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EVALUATION OF THE HEAT OF ADSORPTION OF SOME n-ALKANES ON ALUMINA AND ZEOLITE BY INVERSE GAS CHROMATOGRAPHY

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ABSTRACT

The isosteric heat of adsorption of some n-alkanes (n-C_5 to n-C_8) on some adsorbents(activated alumina, natural zeolite(clinoptilolite) and 13X molecular sieve) were evaluated by inverse gas chromatography using the temperature dependence of adsorption.

The isosteric heat of adsorption of the probes on alumina and clinoptilolite were determined in the finite concentration region, and those on 13X were determined in the infinite dilution region.

It was found that the adsorption isotherms for alumina and clinoptilolite conform with the Langmuir equation, and the isosteric heats of adsorption increase linearly with increasing carbon number of the probes for alumina and 13X.

Key Words: Inverse gas chromatography; Heat of adsorption; n-Alkane adsorption; Alumina; Zeolite.

INTRODUCTION

It is well known today that gas chromatography (GC) offers many possibilities for physicochemical measurements, some of which lead to very precise and accurate results with relatively cheap instrumentation and a simple experimental setup. Many physicochemical properties such as activity coefficient (1), diffusion coefficient (2), Henry's constants (3), surface acidity (4), surface area (5), and adsorption enthalpy, entropy, and free energy (6,7) can be measured by GC.

Gas solid chromatography (GSC) is called inverse gas chromatography (IGC) (8) when applied to the investigation of solid surface properties. This method is based on the study of interactions of gas molecules of known properties with solid surface. 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. Wherever comparison has been made between data obtained by the GC and conventional procedures, aggrement has been encouragingly good.

Heat of adsorption can be determined either directly, by calorimetry, or indirectly, from the temperature dependence of adsorption. In this study, heat of adsorption was evaluated by IGC using the latter method.

The objectives of this study were: a) to construct the adsorption isotherms for n-pentane, n-hexane, n-heptane, and n-octane on alumina and clinoptilolite by finite concentration GC method, b) to determine the isosteric heat of adsorption of the probes on alumina and clinoptilolite in the finite concentration region, c) to determine the isosteric heat of adsorption of the probes on 13X in the infinite dilution region, and d) to investigate the dependency of the isosteric heat of adsorption on the carbon number of the probes.

EXPERIMENTAL

Materials and Columns

Three adsorbents were used: Activated alumina F-1 (Altech), natural zeolite (clinoptilolite from the Bigadiç/TURKEY region), and molecular sieve 13X (Altech). These were named as AL, CL, and 13X, respectively. The surface area of adsorbents was determined by the nitrogen adsorption (B.E.T. 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-meter-long, 5.35 mm i.d. stainless steel column was used in this work. The characteristics of the columns and adsorbents used in this work are given in Table 1.

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Table 1. Description of the Columns and Adsorbents

Adsorbent	Particle Size (Mesh)	Specific Surface Area (m^2/g)	Packing Weight of Adsorbent (g)	Column Temp. (K)	Carrier Gas Flow Rate (ml/min)
AL	80–100	252	19.76	458–488	30–60
CL	60–80	31	12.15	353–383	10–60
13X	80–100	210	1.48	468–568	30–80

The adsorbates (probes) used were n-pentane, n-hexane, n-heptane, and n-octane (Merck, reagent grade) and were employed without further purification.

Instrumentation

The chromatographic experiments were performed with a Unicam 610 gas chromatograph equipped with a thermal conductivity detector. Peak areas and retention times were recorded on a 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).

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 volume."

Calculations

Adsorption Isotherms

In order to obtain adsorption isotherms from the shape of a single gas chromatographic peak, "finite concentration" GC techniques were used (9,10). When adsorption takes place at finite surface coverages, the isotherms are generally nonlinear and hence retention volumes are dependent upon the adsorbate concentration in the gas phase. In addition a nonlinear 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 (10): 1) the isotherm should not have a point of inflection; otherwise, at least two peaks are needed to

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construct the isotherm; and 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.

$$V_N = \text{w.R.T.}\left(\frac{\partial n}{\partial p}\right)_T \tag{1}$$

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

$$n = \frac{1}{\text{w.R.T}} \int_0^p V_N \cdot \text{dp} \tag{2}$$

The V_N/w.R.T 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:

$$V_N = j \cdot V_R' \cdot \frac{T}{T_f} \tag{3}$$

where V_R' is the adjusted retention volume, j is the pressure gradient correction factor, T is the column temperature (K) and T_f is the temperature (K) at which the flowmeter is calibrated (room temperature).

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, Huber, and Keulemans (11,12).

In this study chromatographic peaks recorded for evaluation of adsorption isotherms for AL and CL 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.

Heats of Adsorption

Finite Concentration Region

In this region, the heat of adsorption is calculated using isosteres obtained from adsorption data (i.e., using plots of partial pressures (lnp) versus temperatures (1/T) at constant coverages). The isosteric heat of adsorption at constant coverage (q_{st}) can be calculated from the following equation:

$$\left[\frac{\partial \text{lnp}}{\partial\left(\frac{1}{\text{T}}\right)}\right]_\theta = \frac{\Delta \text{H}_{st}}{\text{R}} \tag{4}$$

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where ΔH_{st} is the differential isosteric enthalpy of adsorption ($q_{st} = -\Delta H_{st}$), and the subscript θ indicates quantities measured at a given value θ (= fractional coverage).

For this equation to be valid the process must be unvariant. This means that Equation (4) can be applied only for constant concentration of adsorbate on the surface, that is, constant θ. If adsorption-equilibrium data are available at different temperatures, the slopes of ln p vs. 1/T curves at constant θ can be used with Equation (4) to calculate ΔH_{st} (13–15).

Infinite Dilution Region(Henry's Law Region)

Chromatographic peaks recorded in this region were virtually symmetrical, with retention times and thus retention volumes being essentially independent of injection sample size. This result indicates that, under the experimental condition employed in the present study, adsorption data obeyed Henry's law.

The isosteric heat of adsorption may be obtained from the temperature dependence of partition coefficient (K) according to the following equation (analogue to the Van't Hoff equation):

$$\frac{d \ln K}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H_{st}}{R} \tag{5}$$

$$K = \frac{\text{weight of adsorbate per gram of adsorbent}}{\text{weight of adsorbate per cc of gas at 0°C}}$$

$$= V_g \text{ (specific retention volume)}$$

V_g was calculated from the following relationship

$$V_g = \frac{V_N}{w} \cdot \frac{273}{T} \tag{6}$$

where V_N is the net retention volume, w is the mass of adsorbent, and T is the column temperature (10,13,16–19).

In this paper, the heat of adsorption of AL and CL were determined in finite concentration region, and the heat of adsorption of 13X was determined in infinite dilution region.

RESULTS AND DISCUSSION

Finite Concentration Region

In this study, the adsorption isotherms of n-pentane, n-hexane, n-heptane, and n-octane on alumina and clinoptilolite were determined by finite concentration method and isosteric heat of adsorption was calculated from the isosteres.

The isotherms are drawn in Figs. 1–8. The isosteric heats of adsorption are tabulated in Table 2.

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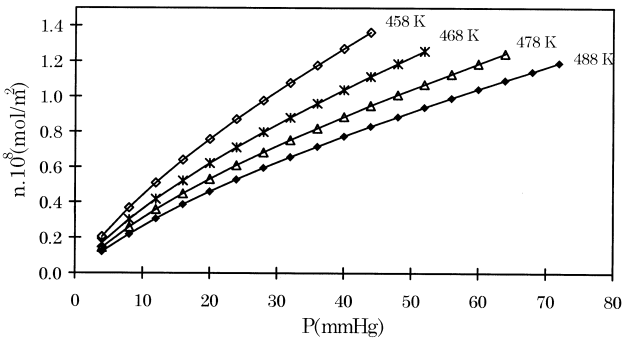

Figure 1. Adsorption isotherms of n-pentane on AL at various temperatures.

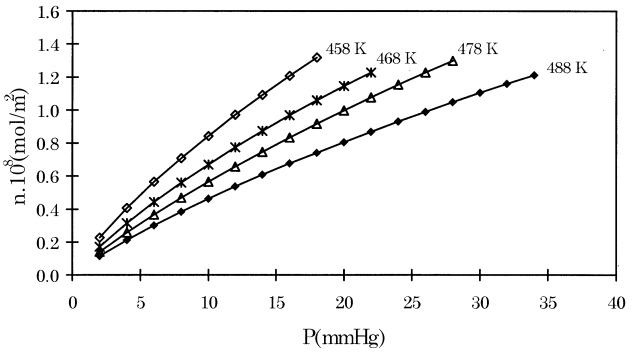

Figure 2. Adsorption isotherms of n-hexane on AL at various temperatures.

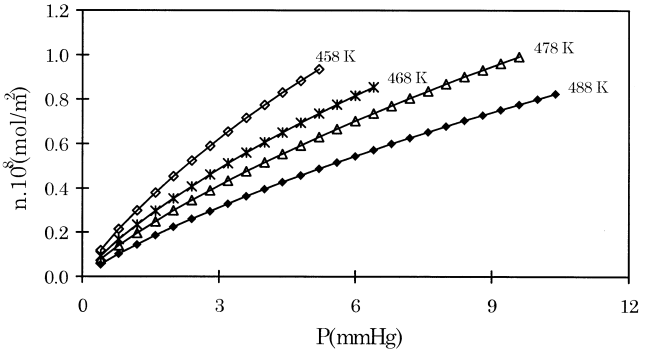

Figure 3. Adsorption isotherms of n-heptane on AL at various temperatures.

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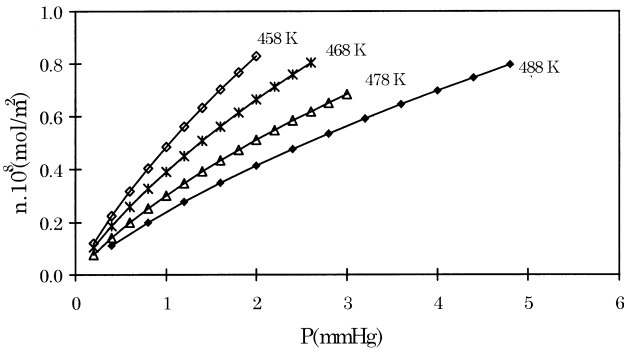

Figure 4. Adsorption isotherms of n-octane on AL at various temperatures.

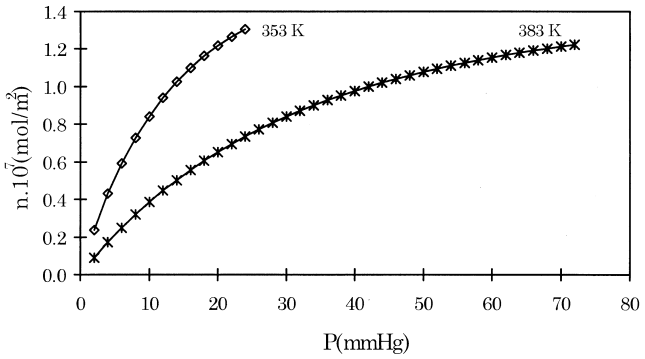

Figure 5. Adsorption isotherms of n-pentane on CL at various temperatures.

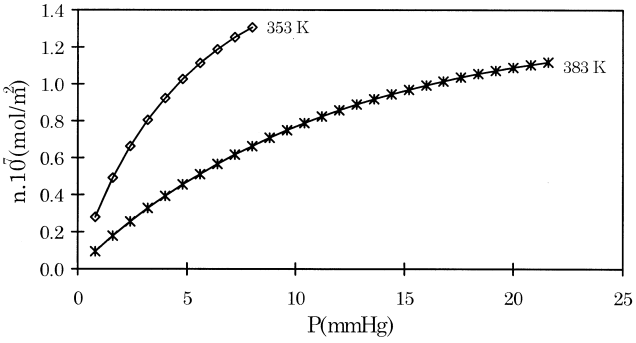

Figure 6. Adsorption isotherms of n-hexane on CL at various temperatures.

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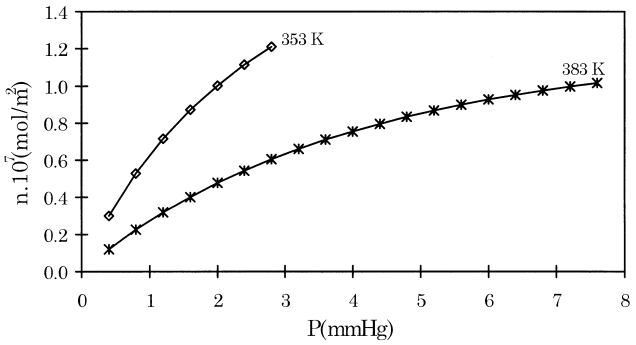

Figure 7. Adsorption isotherms of n-heptane on CL at various temperatures.

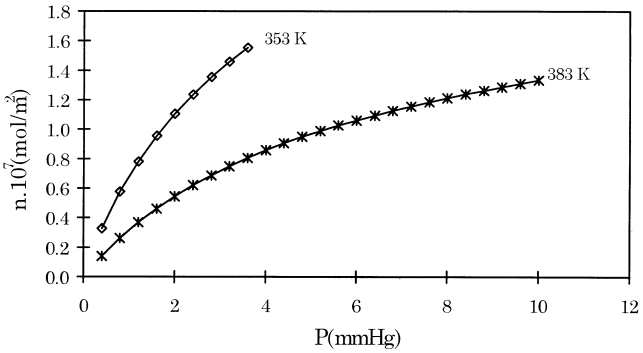

Figure 8. Adsorption isotherms of n-octane on CL at various temperatures.

Isosteric heat of adsorption depends on the extent of surface coverage, mainly because of the adsorbate-adsorbate interaction. In physical adsorption the effect usually appears as a lateral attraction, ascribable to general van der Waals forces acting between adsorbate molecules. Such attractive forces are relatively weak in comparison to chemisorption energies, and it appears that in chemisorption, repulsion effects may be more important (20).

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 2). Analogue results have been reported in the literature (9,14,21–24).

This discrepancy has been attributed to surface heterogeneity (25), attractive adsorbate-adsorbate interactions (26), or changing of the structure of the adsorbed phase (27). Some authors claimed that such results can usually be seen in adsorbate-adsorbent systems where chemisorption appears (21).

Elution peaks with a sharp front and a tailing (diffuse) rear boundary give Langmuir type isotherms (type I according to Brunauer's classification) (10). The same result was observed in this study, and the adsorption data were analyzed according to the Langmuir equation (28,29).

$$\frac{p}{n} = \frac{p}{n_m} + \frac{1}{n_m \cdot b} \tag{7}$$

where p is the partial pressure of probe in mm Hg, n is the amount of probe adsorbed per unit weight (or per unit surface) of adsorbent at p, n_m is the amount adsorbed in the high pressure limit when monolayer covers the entire surface in $mol \cdot g^{-1}$ (or in $mol \cdot m^{-2}$), and b is the adsorption equilibration constant in mm Hg^{-1} (n_m and b are called as Langmuir constants).

The plot of p/n against p should give a straight line of slope $1/n_m$ and the intercept $1/n_m \cdot b$. Straight lines were fitted to the points by the method of least squares, which had highly significant correlation coefficient (r), indicating a good fit to the Langmuir equation. The Langmuir constants and correlation coefficients are tabulated in Tables 3 and 4.

The isosteric heat of adsorption (average) of probes on alumina are plotted against the carbon number of probes in Fig. 9. The isosteric heat of adsorption in-

Table 2. Isosteric Heat of Adsorption of n-Alkanes on AL and CL

	q_{st} ($kj \cdot mol^{-1}$)			
$n \cdot 10^7 (mol \cdot g^{-1})$	n-pentane	n-hexane	n-heptane	n-octane
AL				
5	35.90	44.83	49.85	51.15
10	37.82	45.52	52.17	54.73
15	40.20	46.35	55.39	59.57
20	43.22	47.37	60.11	66.50
Aver.	39.28	46.02	54.38	57.99
CL				
5	38.90	44.75	37.21	34.65
10	39.37	45.04	38.37	35.68
15	39.94	45.39	39.77	36.89
20	40.63	45.82	41.51	38.33
Aver.	39.71	45.25	39.21	36.39

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Table 3. Langmuir Constants and Correlation Coefficients for n-Alkane Adsorption on AL

Probe	T (K)	$n_m \cdot 10^6$ (mol·g^{-1})	$n_m \cdot 10^8$ (mol·m^{-2})	$b \cdot 10^2$ (mm Hg^{-1})	Corr. Coeff.
n-Pentane	458	8.132	3.227	1.589	0.9872
	468	7.187	2.852	1.439	0.9851
	478	6.688	2.654	1.290	0.9844
	488	6.597	2.618	1.089	0.9847
n-Hexane	458	8.660	3.436	3.342	0.9881
	468	8.389	3.329	2.583	0.9897
	478	9.657	3.832	1.772	0.9837
	488	8.104	3.216	1.712	0.9858
n-Heptane	458	5.896	3.340	12.377	0.9887
	468	5.105	2.026	10.899	0.9856
	478	5.625	2.232	7.847	0.9784
	488	5.194	2.061	6.130	0.9848
n-Octane	458	6.227	2.471	24.796	0.9955
	468	4.867	1.931	26.266	0.9846
	478	4.129	1.639	23.041	0.9920
	488	4.811	1.909	14.304	0.9877

creases with increasing C number and that the linear increase was obtained for alumina. In literature there are similar results for silica (6), for microporous carbon (30), carbon fibers (4), graphitized carbon black, macroporous silicagel (9), zeolites (9, 31), and Pt/Al_2O_3 catalyst (32,33).

Table 4. Langmuir Constants and Correlation Coefficients for n-alkane Adsorption on CL

Probe	T (K)	$n_m \cdot 10^6$ (mol·g^{-1})	$n_m \cdot 10^7$ (mol·m^{-2})	$b \cdot 10^2$ (mm Hg^{-1})	Corr. Coeff.
n-Pentane	353	6.874	2.218	6.079	0.9998
	383	5.892	1.901	2.590	0.9994
n-Hexane	353	6.900	2.226	17.804	0.9999
	383	6.096	1.966	6.316	0.9993
n-Heptane	353	7.650	2.468	34.228	0.9998
	383	5.388	1.738	18.934	0.9997
n-Octane	353	9.129	2.945	30.463	0.9992
	383	6.396	2.063	17.884	0.9998

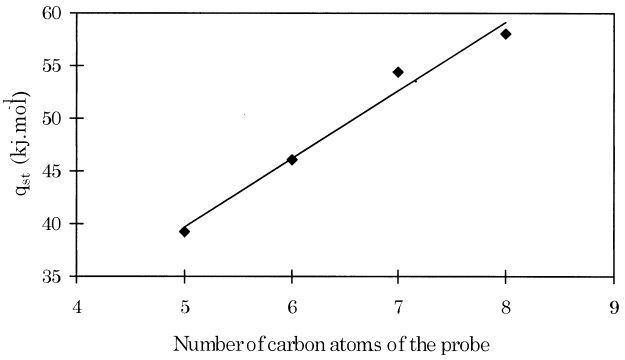

Figure 9. Isosteric heats of adsorption of n-alkanes on AL as a function of the number of carbon atoms in the alkane chain.

In this paper, similar results were not obtained for clinoptilolite. It was attributed to the "retarted exchange" of the probes (34,35). In order to ensure reliable data comparison, it is essential to provide clean adsorbent surfaces prior to the adsorption experiments. Hence thermal cleaning was performed by passing the carrier gas for 4 h at 573 K between two successive injections, but it was concluded that part of the surface, or it may be a fraction of capillaries (clinoptilolite has a pore diameter in the range 0,40 to 0,70 nm) were still occupied with adsorbate that diminishes the adsorption of subsequently injected adsorbate.

It was found that the "*b*" values (adsorption equilibrium constant) increase with increasing carbon number of the probes at the same temperatures for alumina and clinoptilolite (except for n-octane for clinoptilolite). 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 alumina.

In order to characterize the adsorbate-adsorbent interaction, Henry's constants were determined as follows;

Langmuir equation can be rearranged into

$$n = \frac{n_m \cdot b \cdot p}{1 + b \cdot p} \tag{8}$$

In the initial region of the isotherms because $b \cdot p << 1$, the Langmuir equation is close to the Henry equation (21).

$$n = n_m \cdot b \cdot p = K_H \cdot p \tag{9}$$

where K_H is the Henry's constant (in $\text{mol} \cdot \text{g}^{-1} \cdot \text{mm Hg}^{-1}$). The derived values of K_H are shown in Table 5.

Table 5. Henry's Law Constants for n-Alkane Adsorption on AL and CL

	$K_H \cdot 10^7$ (mol·g^{-1}·mm Hg^{-1})					
	AL				CL	
Probe	458 K	468 K	478 K	488 K	353 K	383 K
n-Pentane	1.292	1.034	0.863	0.719	4.179	1.526
n-Hexane	2.894	2.167	1.712	1.387	12.284	3.850
n-Heptane	7.297	5.564	4.414	3.184	26.182	10.202
n-Octane	15.442	12.783	9.514	6.882	27.810	11.439

A comparison of the Henry's constants shows that the adsorption strength decreases in the following sequences: n-octane > n-heptane > n-hexane > n-pentane for both of alumina and clinoptilolite.

Infinite Dilution Region

In this study, the isosteric heats of adsorption of n-pentane, n-hexane, n-heptane, and n-octane on 13X were determined in the infinite dilution region.

The isosteric heats of adsorption(q_{st}) of the probes on 13X in the infinite dilution region were calculated from the slopes of the plots of lnK against 1/T (Fig. 10) according to Eq. (5).

The elution peaks obtained for 13X became broader as the *C* number of the probes increased on account of slow exchange in the fine pores. These symmetri-

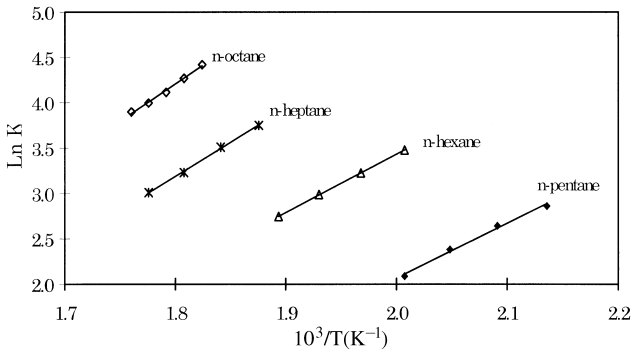

Figure 10. Relationship between ln K and reciprocal temperature for n-alkanes on 13X at infinite dilution.

Table 6. q_{st} Values for n-Alkane Adsorption on AL, CL, and 13X in Different Studies

	q_{st} for AL ($kj \cdot mol^{-1}$)		q_{st} for CL ($kj \cdot mol^{-1}$)		q_{st} for 13X ($kj \cdot mol^{-1}$)	
Adsorbate (Probe)	Present Study	In the Literature	Present Study	In the Literature	Present Study	In the Literature
n-Pentane	39.28 $n_{av} = 12.5.10^{-7}$ mol/g $\theta_{av} = 0.17$	—	39.71 $n_{av} = 12.5.10^{-7}$ mol/g $\theta_{av} = 0.20$	—	50.17 $\theta \rightarrow 0$*	51.92 (9) $\theta \rightarrow 0$ 54.40 (40) calorimetrically $n = 1.10^{-3}$ mol/g
n-Hexane	46.02 $n_{av} = 12.5.10^{-7}$ mol/g $\theta_{av} = 0.14$	30.00 (39) $\theta \rightarrow 0$ 42.30 (15) $n = 35.10^{-7}$ mol/g	45.25 $n_{av} = 12.5.10^{-7}$ mol/g $\theta_{av} = 0.19$	—	53.27 $\theta \rightarrow 0$	45.22 (41) $\theta \rightarrow 0$ 61.55 (9) $\theta \rightarrow 0$ 63.60 (24) calorimetrically $n = 1.10^{-3}$ mol/g
n-Heptane	54.38 $n_{av} = 12.5.10^{-7}$ mol/g $\theta_{av} = 0.23$	—	39.21 $n_{av} = 12.5.10^{-7}$ mol/g $\theta_{av} = 0.19$	—	62.27 $\theta \rightarrow 0$	—
n-Octane	57.99 $n_{av} = 12.5.10^{-7}$ mol/g $\theta_{av} = 0.25$	—	36.39 $n_{av} = 12.5.10^{-7}$ mol/g $\theta_{av} = 0.16$	—	67.93 $\theta \rightarrow 0$	78.80 (42) calorimetrically $n = 1.10^{-3}$ mol/g

* Infinite dilution ($\theta \rightarrow 0$).

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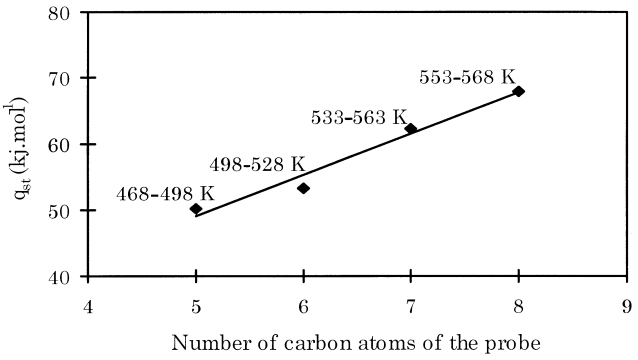

Figure 11. Isosteric heats of adsorption of n-alkanes on 13X as a function of the number of carbon atoms in the alkane chain.

cal but broadened peaks correspond to processes deviating so far from equilibrium. Hence, it would be expected thermodynamic parameters calculated from such peaks via the equilibrium theory to differ from those measured calorimetrically, and that the deviations would increase with the molecular size of the probe (9,36–38). Keibal et al. (38) found that gas chromatographic adsorption heat for zeolites of types CaA, CaX, and NaX(13X) began to deviate from the static ones as the size and adsorption energy of the hydrocarbons increased.

The average isosteric heats of adsorption of probes on 13X are plotted against the *C* number of hydrocarbons in Fig. 11. It was found that the isosteric heats of adsorption increase linearly with increasing *C* number (The column temperature was increased with the molecular size of the probe to reduce the broadening of the peaks).

The results obtained for isosteric heats of adsorption in different studies are summarized in Table 6.

In this study, the dependency of the adsorption heat to the heterogeneity of the adsorbing surface was not investigated, but in recent years this occupies an important domain in adsorption studies (43).

CONCLUSIONS

Heat of adsorption can be determined either directly by calorimetry, indirectly from the temperature dependence of adsorption isosteres as in the finite concentration GC method, or from the temperature dependence of partition coefficient as in the infinite dilution GC method.

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When a linear distribution region is accessible at low adsorbate concentrations, enthalpy of adsorption may be readily derived from the variation in specific retention volumes with temperature. When the distribution isotherms are nonlinear, enthalpy of adsorption can be calculated using plots of partial pressures versus temperatures at constant coverages (isosteres).

Calorimetry gives the more accurate results, but measures only integral heats. Indirect method yields differential heats but is less accurate because it relies on measuring a small difference between quantities at different temperatures. For heats at zero coverage, infinite dilution GC is more reliable method because it requires no extrapolation of data over a region where the heat can be very sensitive to small changes in coverage.

In this paper the adsorption data for AL and CL—obtained in finite concentration region—were found to conform with the Langmuir isotherm, and comparison of the Henry's constants showed that the adsorption strength increases with increasing C number of probes for AL and CL. Also, it was found that the isosteric heats of adsorption increase linearly with increasing C number of probes for AL and 13X(infinite dilution region for 13X).

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