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Evaluation of the Thermodynamic Parameters for the Adsorption of Some Hydrocarbons on Chemically Treated-Bentonites by Inverse Gas Chromatography

R. GÜRKAN*
Department of Chemistry, University of Cumhuriyet, Science and Arts of Faculty, 58140 Sivas-Turkey
rgurkan@cumhuriyet.edu.tr

H. CEYLAN, T. ŞAHAN, A. SAVRAN AND Ş. KUBILAY
Department of Chemistry, University of Yüzüncü Yıl, Science and Arts of Faculty, 65080 Van-Turkey

Abstract. Inverse gas chromatography has been used to evaluate the adsorption parameters (ΔH_a, ΔH_st, ΔS_a and ΔG_a) of some probe molecules, each representing a class of organic (*n*-hexane, cyclohexane, benzene, *n*-octane, 1-octene and isooctane) on bentonite and chemically treated-bentonites. The adsorption parameters of the probes on the bentonite samples were determined in infinite dilution region. Adsorption of the organic species was investigated in the temperature range of 200–275°C, using a flame ionization detector, and nitrogen as a carrier gas. The net retention volumes (V_n) of the probes were determined by the help of the retention times (t_R) observed on gas chromatograms for each probe. Injection was made at least three times for each probe, obtaining reproducible results of $\pm 0.5\%$. It was found that benzene exhibits more negative ΔH than for *n*-hexane and cyclohexane on all of the adsorbents. In addition, it was found that 1-octene exhibits more negative ΔH than for *n*-octane and isooctane on the chemically treated-bentonites, whereas *n*-octane exhibits more negative ΔH than for 1-octene and isooctane on the natural bentonite. Also, interactions of benzene with the natural- and chemically treated-bentonites were found to be stronger than those of *n*-hexane and cyclohexane with the same carbon number. Again, interactions of the 1-octene with the chemically treated-bentonites were found to be stronger those of *n*-octane and isooctane with the same carbon number. On the contrary, interactions of *n*-octane with the untreated-bentonite were found to be stronger than those of 1-octene and isooctane.

Keywords: inverse gas chromatography, thermodynamic parameters, adsorption, bentonite, 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 (Jagiello et al., 1992). 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 (Buckton and Darcy, 1995).

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

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*To whom correspondence should be addressed.

possibilities (Thielman and Baumgarten, 2000). Compared to other techniques (static measurements), IGC has drawn a lot of attention because of its simplicity and the rich information provided (Balard and Papirer, 1993). IGC may be experimentally configured for finite or infinite dilution concentrations of adsorbate (Mukhopadhyay and Schreiber, 1995).

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 also be considered to take place in the linear part of the adsorption isotherms in 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. Therefore, 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 (Balard and Papirer, 1993; Markovic et al., 1989; Conder and Young, 1979; Kiselev and Yashin, 1969).

In this study, the adsorption of some hydrocarbons, each representing a class of organic compound (*n*-hexane, benzene, cyclohexane, *n*-octane, 1-octene and isooctane) on natural bentonite and the chemically treated-bentonites were investigated at infinite dilution region by IGC. This research is a part of our work containing the study of the heats of adsorption of some hydrocarbons on some natural and chemically treated-clays such as bentonite, sepiolite and kaolin.

The purpose of this study was to determine the basic thermodynamic parameters (ΔH, ΔG and ΔS) for the adsorption of some hydrocarbons as probes, each representing a class of organic compounds (*n*-hexane, benzene, cyclohexane, *n*-octane, 1-octene and isooctane) on natural and chemically treated-bentonites with pentanol, HNO_3 and Na_2CO_3 at infinite dilution region by IGC method.

2. Experimental

2.1. Materials and Columns

In this study, the bentonite sample was received from the mine beds in the Kütahya region in Turkey whose basic clay mineral is calcium montmorillonite, and used as stationary phase in the experiments. It was air-dried and passed through a 200 μm sieve. The amounts of metals available in the clay were considered as percentage metal oxide amounts. The percentage of volatile components, on condition of fact that almost all of them are water, was called as ignition loss. After a sample having a certain mass taken from the clay of whose carbonate and moisture was removed, was heated and dried for 2 h at 110°C; the decrease in mass of the sample was considered as ignition loss. The complete chemical composition of metal oxides in the clay sample remained was determined as follows: 71.90% SiO_2, 13.85% Al_2O_3, 0.68% Fe_2O_3, 0.09% TiO_2, 2.42%CaO, 1.27%MgO, 0.39% Na_2O, 1.62% K_2O and 7.50% ignition loss. The chemical analysis was performed with the Unicam 929 atomic absorption spectrophotometer. In addition, for modification of bentonite, pentanol, HNO_3 and Na_2CO_3 chemicals were used, too. In the cleaning of the columns, benzene and acetone were used, and *n*-hexane, cyclohexane, benzene, *n*-octane, 1-octene and isooctane as probes were used for the injection. A further purification was unnecessary because Merck supplied all of the chemicals and reagents. A 180 cm long, 3 mm inner diameter stainless steel column was used in this study.

2.1.1. Surface Areas and CECs of Bentonite Samples. The specific surface areas of the untreated bentonite, and the bentonite treated with HNO_3 and Na_2CO_3 solutions of 1.00 M were determined as 54.14; 54.49 and 57.44 m^2/g by the BET method using nitrogen gas as an adsorbate, respectively. In order to study the effect of the HNO_3 and Na_2CO_3 treatments on the clay structure, the cation exchange capacities (CECs), defined as the milliequivalents of exchangeable cations contained in 100 g bentonite samples before and after acid and base activation were determined by the methylene blue standard procedure (Rytwo et al., 1991). The CECs of the untreated bentonite and treated with HNO_3 and Na_2CO_3 solutions of 0.1 M were 51.85, 33.67 and 34.12 meq/100 g. Neither the surface area nor the CEC value for the bentonite treated with pentanol was studied and calculated.

2.2. Instrumentation

The chromatographic experiments were performed with a Unicam 610 gas chromatograph. The flame ionization detector (FID) was used in the infinite dilution region, in which the gas phase is sufficiently dilute so that intermolecular interaction between probe molecules is considered negligible. 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 flow-meter and was corrected for pressure drop in the column using pressure gradient correction factor (j), correction at column temperature was also made. The flow rates were in the range of 20–30 mL/min for each solid stationary phase studied. The adsorbents were conditioned at the maximum working temperature of 275°C 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 the time or dead time it would take to cross the column without adsorption on the chromatographic support. This latter time is measured using a solute (methane) that scarcely adsorbs under the given experimental conditions. The pressure reactor with temperature controller (4522 Reactor with 4842 controller) was used when the surfaces of the clay samples were treated with alcohol. Also, a vacuum pump was used for filling of the probes into the columns.

2.3. Preparation of Column Packings

For the natural bentonite packing, 25 g clay sample was grinded in a porcelain mortar and then sieved by using the sieve opening of 40–60 meshes, indicating that the size distribution might be in the range of 250–400 μm. The clay sample sieved was kept for 12 h on the oven at 60°C.

For the pentanol treated bentonite packing, 25 g clay sample was mixed with pentanol, indicating that the saturated solution might be obtained. The saturated solution was mixed 30 min by a mechanical stirrer at room temperature. The mixture was kept 15 h in the pressure reactor at a temperature of 200°C. After they were dried at 150°C, the samples were transferred to vacuum desiccators to be filled into the columns.

For the Na_2CO_3 treated bentonite packing, 0.8 g Na_2CO_3 was dissolved in distilled-water until a saturated solution was obtained. Then, the saturated solution was treated with 40 g clay sample and this mixture was mixed 1 h by the mechanical stirrer. After that, the sample was kept 2 h on the furnace at 800°C. The reaction product was washed thoroughly with HCl solution of 3% (w/v) and filtered. The solid was dried at room temperature.

Finally, for the HNO_3 treated bentonite packing, 25 g clay sample was mixed with 0.75 M HNO_3 solution and boiled 1 h under the reflux. Then, the mixture was filtered and subjected to the thermal operation of 15 h at 300°C.

2.4. Package of the Relevant Adsorbents Into the Columns

Indicating that the size of clay samples treated with three different chemical substances ($C_5H_{11}OH$, HNO_3 and Na_2CO_3) was in the range of 250–400 μm, they were passed through the sieve opening of 40–60 meshes. All of the samples including the sample prepared with original clay were brought to a fixed weight before being packed into the columns. The stainless-steel 180 cm long and 3 mm inner diameter column was first cleaned with water, benzene and acetone, respectively and then dried, and after that, packed with the bentonite powder of 2.25 ± 0.1 g by the combined application of an electric vibrator and a vacuum system.

2.5. Purification of the Used Columns

Purify of the stationary phase present in the column assembled into the gas chromatograph is very important in terms of sensitivity of the study. The temperature of the column for cleaning of columns was adjusted to the maximum working temperature. A carrier gas (N_2) was passed through the column during a day. Then, detector and injection temperatures, carrier gas, dry-air and hydrogen flow rate were chosen by determining suitable working conditions. After all of the units are prepared to the analysis, in order to meet the requirement of adsorption at infinite dilution corresponding to zero coverage and GC linearity, the probes were injected, one at a time, by means of a 1 μl Hamilton micro syringe in the range from 0.05 to 0.5 μL. Each adsorbate was injected at least three times, indicating that the amount injected for (ΔH_a) and (ΔG_a) calculations was 0.5 μL, and their average retention times were used for further calculations. Injections were made with the temperature increase of 25°C in the temperature range of 200–275°C. Thus, the retention times were determined

Table 1. Column characteristics of untreated and treated bentonite samples as a function of column temperature at the temperature range of 200–275°C.

		Retention times of probes, t_R (min)						Properties of carrier gas		
Adsorbent	Temperature (°C)	*n*-Hexane	Cyclohexane	Benzene	*n*-Octane	Isooctane	1-Octene	P_i	P_o	F
Untreated Bentonite	200	0.187	0.163	1.718	0.584	0.502	0.501	2952.98	624.20	28.442
	225	0.166	0.133	1.061	0.409	0.421	0.380	2966.98	624.20	27.014
	250	0.133	0.133	0.958	0.261	0.221	0.161	2982.98	624.20	25.723
	275	0.128	0.120	0.457	0.183	0.101	0.120	3000.98	624.20	24.549
Bentonite+Pentanol	200	0.096	0.088	0.115	0.177	0.134	0.199	2922.40	624.35	28.449
	225	0.083	0.079	0.093	0.134	0.107	0.143	2930.40	624.35	27.020
	250	0.077	0.072	0.087	0.113	0.092	0.111	2942.40	624.35	25.729
	275	0.077	0.066	0.076	0.089	0.079	0.091	2956.40	624.35	24.555
Bentonite+HNO_3	200	0.242	0.196	0.375	0.844	0.445	0.906	2924.00	625.70	28.510
	225	0.190	0.157	0.326	0.656	0.323	0.529	2936.00	625.70	27.079
	250	0.170	0.141	0.260	0.534	0.255	0.344	2949.00	625.70	25.784
	275	0.132	0.123	0.195	0.270	0.179	0.171	2964.00	625.70	24.608
Bentonite+Na_2CO_3	200	0.107	0.098	0.122	0.154	0.110	0.186	2894.60	624.95	28.476
	225	0.101	0.097	0.122	0.118	0.110	0.148	2904.60	624.95	27.046
	250	0.101	0.096	0.110	0.116	0.102	0.129	2917.60	624.95	25.753
	275	0.100	0.082	0.102	0.102	0.101	0.102	2933.60	624.95	24.579

Note: P_i is the inlet pressure as mm-Hg, P_o is the outlet pressure as mm-Hg, and F is the flow rate of carrier gas as mL min^{-1}.

for each probe at four different temperatures. They are given for the retention of the investigated hydrocarbons as probe on the untreated- and chemically treated-bentonite samples as a function of column temperature at the temperature range of 200–275°C in Table 1.

2.6. 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 that, under the experimental conditions used, adsorption data obeyed Henry's law. The net retention volume, V_n can be expressed in terms of changes of thermodynamic functions like enthalpy and entropy of adsorption by the measuring the net retention volumes, V_n of probes at different temperatures, T and plotting ln V_n against $1/T$:

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

Here, R is the gas constant, n_s (mol) the total amount of solute in the adsorbed state and ΔH, ΔS the differential enthalpy and differential entropy of adsorption, respectively (Katsanos et al., 1978, 1998, 1999).

The net retention volume (V_n) can be calculated from the following relation (Conder and Young, 1979; Grob, 1995):

$$V_n = (t_R - t_m)F_a \frac{T}{T_a} j \qquad (2)$$

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

By determining V_n at different temperatures, one can calculate ΔH (differential enthalpy of adsorption) from the slope and ΔS value from the intercept of the plot of ln V_n versus $1/T$, provided that the range of T is narrow enough for ΔH and ΔS 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. ΔH, which is calculated by Eq. (1), is the "differential" enthalpy of adsorption (it is not the isosteric) (Katsanos et al., 1998). A similar way for calculating differential enthalpy of adsorption by GSC has been described by Milonjic and Kopecni (1984). It is known for along time (Katsanos et al., 1999; Milonjic and Kopecni, 1984) that the differential enthalpy of adsorption (ΔH) is related to the isosteric enthalpy of adsorption (ΔH_{st}) by the equation:

$$|\Delta H_{\mathrm{st}}| = |-\Delta H| + RT_{\mathrm{av}} \tag{3}$$

Here, T_{av} is the average temperature for the interval studied. The isosteric heats of adsorption, q_{st} or ΔH_{st} is defined as the differential change in energy dQ that occurs when an infinitesimal number of molecules dN are transferred at constant pressure P, temperature T, and adsorbent surface area A from the bulk gas phase to the adsorbed phase for fixed adsorbed amount: $q_{\mathrm{st}} = (dQ/dN)_{P,T,A}$. 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 is $[-(\Delta H_{\mathrm{st}}/R)]$ (Conder and Young, 1979; Kiselev and Yashin, 1969; Milonjic and Kopecni, 1984; Gozdz and Weigmann, 1984).

Here, It should be noted 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 (Conder and Young, 1979; Milonjic and Kopecni, 1984). 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 ΔH. Therefore, both linear relations may also practically be used for analysis of IGC data although the plot of ln(V_n/T) versus $1/T$ provides a better linear dependence for the calculation of thermodynamic quantities. This fact was clearly pointed out by Habgood and Hanlan (1959).

3. Results and Discussion

In the case of bentonite treated with Na_2CO_3, the retention times of several probes at especially high temperatures are the same in Table 1. This may be due to be fact that they have very little retention or elute at the dead time. However, the reason of the fact that 1-octene has a higher retention time according to *n*-octane and isooctane, may have its increasing acidity or polarity due to increasing s-character or π-bonding when it is compared with other probes.

In this study, the thermodynamic parameters for adsorption of *n*-hexane, cyclohexane, benzene, *n*-octane, 1-octene and isooctane on the natural bentonite and bentonites, chemically treated with pentanol, HNO_3 and Na_2CO_3 were determined in the infinite dilution region by means of the net retention volumes of probes. The net retention volumes are given for the adsorption of the investigated hydrocarbons as probe on the untreated- and treated-bentonite samples as a function of column temperature at the temperature range of 200–275°C in Table 2.

Differential enthalpy of adsorption and entropy of adsorption were calculated from the slopes and intercepts of the plots of ln V_n versus $1/T$ according to Eq. (1). The plot is given for the adsorption onto the natural bentonite in Fig. 1. Isosteric enthalpies of adsorption

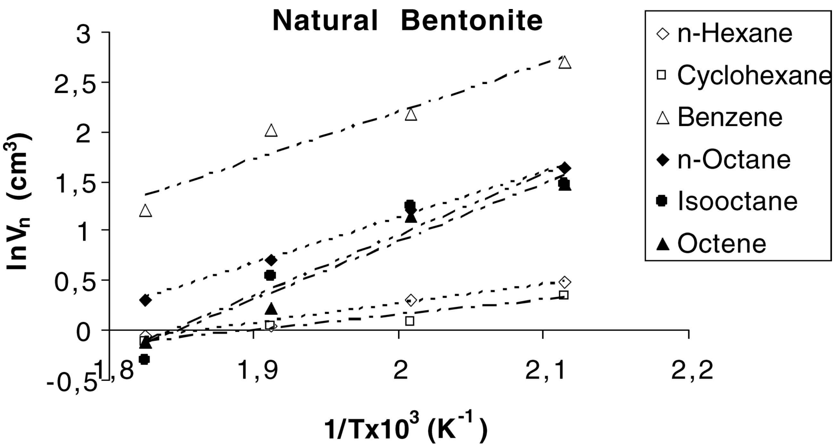

Figure 1. The plot of ln V_n versus $1/T$ for the adsorption of the probes investigated such as *n*-hexane, cyclohexane, benzene, *n*-octane, isooctane and 1-octene on natural bentonite.

Table 2. Specific retention volumes for some hydrocarbons on untreated- and chemically treated-bentonite samples as a function of column temperature at the temperature range of 200–275°C.

		Specific retention volumes of probes, V_n (cm^3)					
Adsorbent	Temperature (K)	*n*-Hexane	Cyclohexane	Benzene	*n*-Octane	Isooctane	1-Octene
Untreated Bentonite	200	1.626	1.418	14.942	5.079	4.366	4.357
	225	1.365	1.094	8.726	3.364	3.462	3.125
	250	1.036	1.036	7.465	2.034	1.721	1.254
	275	0.946	0.887	3.379	1.353	0.746	0.887
Bentonite + Pentanol	200	0.844	0.773	1.010	1.555	1.177	1.749
	225	0.691	0.658	0.774	1.115	0.891	1.190
	250	0.608	0.569	0.687	0.892	0.726	0.876
	275	0.578	0.495	0.570	0.668	0.597	0.683
Bentonite + HNO_3	200	2.134	1.728	3.307	7.443	3.924	7.990
	225	1.585	1.310	2.720	5.474	2.695	4.414
	250	1.345	1.116	2.057	4.225	2.018	2.643
	275	0.992	0.924	1.466	2.029	1.343	1.285
Bentonite + Na_2CO_3	200	0.950	0.870	1.084	1.368	0.977	1.652
	225	0.849	0.816	1.026	0.992	0.925	1.244
	250	0.805	0.765	0.877	0.925	0.813	1.029
	275	0.757	0.621	0.772	0.772	0.765	0.772

(ΔH_{st}) were calculated by using both a plot of $\ln(V_n/T)$ against $1/T$, which the slope is $-(\Delta H_{st}/R)$ and Eq. (3). The plot is also given in Fig. 2. Since the remained plots for the chemically treated bentonite samples could be easily made on the basis of data given in Table 1–4, it was considered that it is sufficient to show one figure for $\ln V_n$ vs. $1/T$ and another figure for $\ln(V_n/T)$ vs. $1/T$ dependence.

Therefore, it was investigated that isosteric enthalpies of adsorption ($\Delta H_{st,measured}$ and $\Delta H_{st,calculated}$), which is measured and calculated are significant. Free energies of adsorption (ΔG) were calculated from the following equation:

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

Thermodynamic parameters are given for each probe in Tables 3 and 4.

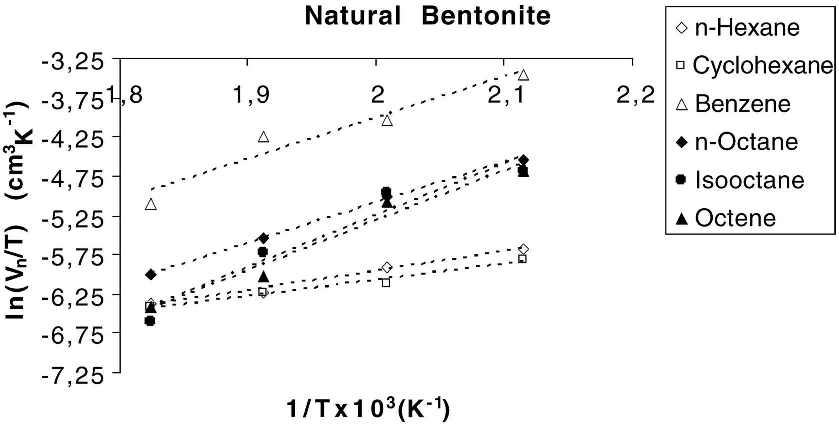

Figure 2. The plot of ln (V_n/T) versus $1/T$ for the adsorption of the probes investigated such as *n*-hexane, cyclohexane, benzene, *n*-octane, isooctane and 1-octene on the natural bentonite.

Table 3. Thermodynamic parameters for the adsorption of the probes such as *n*-hexane, cyclohexane and benzene on the untreated-bentonite and the chemically treated-bentonite samples.

Adsorbent	Probes	$-\Delta H$ (kJ mol^{-1})	$-\Delta H_{\text{st,measured}}$ (kJ mol^{-1})	$-\Delta H_{\text{st,calculated}}$ (kJ mol^{-1})	%Error	$-\Delta S$ (J mol^{-1} K^{-1})	$-\Delta G$ (kJ mol^{-1})
Bentonite	*n*-Hexane	16.419	20.644	20.663	−0.092	39.640	5.002
	Cyclohexane	12.656	16.878	16.900	0.126	24.130	4.764
	Benzene	39.521	43.745	43.696	0.112	60.820	12.716
Bentonite + Pentanol	*n*-Hexane	11.003	15.226	15.247	−0.136	24.920	2.507
	Cyclohexane	12.781	17.007	17.025	−0.108	29.150	2.125
	Benzene	15.872	20.100	20.117	−0.083	33.640	2.925
Bentonite + HNO_3	*n*-Hexane	21.188	25.414	25.433	−0.072	38.500	5.761
	Cyclohexane	17.617	21.840	21.861	−0.095	32.850	5.070
	Benzene	23.293	27.519	27.537	−0.067	38.910	7.658
Bentonite + Na_2CO_3	*n*-Hexane	6.373	10.598	10.617	−0.181	13.990	3.453
	Cyclohexane	9.148	13.373	13.392	−0.143	20.230	3.064
	Benzene	10.030	14.254	14.274	0.146	20.290	3.892

Table 4. Thermodynamic parameters for the adsorption of the probes such as *n*-octane, isooctane and 1-octene on the untreated-bentonite and the chemically treated-bentonite samples.

Adsorbent	Probes	$-\Delta H$ (kJ mol^{-1})	$-\Delta H_{\text{st,measured}}$ (kJ mol^{-1})	$-\Delta H_{\text{st,calculated}}$ (kJ mol^{-1})	% Error	$-\Delta S$ (J mol^{-1} K^{-1})	$-\Delta G$ (kJ mol^{-1})
Bentonite	*n*-Octane	38.481	42.707	42.656	0.119	67.600	8.215
	Isooctane	51.097	55.323	55.341	−0.040	94.230	7.248
	Octene	48.917	53.142	53.092	0.096	90.460	6.963
Bentonite + Pentanol	*n*-Octane	23.788	28.013	28.092	−0.068	46.670	4.189
	Isooctane	19.887	23.590	24.131	2.243	39.690	3.330
	Octene	27.028	33.382	31.272	6.748	52.650	6.496
Bentonite + HNO_3	*n*-Octane	35.429	39.652	39.674	−0.054	57.440	10.330
	Isooctane	30.145	34.371	34.389	−0.053	52.250	7.696
	Octene	49.609	55.714	53.853	3.455	87.660	10.962
Bentonite + Na_2CO_3	*n*-Octane	15.487	19.713	19.732	−0.093	30.490	4.147
	Isooctane	7.425	11.651	11.666	−0.130	15.790	3.592
	Octene	21.270	25.497	25.515	−0.068	40.770	4.683

It was found that benzene exhibits more negative ΔH than those for *n*-hexane and cyclohexane on both the natural bentonite and the chemically treated bentonites. Also, interactions of benzene with the natural bentonite were found to be stronger than those on the chemically treated bentonites. It is evident from the data that benzene exhibits more negative ΔH than the corresponding values for aliphatic and alicyclic hydrocarbons with the same carbon number, *n*-hexane and cyclohexane. The more negative the ΔH, 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 all of the adsorbents used, increase according to the following sequence: benzene $>$ *n*-hexane $>$ cyclohexane.

Additionally, it was found that 1-octene exhibits more negative ΔH than those for *n*-octane and isooctane on both the natural bentonite and chemically treated bentonites. Also, interactions of 1-octene with bentonite, chemically treated with pentanol, HNO_3 and Na_2CO_3 were found to be stronger than those on the natural bentonite. However, interactions of 1-octene with the natural bentonite were lower from those of isooctane with a $\Delta\,(\Delta H)$ difference of 2.180 kJ mol^{-1}. Again, it is evident from the data that 1-octene exhibits more negative ΔH than the corresponding values for n-octane and isooctane with the same carbon number due to having its π-electrons except for adsorption on the natural bentonite. It was observed that all thermodynamic parameters (ΔH_{st}, ΔH, ΔS and ΔG) of the probes on all of the bentonite samples used, increase according to the following sequence: 1-octene > isooctane > n-octane. Addition to, benzene, n-hexane and cyclohexane molecules have kinetic diameters of 5.230, 5.909 and 6.093 Å, respectively (Ma and Lin, 1985). The ease of benzene molecule to enter the bentonite channels or the inner parts of bentonite structure due to its smaller size may account for its higher adsorption capacity and differential adsorption enthalpy according to the n-hexane and cyclohexane molecules. It was observed that the higher ΔH values were also obtained for the studied probes onto the natural bentonite and the bentonite with acid activation. The reason of this change may be the breakage of Si—O—Si bonds in its structure and gain a more polar structure when the bentonite was treated with pentanol and Na_2CO_3. It was established that these bridges are broken off as follows in which the clays containing Si—O—Si bridges in their structures interacted with carbonate, ammonia and alcohol by Papirer et al. (1992). They have determined the surface properties and some thermodynamic parameters of Talc after surface modification in their studies by using IGC method. They had used different alkanes and alkenes as probes. Therefore, the retention times of non-polar probes contacting with this polar structure decrease.

$$\equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{Na_2CO_3}$$

$$\xrightarrow{600^\circ\mathrm{C}} 2\ \equiv\mathrm{Si{-}ONa} + \mathrm{CO_2} \xrightarrow{\mathrm{H_3O}} 2\equiv\mathrm{Si{-}OH}$$

or

$$\equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{ROH} \xrightarrow{200^\circ\mathrm{C}} \equiv\mathrm{Si{-}OR} + \equiv\mathrm{Si} - \mathrm{OH}$$

Consequently, the specific retention volume (V_n), and free adsorption enthalpy (ΔG) and differential adsorption enthalpy (ΔH) of the probes decrease, too. Contrary to, the reason of the fact that the higher ΔH values are obtained for the probes adsorbed onto the bentonite treated with HNO_3 is to cause the increase of specific pore volume of metallic cations removing from the montmorillonite mineral during acid activation. By the way, the adsorption capacity of clay surface having larger pore structure also has increased.

Choudhary and Menon (1976) determined the heats of adsorption of C_5—C_8 hydrocarbons on platinum-alumina and found the adsorption enthalpy of benzene to be higher than that of n-hexane. A similar study was also done by Gönenç et al. (1993). They determined the adsorption parameters of some C_5—C_8 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. (1978) obtained the same results for aluminum oxide activated at different temperatures.

The sequence obtained for the natural bentonite and the bentonite with acid activation is similar to that obtained for silica surfaces and 13X (Milonjic and Kopecni, 1984; İnel et al., 2002), benzene > n-hexane > cyclohexane. But the same sequence wasn't obtained for the bentonite treated with pentanol and Na_2CO_3. The sequence obtained for the bentonite treated with pentanol and Na_2CO_3 is similar to that obtained for 4A; benzene > cyclohexane > n-hexane (İnel et al., 2002). The studies on the heats of adsorption of the C_6-hydrocarbons on the investigated adsorbents in the literature generally refer to the natural bentonite and the bentonite treated with HNO_3. Some of the isosteric enthalpy data available are as follows: (1) AL- n-hexane 37.10 kJ mol^{-1} [18,19], 30.00 kJ mol^{-1} (Todorovic et al., 1988), 46.02 kJ mol^{-1} (Aşkı n and İnel, 2001), 42.30 kJ mol^{-1} (Baumgarten et al., 1977), AL-cyclohexane 31.7 kJ mol^{-1} (Baumgarten et al., 1977; Gönenç et al., 1993), 30.00 kJ mol^{-1} (Todorovic et al., 1988), AL-benzene 51,78 kJ mol^{-1} (Choudhary and Menon, 1976), 39.00 kJ mol^{-1} (Todorovic et al., 1988), 46.50 kJ mol^{-1} (Baumgarten et al., 1977). (2) 3A-hexane 33.98 kJ mol^{-1} (Tümsek and İnel, 2003). (3) 5A-hexane 58.60 kJ mol^{-1} (Silva and Rodrigues, 1999; Miano, 1996), 32.51 kJ mol^{-1} (Tümsek and İnel, 2003).

The contribution of the interaction between the π-electrons of the benzene ring and bentonite surface can be evaluated considering $\Delta\ (\Delta\ G)$ values. For the pair benzene-n-hexane, $\Delta(\Delta G) = \Delta G_{\mathrm{benzene}} - \Delta G_{n\text{-hexane}}$. This value represents the difference in the interaction ability between benzene and n-hexane with adsorbents. The values of $\Delta\ (\Delta G)$ for the natural bentonite, the bentonites treated with pentanol, HNO_3 and Na_2CO_3 are -7.714, -0.418, -1.897 and -0.439 kJ mol^{-1}, respectively. Interaction of benzene ring with the natural bentonite was found to be stronger in comparison to the interaction with the bentonites treated with pentanol, HNO_3 and Na_2CO_3. Comparison of the pair benzene-cyclohexane leads to the similar conclusion. Again, the contribution of the interaction between the π-electrons of unsaturated 1-octene and bentonite surface can be evaluated considering Δ (Δ G). For the pair 1-octene-n-octane, $\Delta(\Delta G) = \Delta G_{\text{1-octene}} - \Delta G_{n\text{-octane}}$.

This value represents the difference in the interaction ability between 1-octene and n-octane with adsorbents. The values of Δ (Δ G) for all of the adsorbents used are -1.252, -2.307, 0.632 and 0.536 kJ mol^{-1}, respectively. Interaction of 1-octene with bentonite treated with pentanol was found to be stronger in comparison to the interaction with the natural bentonite and the bentonites treated with HNO_3 and Na_2CO_3. Contrary to, the comparison of the pair 1-octene-isooctane leads to the various conclusion. Interaction of 1-octene with the bentonite treated with HNO_3 was found to be stronger in comparison to the interaction with the remained adsorbents when the Δ (Δ G) values of -0.285, -3.166, -3.266 and 1.091 kJ mol^{-1} was considered for each adsorbent, respectively.

4. Conclusions

Dynamic measurements give less accurate results when compared with static methods because they rely on measuring a small difference between quantities at different temperatures. However, for heats at zero coverage, infinite dilution gas chromatography is a 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 Δ H began to deviate from the static ones as the size and adsorption energy of the hydrocarbons increased, as reported by Kiselev and Yashin (1969). As a consequence, this work has shown that IGC is an efficient tool to study the interactions between the polar or non-polar-hydrocarbon compounds and untreated- or treated-bentonite samples. This study may also allow us to evaluate the nature of other types of interactions such as hydrogen bonding and dipole-dipole interactions based on electron donor-acceptor mechanisms besides non-polar and polar interactions if appropriate probes are used, and to understand the different behaviors of hydrocarbon compounds with bentonite or modified-bentonite considering their chemical structure and function.

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