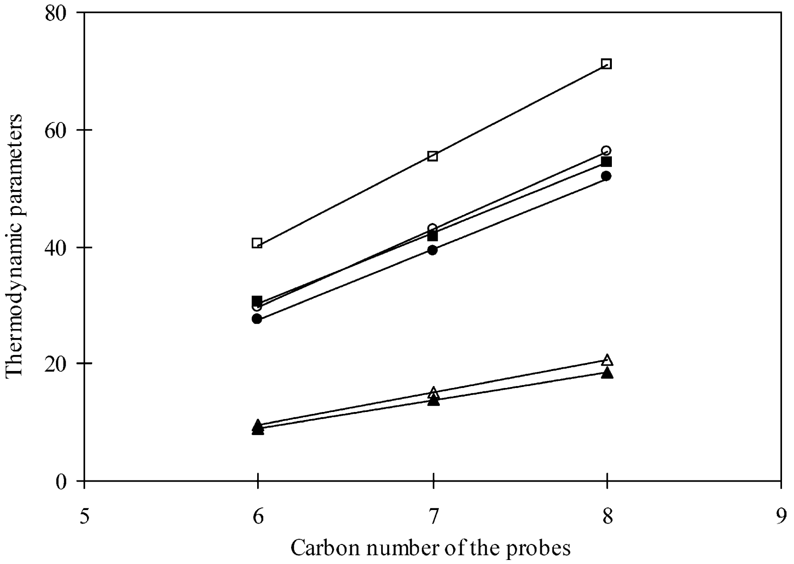

Fig. 13. Relationship between thermodynamic parameters and carbon number of the probes: (○) $-\Delta H$ for 3A; (□) $-\Delta S \times 10^3$ for 3A; (△) $-\Delta G$ for 3A; (●) $-\Delta H$ for 5A; (■) $-\Delta S \times 10^3$ for 5A; (▲) $-\Delta G$ for 5A.

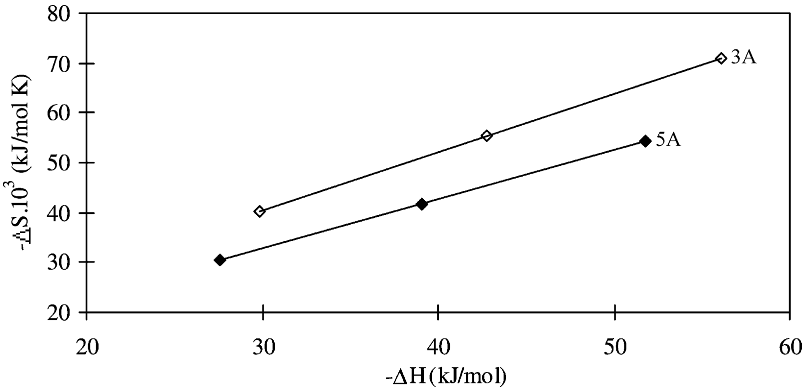

Fig. 14. The dependence of ΔS on ΔH for 3A and 5A.

high alkanes. Eder and Lercher [35] studied the adsorption of light alkanes on the acidic zeolites and found that the heat of adsorption of alkanes increases with decreasing pore size.

It has been suggested that the heat of adsorption is a function of the framework density, which usually increases with decreasing pore size [35]. The higher framework densities lead to an increase in the strength of interaction between zeolite lattice and sorbed alkanes.

Acknowledgements

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