



# Evaluation of the thermodynamic parameters for the adsorption of some hydrocarbons on alumina and molecular sieves 3A and 5A by inverse gas chromatography

Ceyda Bilgiç\*, Ayşegül Aşkın

*Department of Chemical Engineering, Faculty of Engineering and Architecture, Osmangazi University, 26480 Eskişehir, Turkey*

## 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 organic compounds (*n*-hexane, cyclohexane and benzene) on some adsorbents (activated alumina, and molecular sieves 3A and 5A). It was found that benzene exhibits more negative  $\Delta H$  than for *n*-hexane and cyclohexane on molecular sieves 3A and 5A and alumina. Also, interactions of the benzene with molecular sieves 3A and 5A were found to be stronger than that on alumina. On the contrary, interactions of the hexane with alumina were found to be stronger than those on molecular sieves 3A and 5A.

© 2003 Elsevier B.V. All rights reserved.

**Keywords:** Thermodynamic parameters; Molecular sieves; Inverse gas chromatography; Heat of adsorption; Adsorption; Alumina; Zeolites; Hexane; Cyclohexane; Benzene; Hydrocarbons

## 1. Introduction

Gas–solid chromatography (GSC), when applied to the investigation of solid surface properties, is usually called inverse gas chromatography (IGC). This method is based on the study of physical adsorption of appropriate molecular probes by means of chromatographic (dynamic) experiments [1].

In contrast to static methods, dynamic systems utilize a flowing gas system. The most common flow methods are IGC, gravimetric instruments, and permeability measurement systems.

The principle of dynamic gravimetric systems is the measurement of the amount of solute adsorbed from a flowing gas stream using a microbalance [2].

In comparison to static sorption equipment, the main benefits of the dynamic sorption technique are shorter measurement time and a wider range of experimental possibilities [3].

Compared to other techniques (static measurements), IGC has attracted a lot of attention because of its simplicity and the rich information provided [4]. IGC may be experimentally configured for finite or infinite dilution concentrations of the adsorbate [5].

In the finite concentration region, retention volumes depend on the adsorbate concentration in the gas phase. In the infinite dilution conditions of the IGC method, a few molecules are injected into the column to approach zero surface coverage. Under this condition the lateral interactions between the adsorbed molecules on the surface can be neglected and the thermodynamic functions depend only on the adsorbate–adsorbent interactions. Adsorption can be

\*Corresponding author. Tel.: +90-222-239-2850; fax: +90-222-239-3613.

E-mail address: [cbilgic@ogu.edu.tr](mailto:cbilgic@ogu.edu.tr) (C. Bilgiç).

considered to take place in the linear part of the adsorption isotherms (Henry's law region). The attainment of the Henry's law region is indicated by the symmetry of the chromatographic peaks and by the constancy of the retention times measured over a significant range of the sample sizes. Hence, the net retention volumes for a given adsorbate are independent of its gas phase concentration. From the measured retention volume of a given probe passing through the column, different thermodynamic parameters can be deduced, such as free energy of adsorption, adsorption enthalpy and entropy, dispersive and polar components of surface energy and even surface morphology at the molecular level [4,6–8].

In this study, the adsorption of some hydrocarbons (probes), each representing a class of organic compounds (*n*-hexane, cyclohexane and benzene) on two molecular sieves (5A, 3A) and alumina (AL) were investigated at 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 synthetic and natural zeolites [9,10].

The objective of this study was to determine the basic thermodynamic parameters ( $\Delta H$ ,  $\Delta G$ ,  $\Delta S$ ) for the adsorption of some hydrocarbons (probes), each representing a class of organic compounds (*n*-hexane, cyclohexane and benzene) on two molecular sieves (5A and 3A) and AL at infinite dilution region by IGC.

## 2. Experimental

### 2.1. Materials and columns

Three adsorbents were used: activated alumina F-1 (Alltech), molecular sieve 3A (Greyhound), and molecular sieve 5A (Greyhound). The surface area

of the adsorbents was determined by nitrogen adsorption (BET method) with a Micromeritics-Flow-sorb II 2300 instrument. The measurements were performed in the laboratories of the Tübitak (Scientific and Technical Research Council of Turkey) Research Institute.

A 2.00 m×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*-hexane, cyclohexane, and benzene (Merck, reagent grade) and were employed without further purification.

### 2.2. Instrumentation

The chromatographic experiments were performed with a Unicam 610 gas chromatograph equipped with a flame ionization detector. 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 James–Martin gas compressibility 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

Chromatographic peaks recorded in infinite dilution region were symmetrical with retention times and thus retention volumes being essentially independent of the injected amount. This result indicates

Table 1  
Description of the columns and adsorbents

Adsorbent	Particle size (mesh)	Specific surface area (m <sup>2</sup> /g)	Packing mass of adsorbent (g)	Column temperature (K)	Carrier gas flow-rate (ml/min)
AL	80–100	252	26.47	513–543	40
3A	80–100	21.7	28.60	643–673	50, 15, 60
5A	80–100	39	19.16	613–643	15, 60

that, under the experimental conditions employed, adsorption data obeyed Henry's law.

The net retention volume,  $V_N$  can be expressed in terms of changes in thermodynamic functions, like enthalpy and entropy of adsorption [11,12]:

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

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

The net retention volume ( $V_N$ ) can be calculated from the following relation [7,13]:

$$V_N = (t_R - t_m) \cdot F_a \cdot \frac{T}{T_a} \cdot j \quad (2)$$

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

By determining  $V_N$  at various temperatures, one can calculate  $\Delta H$  (differential enthalpy of adsorption) 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.

$\Delta H$  which is calculated by Eq. (1) is the “differential” enthalpy of adsorption (it is not the “isosteric”) [11]. An analogous way for calculating differential enthalpy of adsorption by GSC has been described by Milonjić and Kopećni [14].

It is known for a long time [12,14] that the differential enthalpy of adsorption ( $\Delta H$ ) is related to the isosteric enthalpy of adsorption ( $\Delta H_{st}$ ) by the equation:

$$|\Delta H_{st}| = |\Delta H| + RT_{av} \quad (3)$$

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  $1/T$  which the slope is  $[-(\Delta H_{st}/R)]$  [7,8,14,15].

#### 4. Results

In this study, thermodynamic parameters for adsorption of *n*-hexane, cyclohexane and benzene on alumina, molecular sieves 3A and 5A 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. (1). These plots are given in Figs. 1–3.

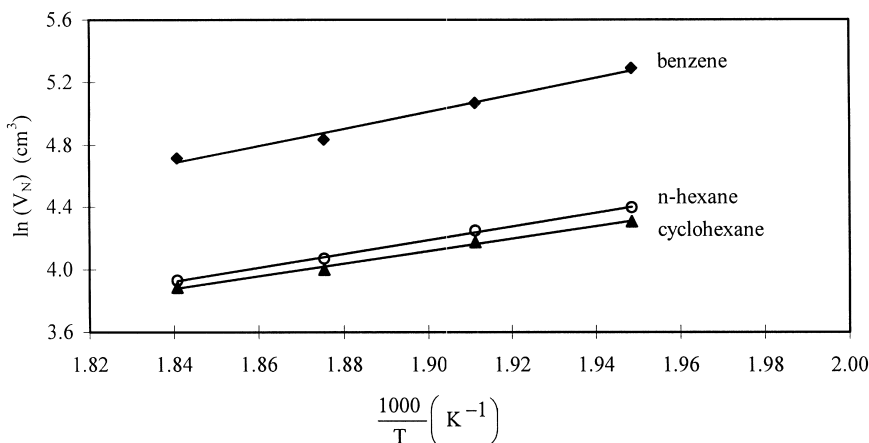


Fig. 1. The plot of  $\ln V_N$  versus  $1/T$  for *n*-hexane, cyclohexane, benzene adsorption on AL.

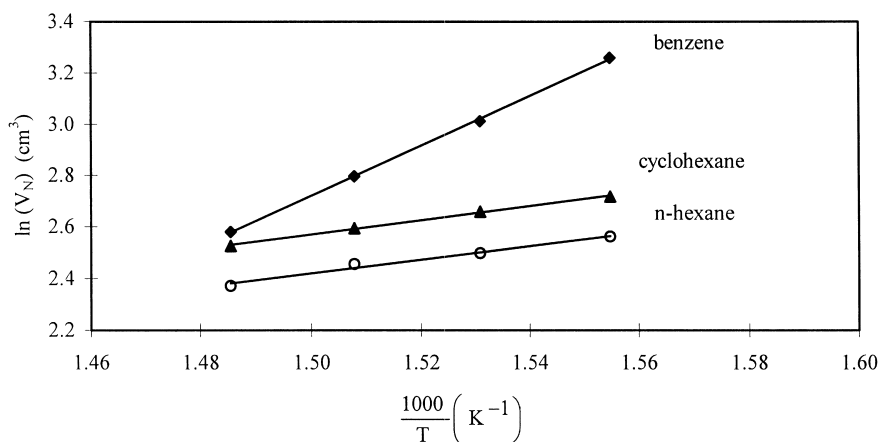


Fig. 2. The plot of  $\ln V_N$  versus  $1/T$  for *n*-hexane, cyclohexane, benzene adsorption on 3A.

Isosteric enthalpies of adsorption ( $\Delta H_{st}$ ) were calculated by Eq. (3). Free energies of adsorption ( $\Delta G$ ) were calculated from the following equation:

$$\Delta G = \Delta H_{st} - T_{av} \Delta S \quad (4)$$

Thermodynamic parameters are tabulated in Table 2.

## 5. Discussion

It was found that benzene exhibits more negative  $\Delta H$  than for *n*-hexane and cyclohexane on 3A, 5A

and AL. Also, interactions of benzene with 3A and 5A were found to be stronger than those on AL. On the contrary, interactions of the hexane with alumina were found to be stronger than those on 3A and 5A.

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 adsorbent.

It was observed that all thermodynamic parameters (isosteric enthalpy, entropy and free energy of adsorption) of the probes on AL increase according to the following sequence: cyclohexane < *n*-hexane <

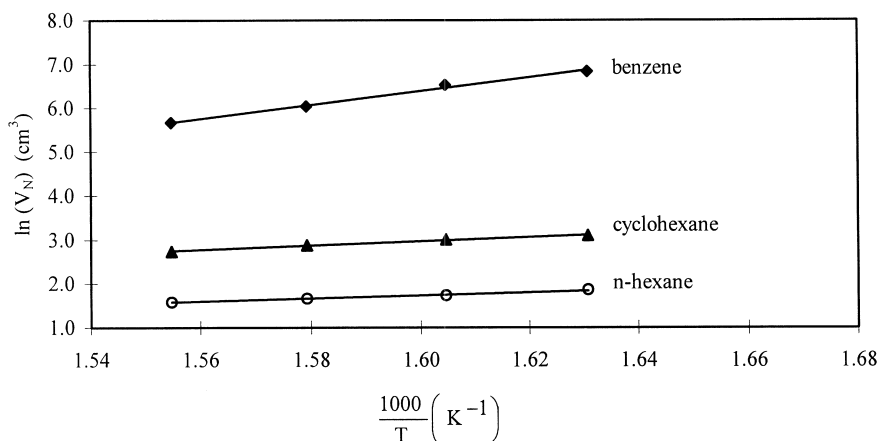


Fig. 3. The plot of  $\ln V_N$  versus  $1/T$  for *n*-hexane, cyclohexane, benzene adsorption on 5A.

Table 2  
Thermodynamic parameters for the adsorption of the probes on AL, 3A and 5A

Adsorbent	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> )
AL	<i>n</i> -Hexane	41.012	$34.770 \cdot 10^{-3}$	22.646
	Cyclohexane	37.738	$29.139 \cdot 10^{-3}$	22.347
	Benzene	49.715	$44.460 \cdot 10^{-3}$	26.231
3A	<i>n</i> -Hexane	27.467	$12.880 \cdot 10^{-3}$	18.989
	Cyclohexane	28.554	$13.256 \cdot 10^{-3}$	19.829
	Benzene	86.372	$98.737 \cdot 10^{-3}$	21.383
5A	<i>n</i> -Hexane	34.723	$32.781 \cdot 10^{-3}$	14.130
	Cyclohexane	45.220	$39.321 \cdot 10^{-3}$	20.519
	Benzene	135.145	$154.784 \cdot 10^{-3}$	37.910

benzene. Similar results were obtained by Baumgarten et al. [16]. They studied adsorption of some C<sub>6</sub> hydrocarbons on AL in the finite concentration region.

Activated alumina is a porous high-area form of aluminum oxide, prepared either directly from bauxite (Al<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O) or from the monohydrate by dehydration and recrystallization at elevated temperature. The surface is more strongly polar than that of silica gel and has both acidic and basic character, reflecting the amphoteric nature of the metal [17].

Activated carbons, activated alumina, and silica gel do not possess an ordered crystal structure and consequently the pores are nonuniform. The distribution of the pore diameters within the adsorbent particles may be narrow (20 to 50 Å) or it may range widely (20 to several thousand Å) as is the case for some activated carbons. Hence, all molecular species, with the possible exception of high-molecular-mass polymeric materials, may enter the pores [18]. Benzene, *n*-hexane and cyclohexane molecules have kinetic diameters of 5.23, 5.909, and 6.093 Å, respectively [19]. The ease of benzene molecule to enter the AL channels due to its smaller size may account for its higher adsorption capacity and  $\Delta H$ .

The molecular sieves 3A and 5A have very small pores, and the outer surfaces of these crystals provide sharper and more rapid separation of aromatic hydrocarbons than does the internal surface of AL. Molecular sieves 3A and 5A have pores of uniform sizes of 2.9 and 4.4 Å, respectively, which are uniquely determined by the unit structure of the crystal [17]. These pores will completely exclude molecules which are larger than their diameters.

Therefore, 3A and 5A pores cannot be invaded by the studied probes. These molecules may still be adsorbed on the external surface. The external surface of 3A and 5A corresponds to the zone of meso-porosity, characterized by extra-crystalline pores of larger dimensions than the micro-pores.

Choudhary and Menon [20] determined the heats of adsorption of C<sub>5</sub>–C<sub>8</sub> hydrocarbons on platinum–alumina and found the adsorption enthalpy of benzene to be higher than that of *n*-hexane. A similar study was done by Gönenç et al. [21]. They determined the adsorption parameters of some C<sub>5</sub>–C<sub>8</sub> hydrocarbons on platinum–alumina by gas chromatographic pulse techniques and found enthalpy and entropy values of *n*-hexane higher than cyclohexane. Also, Katsanos et al. [22] obtained the same results for aluminum oxide activated at different temperatures.

The sequence obtained for AL is similar to that obtained for silica surfaces and 13X [14,10]. But the same sequence was not obtained for 3A and 5A. The sequence obtained for 3A and 5A is similar to that obtained for 4A [10].

The studies on the heats of adsorption of the C<sub>6</sub> hydrocarbons on the studied adsorbents in the literature generally refer to AL. Some of the isosteric enthalpy data available are as follows: (1) AL–*n*-hexane 37.1 kJ mol<sup>-1</sup> [20,21], 30.00 kJ mol<sup>-1</sup> [23], 46.02 kJ mol<sup>-1</sup> [9], 42.30 kJ mol<sup>-1</sup> [16]; AL–cyclohexane 31.7 kJ mol<sup>-1</sup> [16,21], 30.00 kJ mol<sup>-1</sup> [23]; AL–benzene 51.78 kJ mol<sup>-1</sup> [20], 39.00 kJ mol<sup>-1</sup> [23], 46.5 kJ mol<sup>-1</sup> [16] (2) 3A–hexane 33.98 kJ mol<sup>-1</sup> [24]. (3) 5A–hexane 58.60 kJ mol<sup>-1</sup> [25,26], 32.51 kJ mol<sup>-1</sup> [24].

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 adsorbates. The values of  $\Delta(\Delta G)$  for AL, 3A and 5A are  $-3.884$ ,  $-1.554$  and  $-17.591$ , respectively. Interaction of the benzene ring with 5A was found to be stronger in comparison to the interaction with AL and 3A. Comparison of the pair benzene–*n*-hexane leads to the same conclusion.

Dynamic measurements give less accurate results when compared with static methods because it relies on measuring a small difference between quantities at different temperatures. However, for heats at zero coverage, infinite dilution gas chromatography 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.

Static measurement values sufficient to compare to our results could not be found in the literature for studied adsorbents and probes. However, the gas chromatographic  $\Delta H$  began to deviate from the static ones as the size and adsorption energy of the hydrocarbons increased, as reported by Kiselev and Yashin [8].

## 6. Nomenclature

$F_a$	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
$n_s$	Amount adsorbed (mol)
$R$	Universal gas constant
$\Delta S$	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

## References

- [1] J. Jagiello, T.J. Bandosz, J.A. Schwarz, *Carbon* 30 (1) (1992) 63.
- [2] G. Buckton, P. Darey, *Int. J. Pharm.* 123 (1995) 265.
- [3] F. Thielmann, E. Baumgarten, *J. Colloid Interface Sci.* 229 (2000) 418.
- [4] H. Balard, E. Papirer, *Prog. Org. Coating* 22 (1993) 1.
- [5] P. Mukhopadhyay, H.P. Schreiber, *Colloids Surf. A* 100 (1995) 47.
- [6] M.M. Markovic, M.M. Kopecni, S.K. Milonjic, *J. Chromatogr.* 463 (1989) 281.
- [7] J.R. Conder, C.L. Young, in: *Physicochemical Measurement by Gas Chromatography*, Wiley-Interscience, New York, 1979, Chapter 10.
- [8] A.V. Kiselev, Y.I. Yashin, in: *Gas Adsorption Chromatography*, Plenum Press, New York, 1969, Chapter 4.
- [9] A. Aşkın, O. İnel, *Sep. Sci. Technol.* 36 (3) (2001) 381.
- [10] O. İnel, D. Topaloğlu, A. Aşkın, F. Tümsek, *Chem. Eng. J.* 4008 (2002) 1.
- [11] N.A. Katsanos, R. Thede, F. Roubani-Kalantzopoulou, *J. Chromatogr. A* 795 (1998) 133.
- [12] N.A. Katsanos, N. Rakintzis, F. Roubani-Kalantzopoulou, E. Arvanitopoulou, A. Kalantzopoulous, *J. Chromatogr. A* 845 (1999) 103.
- [13] R.L. Grob (Ed.), *Modern Practice of Gas Chromatography*, Wiley-Interscience, New York, 1995, Chapter 9.
- [14] S.K. Milonjic, M. M Kopecni, *Chromatographia* 19 (1984) 342.
- [15] A.S. Gozdz, H.D. Weigmann, *Appl. Polym. Sci.* 29 (1984) 3965.
- [16] E. Baumgarten, F. Weintrauch, H. Höffkes, *J. Chromatogr.* 138 (1977) 347.
- [17] D.M. Ruthven, in: *Principles of Adsorption and Adsorption Processes*, Wiley-Interscience, New York, 1984, Chapter 1.
- [18] D.W. Breck (Ed.), *Zeolite Molecular Sieves, Structure, Chemistry and Use*, R.E. Krieger, Malabar, FL, 1984, Chapter 1.
- [19] Y.H. Ma, Y.S. Lin, in: *AIChE Symposium Series. No. 2, Vol. 81*, American Institute of Chemical Engineers, New York, 1985, p. 39.
- [20] V.R. Choudhary, P.G. Menon, *J. Chromatogr.* 116 (1976) 431.
- [21] Z.S. Gönenç, R. Yıldırım, A.B. Beler-Baykal, Z.I. Önsan, *Appl. Catal. A* 103 (1993) 35.
- [22] N.A. Katsanos, A. Lycourghiotis, A. Tsiatsios, *J. Chem. Soc., (Faraday Trans. 1)* 74 (1978) 575.
- [23] M. Todorovic, M. M Kopecni, J.J. Comor, R.J. Laub, *J. Chromatogr.* 442 (1988) 105.
- [24] F. Tümsek, O. İnel, *Chem. Eng. J.* (2003) in press.
- [25] J.A.C. Silva, A.E. Rodrigues, *Ind. Eng. Chem. Res.* 38 (1999) 2434.
- [26] F. Miano, *Colloids Surfaces A* 110 (1996) 95.