

## Determination of the Surface Properties of Bentonite by Inverse Gas Chromatography

Ceyda Bilgiç<sup>1\*</sup>

<sup>1</sup>Department of Chemical Engineering, Faculty of Engineering and Architecture,  
Osmangazi University, 26480 Eskişehir, Turkey

\*cbilgic@ogu.edu.tr

### ABSTRACT

*Inverse gas chromatography (IGC) was applied to characterize the surface of bentonite. The adsorption thermodynamic parameters (the standard enthalpy ( $\Delta H^0$ ), entropy ( $\Delta S^0$ ) and free energy of adsorption ( $\Delta G^0$ ), the dispersive component of the surface energy ( $\gamma_s^d$ ), and the acid/base character of bentonite surface were estimated by using the retention time of different non-polar and polar probes at infinite dilution region. The specific free energy of adsorption ( $\Delta G^{sp}$ ), the specific enthalpy of adsorption ( $\Delta H^{sp}$ ), and the specific entropy of adsorption ( $\Delta S^{sp}$ ) of polar probes on bentonite were determined.  $\Delta G^{sp}$  were correlated with the donor and modified acceptor numbers of the probes to quantify the acidic  $K_A$  and the basic  $K_D$  parameters of the bentonite surface. The values obtained for the parameters  $K_A$  and  $K_D$  indicated a basic character for bentonite surface.*

**Keywords:** Inverse gas chromatography, Adsorption thermodynamic parameters, Acid-base surface characteristics, Bentonite.

### INTRODUCTION

Clay minerals have been used for years in many applications such as nanocomposites (Ray and Okamoto, 2003), catalysts (Nagendrappa, 2011), adsorbents for removal of hazardous compounds (Dąbrowski, 2001), supports for highly fluorescent probes (Danko et al., 2013) to name but a few. The demand for clays in diverse scientific and technological areas lies in their low cost and natural abundance, high adsorption and absorption capacities, and fire retardancy among other properties. However, in most cases clays cannot be employed as received and performances of clay-based materials rests on appropriate chemical modification by arrangement of molecular and macromolecular compounds. The clays always contain exchangeable ions on their surface and give important role in the environment by acting as a natural scavenger of contaminants by taking up cations and/or anions through either ion exchange or adsorption. (Babel and Kurniawan 2003). They are classified by their differences in layered structures. Some classes of clays are smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pyrophyllite (talc), vermiculite and sepiolite.

Bentonite is usually formed from weathering of volcanic ash, most often in the presence of water. However, the term bentonite, as well as similar clay called tonstein, has been used to describe clay beds of uncertain origin. Bentonites have excellent rheological and absorbent properties. Bentonite expands when wet, absorbing as much as several times its dry mass in water. Because of its excellent colloidal properties, it is often used in drilling mud for oil and gas wells and for geotechnical and environmental investigations. Bentonites are environmentally safe providing dust abatement procedures which are used in processing and handling (Murray 2002). Bentonite also has the interesting property of adsorbing relatively large amounts of protein molecules from aqueous solutions. Bentonite can also be used as a

desiccant due to its adsorption properties. Bentonite desiccants have been successfully used to protect pharmaceutical, nutraceutical and diagnostic products from moisture degradation and extend shelf life. In fact, in most common packaging environments, bentonite desiccants offer a higher adsorption capacity than silica gel desiccants. The abundance and availability of bentonite reserves as a raw material sources and relatively low cost guarantee their continued utilization in the future and most of the world's reserves are found in Turkey.

Major clay minerals in bentonites are smectites such as montmorillonite, beidellite, nontronite, hectorite, and saponite which are 2:1 phyllosilicates (Churchman, et al., 2006; Grim, 1968; Bergaya, et al., 2006). Each 2:1 layer of smectites has two silica tetrahedral (T) sheets bonded to a central alumina octahedral (O) sheet. The net negative electric charge of the 2:1 (T–O–T) layers arising from the isomorphous substitution of  $Al^{3+}$  with  $Fe^{2+}$  and  $Mg^{2+}$  in the octahedral sites and  $Si^{4+}$  with  $Al^{3+}$  in the tetrahedral sites, is naturally balanced by hydrated inorganic cations such as  $Na^+$  and  $Ca^{2+}$  located interlayers and surrounding the edges. These cations can be replaced reversibly; therefore  $Na^+$  and  $Ca^{2+}$  are called exchangeable cations. The ideal mineral formula for montmorillonite is (Grim, 1968)  $(Na, Ca)_{0.33}(Al_{1.67}, Mg_{0.33})Si_4O_{10}(OH)_2 \cdot nH_2O$ .

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. 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 (Jagiello et al., 1992). 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 (Buckton and Darey, 1995). Compared to other techniques (static measurements), IGC has attracted a lot of attention because of its simplicity and the rich information provided (Ballard and Papirer, 1993). Inverse gas chromatography (IGC) is a dynamic sorption technique. Unlike conventional gas chromatography, IGC focuses primarily on the solid material which is filled inside the column in the form of a powder, fiber or film, and non-volatile compounds are also injected into the column. The surface characteristics of various types of clay, such as illite (Saada et al., 1995), bentonite (Hamdi et al., 1999), attapulgite (Boudriche et al., 2010), sepiolite (Morales et al., 1991, Lazarevic et al., 2009) and kaolinite (Saada et al., 1995; Price and Ansari, 2003; Kubilay et al., 2006), are analyzed using inverse gas chromatography.

In the present study, we applied IGC method at infinite dilution to the investigation of surface properties of bentonite. The objectives of this study were, (a) to calculate basic thermodynamic parameters of adsorption, (b) to estimate the dispersive (London) component of the surface energy, (c) to determine the degree of acidity/ basicity of the bentonite surface, and (d) to demonstrate that the IGC method provides a convenient way to evaluate surface properties of clay minerals.

## MATERIALS AND METHODS

### Materials

The bentonite was obtained from the Uşak region (Turkey). The cation exchange capacities (CEC) of the samples were determined by  $NH_4^+$  saturation using Kjeldhal distillation. The value determined for bentonite was 32.35 meq/100 g. The chemical composition of this clay obtained by X-ray florescence (XRF) is 64.94%  $SiO_2$ , 16.93%  $Al_2O_3$ , 0.44%  $Na_2O$ , 1.95%  $Fe_2O_3$ , 0.72%  $CaO$ , 1.60%  $K_2O$ , 0.65%  $MgO$  and 11.09% loss ignition. The natural bentonite was received as it was taken out of the ground, without having

been processed, it contained many impurities. In order to purify it a decantation and centrifugation process was applied. About fifty grams of raw bentonite were agitated for 60 min in 1 L of distilled water clay is mixed until fully dissolved. This was continuously stirred by a magnetic stirrer for 2 h and then left and then it was heated covered over two days. Colloidal solution is formed in the upper and middle part of the bottle bentonite container with water and precipitated impurities in natural bentonite. The separated colloidal solution is taken to another container and stored for two days. The same process was repeated at ten times on the successive settled solid fraction. The clay is in the colloidal solution from the most recent transaction was poured into 50 mL polyethylene centrifuge bottles, closed with screw-on caps, and then centrifuged for 20 min and centrifuge. The clay into the bottom of the tube taking the help of a spatula is collected in a clean petri dish. It was dried overnight at 80 °C in an oven and then ground to fine powder.

The chromatographic experiments were performed with Agilent 7890 gas chromatography equipped with a flame ionization detector (FID). A vacuum pump was used for packing the solids into the columns. High purity nitrogen was used as the carrier gas with a flow rate of about 40 mL/min. The flow rate of carrier gas was corrected for pressure drop and temperature change in the column using James-Martin gas compressibility factor. A stainless steel column (2.00 m long, 5.35 mm I.D.) previously washed with methanol and acetone was packed with kaolinite powders. The column was stabilized overnight in stream of nitrogen at 260°C. The dead volumes of the columns were determined by injecting methane. At least three replicate determinations were used in averaging the net retention volume ( $V_N$ ). For the IGC analysis, the polar probes used were *n*-hexane *n*-heptane, *n*-octane, *n*-nonane. The polar probes used were tetrahydrofuran (THF), acetone (AC), diethyleter (DEE), trichloromethane (TCM), and ethyl acetate (Et.Ac.). All of these chemicals were analytical reagent grade and used without further purification. Properties were taken from literature of the probes (Cordeiro et al., 2011). These probes are commonly used for solid surface characterizations by IGC method.

The FTIR spectra of bentonite was recorded on a Perkin Elmer 100 FTIR spectrometer in the 4000 to 400  $\text{cm}^{-1}$  wave number range using DRIFT (Diffuse Reflectance Infrared Fourier Transform) technique. FTIR studies were carried out using spectrometer equipped with a standard DTGS detector. All standards and technological samples were prepared using KBr technique. The spectra were collected with 4  $\text{cm}^{-1}$  resolution in transmission mode and were taken in the frequency region from 4000 to 400  $\text{cm}^{-1}$ .

## Calculations

IGC is used to study the surface free energy and acid–base properties of solids; the study is generally performed in the area of infinite dilution where the interactions between the adsorbed probe molecules are negligible. The basic value in IGC is the net retention volume. The net retention volume is the volume of carrier gas required to elute a given probe. The net retention volume ( $V_N$ ) is calculated using the following equation:

$$V_N = (t_R - t_m)F_a \cdot \frac{T}{T_a} \cdot j \quad (2.1)$$

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

When adsorption takes place in the Henry's law region, the standard free energy of adsorption ( $\Delta G^0$ ), as a function of  $V_N$ , can be determined from:

$$\Delta G^0 = -RT \ln \left( \frac{V_N P_0}{m S \pi_0} \right) \quad (2.2)$$

where R is the ideal gas constant, m is the mass of adsorbent in the column, S is the specific surface area of adsorbent,  $P_0$  is the adsorbate vapor pressure in the gaseous standard state having a value of 101.3 kN/m<sup>2</sup> (1 atm) and  $\pi_0$  is the reference two-dimensional surface pressure whose standard state is arbitrary. The standard reference state was taken as  $\pi_0 = 0.338 \text{ mJ/m}^2$  proposed by de Boer (De Boer, 1953).

Therefore,  $\Delta G^0$  can be written as:

$$\Delta G^0 = -RT \ln V_N + C \quad (2.3)$$

At zero surface coverage  $\Delta H^0$  is the differential heat of adsorption of the probe and it is estimated from the changes in  $V_N$  with temperature, i.e.:

$$\Delta H^0 = -R \frac{d \ln V_N}{d(1/T)} \quad (2.4)$$

The standard entropy change of adsorption of the probe at zero coverage,  $\Delta S^0$ , can be calculated the following equation:

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \quad (2.5)$$

Provided that  $\Delta H^0$  is temperature independent in the investigated temperature range, Eq. (2.5) predicts a linear relationship between  $\Delta G^0$  and  $\Delta H^0$  (Vidal et al., 1987, Rodriguez et al., 1997, Chappell and Williams, 1989)

Generally, surface free energy of a solid ( $\gamma_s$ ) can be split into two components: the dispersive component ( $\gamma_s^d$ ), and the specific component ( $\gamma_s^{sp}$ ). The dispersive component depends on the van der Waals dispersion forces which are relatively weak, while the specific component contains all the polar forces (Milonjic, 1999, Ansari and Price, 2004).

$$\gamma_s = \gamma_s^d + \gamma_s^{sp} \quad (2.6)$$

There are various methods for calculating the dispersive component of the surface free energy using IGC, but two of these are the most widely used. These are the Dorris–Gray and Schultz methods. In both these methods, when calculating  $\gamma_s^d$ , a homologue alkane series in extremely small concentrations (infinite dilution) and in isothermal conditions is injected into the column in sequence. A single numerical  $\gamma_s^d$  value is calculated from the acquired alkane series retention time data at studied column temperature (Ylä-Mäihänen et al., 2008). The calculation of  $\gamma_s^d$  according to the Schultz method, using infinite dilution measurements, is done using the following equation (Shi et al., 2011).

$$RTL \ln V_N = 2N \cdot (\gamma_s^d)^{1/2} \cdot a \cdot (\gamma_L^d)^{1/2} + C \quad (2.7)$$

where  $V_N$  is the net retention volume of the n-alkane probe, R is the gas constant, T is the absolute column temperature (K), a is the molecular surface area coated with a kind of adsorbed alkane, N is Avogadro's number, and C is the constant. In this equation,  $\gamma_S^d$  is the dispersive component of the surface free energy of the solid phase, and  $\gamma_L^d$  is the dispersive component of the surface free energy of the probe. The plot of  $(RT \ln V_N)$  versus  $a(\gamma_L^d)^{1/2}$  can be useful. Such a plot is linear and the slope of the lines gives dispersive free energy of the solid phase. The values of  $a(\gamma_L^d)^{1/2}$  are necessary for the calculations and can be easily found in the literature. The free energy of adsorption ( $\Delta G^0$ ) for any probe is composed of the dispersive ( $\Delta G^d$ ) and the specific ( $\Delta G^{sp}$ ) components (Lindsay, 2007):

$$\Delta G^0 = \Delta G^d + \Delta G^{sp} \quad (2.8)$$

The specific component free energy of adsorption ( $\Delta G^{sp}$ ) is related to the solid phase's ability to act as an acceptor or donor of electrons. For alkane probes, because there are no polar interactions,  $\Delta G^{sp}$  is equal to zero. Thus  $\Delta G^0$  is composed of only the dispersive component.

$$\Delta G^{sp} = -RT \ln\left(\frac{V_N}{V_{N_{ref}}}\right) \quad (2.9)$$

To evaluate the  $\Delta G^{sp}$ ,  $RT \ln(V_N)$  for each probe (including the alkanes) is plotted against  $a(\gamma_L^d)^{1/2}$ . This plot gives a straight line for alkane series which is used as the reference line. The vertical distance between the n-alkane line and the point where the polar probe is gives the  $-\Delta G^{sp}$  value of that polar probe. In Eq. (9),  $V_N$  is the net retention volume of the polar probe, while  $V_{N_{ref}}$  is the hypothetical net retention volume in the n-alkane line (Thielmann, 2004, Santos and Guthrie, 2005). According to the following equation, specific components of the adsorption enthalpy ( $\Delta H^{sp}$ ) and entropy ( $\Delta S^{sp}$ ) can be determined from  $\Delta G^{sp}$ 's relationship with the temperature:

$$\frac{\Delta G^{sp}}{T} = \frac{\Delta H^{sp}}{T} - \Delta S^{sp} \quad (2.10)$$

A plot of  $\Delta G^{sp} / T$  versus  $1/T$  should yield a straight line with slope  $\Delta H^{sp}$  and intercept  $\Delta S^{sp}$ . The acidic–basic parameters can be obtained from the calculated  $\Delta H^{sp}$  values using the following equation (Lazarevic et al., 2009).

$$-\frac{\Delta H^{sp}}{AN^*} = K_A \frac{DN}{AN^*} + K_D \quad (2.11)$$

where  $K_A$  and  $K_D$  parameters define the analyses surface's acid and base constants respectively,  $AN^*$  is the modified acceptor number of the adsorbed probe while DN is the donor number. The  $K_A$  and  $K_D$  values can be calculated with the aid of probes which have acidic, basic and amphoteric properties. According to the above equation, representing the

$-\Delta H^{sp} / AN^*$  versus  $DN / AN^*$ , one gets  $K_A$  as the slope and  $K_D$  as the intercept (Santos and Guthrie, 2005). Finally, a general definition of the nature of a solid surface can be obtained through the determination of the  $S_C$  parameters known as  $K_D/K_A$ . According to the values obtained from these parameters, it is accepted that  $S_C \leq 0.9$  means surface is acidic,  $S_C \geq 1.1$  means basic, and if it is between 0.9 and 1.1, the surface is amphoteric (Santos, 2002).

## RESULTS AND DISCUSSION

The chromatographic peaks were symmetric and had maxima that were independent of the amount injected. It is assumed that the adsorption occurs in the Henry's law region (at zero surface coverage) where lateral interactions between the adsorbates at the surface can be neglected. The net retention volumes,  $V_N$ , were obtained from the maxima of the chromatographic peaks and the dead time volume.

In this study, thermodynamic parameters for adsorption of polar probes on bentonite were determined in the infinite dilution region. Standard free energies changes of adsorption ( $\Delta G^0$ ) were calculated by Eq. (2.2). Differential heats of adsorption ( $\Delta H^0$ ) were calculated from plots of  $\ln V_N$  against  $1/T$ . The slopes of the lines are  $[-(\Delta H^0/R)]$  according to Eq. (2.4). Standard entropies of adsorption ( $\Delta S^0$ ) were calculated by Eq. (2.5). Thermodynamic parameters (average values) are given in Table 1. The values of  $\Delta H^0$ ,  $\Delta S^0$  and  $\Delta G^0$  increase with increasing carbon number and the linear increase was obtained for the n-alkanes. This is due to the increase in the boiling points of n-alkanes and to the stronger interaction between the solute and adsorbent surface. The more negative the heat of adsorption, the greater the interaction between the adsorbate and the adsorbents. The  $-\Delta H^0$  values of polar probes increase in the following order: Acetone < TCM < DEE < Et. Ac. < THF.

Table 1. Thermodynamic parameters for bentonite

	$-\Delta H^0 (kJ/mol^{-1})$	$-\Delta S^0 (kJ/mol^{-1}K^{-1})$	$-\Delta G^0 (kJ/mol^{-1})$
n-Hexane	41.15	65.81	7.05
n-Heptane	82.14	138.19	10.53
n-Octane	80.46	128.50	13.88
n-Nonane	91.54	143.06	17.41
TCM	58.45	97.16	8.10
DEE	61.66	87.73	17.16
Acetone	56.94	69.30	21.03
THF	73.85	98.17	22.98
Et. Ac.	73.30	98.11	22.66

The dispersive component of the surface free energy,  $\gamma_s^d$ , was determined by injection of a homologous series of n-alkanes having between 6 and 9 carbon atoms. One of the most commonly measured parameters for the description of the energy situation on the surface of a solid is the surface energy. The surface energy can affect, e.g. catalytic activity or the strength of particle-particle interaction. The dispersive components of bentonite at experimental temperatures were calculated from Eq. (2.7), (Fig. 1). The variation of  $\gamma_s^d$  calculated as a function of temperature. It was observed that  $\gamma_s^d$  values decrease with temperature. The

obtained  $\gamma_s^d$  values for bentonite were compared to the corresponding values of different clay types reported by various authors and listed in Table 2.

The values reported for MMT indicate that we tackle high energy materials as demonstrated elsewhere: 155mJ/m<sup>2</sup> for untreated Na-MMT (Bandosz et al., 1993), 114mJ/m<sup>2</sup> for untreated MMT at 150 °C (Saada et al., 1995) and 216.0mJ/m<sup>2</sup> for pure MMT at 150 °C (Mravcakova et al., 2006). For untreated MMT, the  $\gamma_s^d$  value of 114 mJ/m<sup>2</sup> is slightly lower than the value of 155 mJ/m<sup>2</sup> obtained by Bandosz et al. for a Na-montmorillonite at 150 °C (Bandosz et al., 1993), however, after a thorough 15 h activation at 200 °C. It follows that the increase of the surface energy of MMT with temperature denotes most probably an activation of the clay surface. This has also been reported for illites and kaolinites (Saada et al., 1995), and sepiolite (Morales et al., 1991).

Table 2. Comparison of the present and reported dispersive component of surface energy

T (°C)	Illite	Sepiolite		Kaolinite			Bentonite	
	from ref. (Saada et al., 1995)	from ref. (Lazarevic et al., 2009)	from ref. (Morales et al., 1991)	from ref. (Kubilay et al., 2006)	from ref. (Price, and Ansari, 2003)	from ref. (Saada et al., 1995)	from ref. (Hamdi, et al., 1999)	Present study
80	138.17				165	154.21		
90					156			
100	147.17		54		149	167.20	155	
110			60					
120	145.17		66		151	156.21		
130			74					
140	142.16				147	160.21		
150							165	
160	141.17					161.23		
180	138.16					158.22		
200				15.39			170	
210		149.9						
220		143.6						
225				10.85				
230		136.0						34.237
240		130.4						30.875
250				6.38				27.636
260								24.556
275				6.99				
280							155	

A comprehensive insight into the Lewis acid-base surface interactions provides a better understanding of the influence of the catalytic and sorption capabilities of bentonite, as well as their ability to change via chemical modifications, which is of great importance for their applications. The application of the Schultz's method to our experimental results (Fig.1 and 2) gave us the value of  $\Delta G^{sp}$ . The variation of free energy of specific interactions,  $\Delta G^{sp}$ ,

bentonite and polar probes for different temperatures is given Table 3. The average  $-\Delta G^{sp}$  values of polar probes and kaolinite in the following order: TCM < DEE < Et. Ac < THF < Acetone.

The values of  $K_A$  and  $K_D$  were calculated using Eq. (11). Representing  $-\Delta H^{sp} / AN^*$  versus  $DN / AN^*$ , one gets  $K_A$  as the slope and  $K_D$  as the intercept (Fig 2). The values of  $K_A$  and  $K_D$  for bentonite found to be 0.12 and 0.21 with the correlation coefficient of 0.9961. The overall acid-base character of kaolinite can be evaluated from  $K_D / K_A$  ratio. According to the values obtained for of  $K_A$  and  $K_D$ , the surface of bentonite exhibits largely basic character with the ratio of  $K_D / K_A = 1.62$ .

Table 3. The variation of  $\Delta G^{sp}$  with temperature, and  $\Delta H^{sp}$  and  $\Delta S^{sp}$  values of polar probes on bentonite

Adsorbent	Polar probes	$-\Delta G^{sp}$ (kJ mol <sup>-1</sup> )				$-\Delta H^{sp}$ (kJ mol <sup>-1</sup> )	$-\Delta S^{sp} 10^3$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )
		230 °C	240 °C	250 °C	260 °C		
Bentonite	TCM	0.532	0.522	0.470	0.397	-2.80	4.52
	DEE	10.504	10.495	10.428	10.428	-12.80	4.53
	Acetone	12.456	12.533	12.573	12.519	-11.28	-2.4
	THF	11.179	11.181	11.179	11.144	-11.39	-4.61
	Et. Ac	11.044	11.004	11.057	10.974	-11.81	-1.53

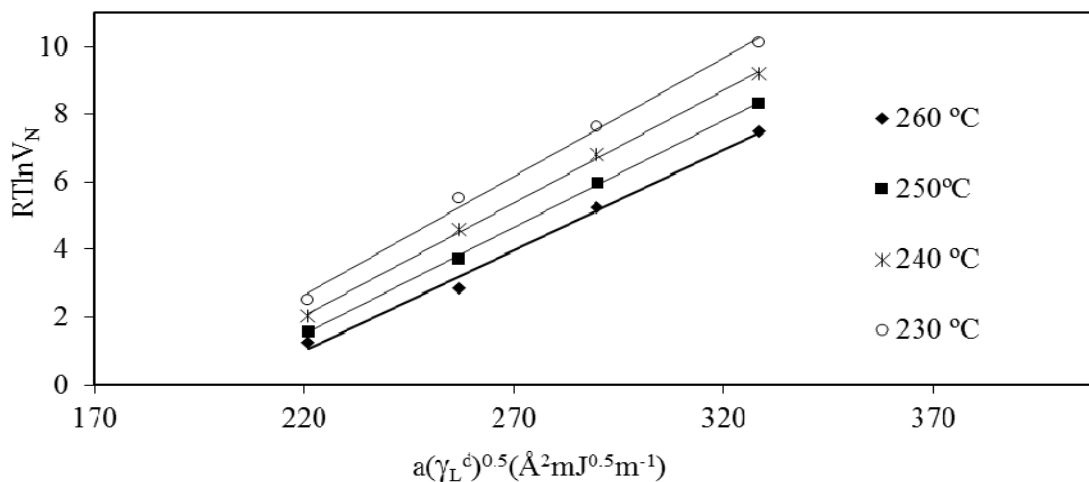


Figure 1. The  $RT \ln(V_N) - a(\gamma_L^d)^{1/2}$  graphs for bentonite



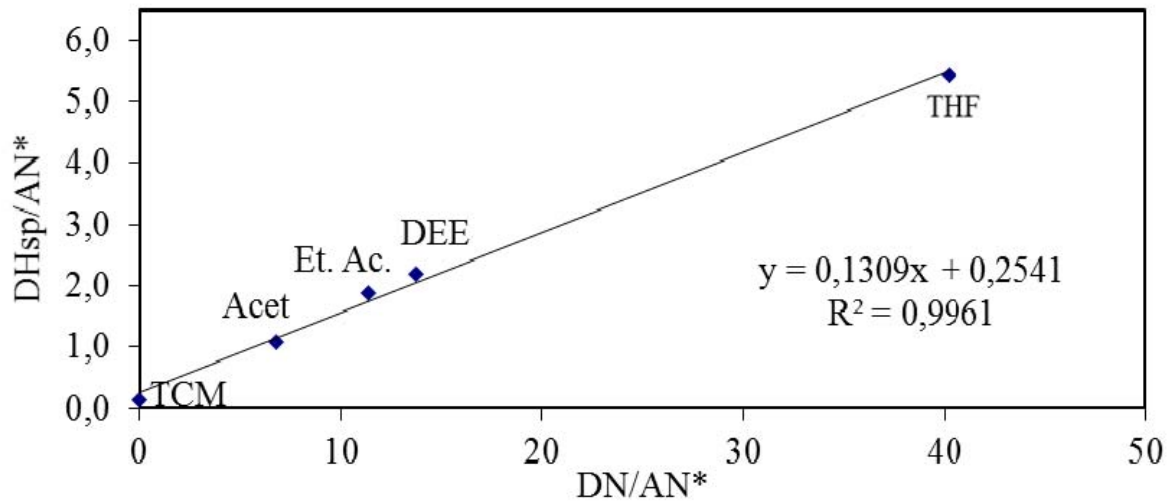


Figure 2. Plots of  $\Delta H^{sp}/AN^*$  versus  $(DN/AN^*)$  for bentonite

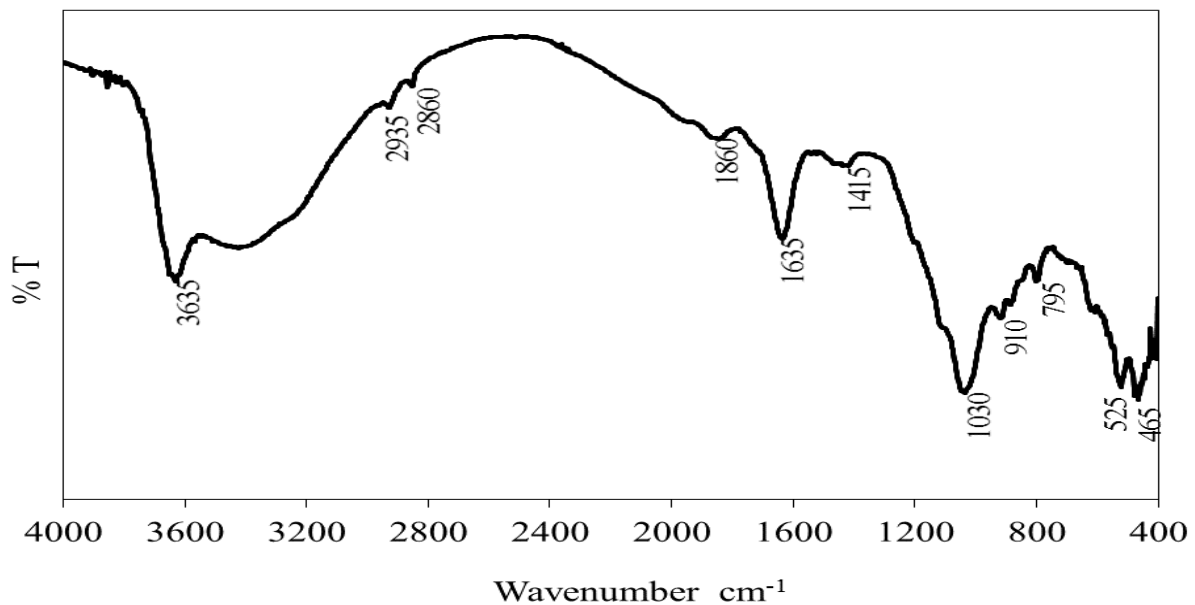


Figure 3. FTIR spectra of the purified bentonite

Vibrational spectroscopic investigations yield useful information about hydration characteristics, interlayer cations and moisture content in clays (Paluszkievicz et al., 2008). In addition, it is a useful tool to study changes in the Si-O vibrations resulting from changes crystal symmetry due to swelling. FTIR spectroscopy applied to study of bentonites is a very sensitive technique that provides information on chemical composition of the analyzed material. The FTIR spectrum of bentonite presented in Figure 3 reveals the bands belonging to bentonite: those assigned to Si-O in-plane and out-of-plane stretching vibrations at 1030 and 1415  $cm^{-1}$ , respectively. In this spectrum also the bands at 960, 1000, 1170 and 1277  $cm^{-1}$  which can be probably attributed to Si-O vibrations of other silicates, such as kaolinite or/and illite present in the samples as impurities can be seen. The bands near 465, 525, and 1030  $cm^{-1}$  are assigned to the hydroxyl bending vibrations of water and stretching vibration of the structural hydroxyl group of smectites, respectively. The band at 525  $cm^{-1}$  was from Si-O-Al (where Al is an octahedral cation), in the bentonite. The band at 1635  $cm^{-1}$  belongs to the stretching vibration of the H-OH bonds located in water molecule cations (Önal, 2007). The

peaks between 3500 and 3700  $\text{cm}^{-1}$  and near 3400  $\text{cm}^{-1}$  are indicative of montmorillonite-rich smectite clay. Peaks at 3635  $\text{cm}^{-1}$  is due to –OH band stretch for Al-OH and Si-OH. The shoulders and broadness of the –OH bands are mainly due to contributions of several structural –OH groups occurring in smectite.

## CONCLUSION

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. In this study, purified bentonite was prepared by decantation and centrifugation process was applied. The structural and morphological characteristics of the bentonites produced were studied with FTIR analysis, and surface properties were investigated by IGC. We showed that inverse gas chromatography is a powerful analytical technique very useful for studying the surface properties of zeolite and for monitoring adsorption processes. Thermodynamic information on adsorption was obtained from the temperature variation of the partition coefficients for probes at zero coverage. The high value of the dispersive component of free energy of adsorption  $\gamma_s^d$  probably was related to structural heterogeneities on the lateral surfaces, as well as to the channels and pores present at 230–260 °C. The values of  $K_A$  and  $K_D$  indicated that bentonite surface is basic.

The results obtained show that FTIR method can be successfully applied for fast determination of structural defects occurring in bentonites and thus it is a good tool to control technological process. The FTIR measurements a bentonite characterization was carried out for the possible identification of properties which are characteristic with respect to their origin. The quality of bentonitic raw materials depends on numerous parameters such as colour, rheological and exchange properties, adsorption abilities and swelling behaviour. The mineralogical and chemical composition of bentonite as well as the morphological parameters of smectites influences these properties. FTIR spectroscopy also provides information on the chemical composition of the octahedral sheets of clay minerals as the occupancy of the octahedra by different central atoms has an effect on the positions of the OH stretching and bending bands.

## ACKNOWLEDGEMENTS

This work was financially supported by Eskişehir Osmangazi University Scientific Research Projects Commission (project no: 2017-1426).

## REFERENCES

- Ansari D.M., and Price G.J., 2004. Chromatographic estimation of filler surface energies and correlation with photo degradation of kaolin filled polyethylene. *Polymer*, 45,1823-1831.
- Babel, S. and Kurniawan T.A., 2003. Low-cost Adsorbents for Heavy Metals Uptake from Contaminated Water: a review. *J Hazard Mater*, 97(1), 219–43.
- Ballard, H., Papirer, E., 1993. Characterization and modification of fillers for paints and coatings, *Progress in Organic Coatings*, 22 (1-4), 1-17.
- Bandosz T.J., Putyera K., Jagiello J., Schwarz JA., 1993. Application of inverse gas chromatography to the study of surface properties of modified layered materials. *Microporous Mater*, 1, 73–79.

- Bergaya, F., Theng, B.K.G., Lagaly, G., 2006. Handbook of Clay Science, Development in Clay Science, vol. 1, Elsevier, Amsterdam.
- Boudriche, L., Hamdi, B., Kessaissia, Z., Calvet, R., Chamayou, A., Dodds, J. A., Balard, H., 2010. An Assessment of the Surface Properties of Milled Attapulgite Using Inverse Gas Chromatography. *Clays Clay Minerals*. 58 (2), 143-153.
- Buckton, G., Darey, P., 1995. The use of gravimetric studies to assess the degree of crystallinity of predominantly crystalline powders, *International Journal of Pharmaceutics*, 123(2), (1995) 265-271.
- Chappell, P.J.C. and Williams, D.R., 1989. Determination of poly(*p*-phenylene terephthalamide) fiber surface cleanliness by inverse gas chromatography *Journal of Colloid and Interface Science*, 128, 450-457.
- Churchman, G.J., Gates, W.P., Theng B.K.G., Yuan, G., 2006. Clays and clay minerals for pollution control, in: Bergaya, F., Theng, B.K.G., Lagaly G. (Eds.), *Handbook of Clay Science, Developments in Clay Science*, vol. 1, Elsevier, pp. 625–675.
- Cordeiro, N., Gouveia C., John, M.J., 2011. Investigation of Surface Properties of Physico-Chemically Modified Natural Fibres Using Inverse Gas Chromatography, *Industrial Crops and Products*, 33, 108-115.
- Dabrowski A., 2001. Adsorption-from theory to practice. *Adv Colloid Interface Sci*, 93, 135–224.
- Danko M., Micusik M., Omastova M., Bujdak J., Chorva tD. 2013. Spectral characterization of new organic fluorescent dyes with an alkoxy silane moiety and their utilisation for the labelling of layered silicates. *Chem Pap*, 67, 18–28.
- De Boer, J.H., 1953. *The Dynamic Character of Adsorption*, Oxford University Press, London.
- Grim, R.E., 1968. *Clay Mineralogy*, 2nd ed., McGraw-Hill, New York, p.79.
- Hamdi, B., Kessaissia, Z., Donnet, J.B., Wang, T.K., 1999. Variation De L'énergie Superficielle D'une Bentonite Par Traitement Chimique Et Thermique, *Annales de Chimie Science des Matériaux*, 24(1), 63-73.
- Jagiello J., Badosz, T.J., Schwarz J.A., 1992. Application of inverse gas chromatography at infinite dilution to study the effects of oxidation of activated carbons, *Carbon*, 30 (1), 63-69.
- Kubilay, S.; Gurkan, R.; Savran, A.; Yalcinkaya, Z., 2006. Determination of the Surface Properties of Untreated and Chemically Treated Kaolinites by Inverse Gas Chromatography. *Colloid Journal*. 68, 274-284.
- Lazarevic S., Radovanovic Z., Veljovic Dj., Onjia A., Janackovic Dj., Petrovic R., 2009. Characterization of sepiolite by inverse gas chromatography at infinite and finite surface coverage. *Applied Clay Science*, 43, 41–48.
- Lindsay B., Abel M.L., Watts J.F., 2007. A study of electrochemically treated PAN based carbon fibres by IGC and XPS, *Carbon*, 45, 2433-2444.
- Milonjic, S.K., 1999. Surface Properties of Metal Ions Modified Silicas, *Colloid Surf. A.*, 149, 461-466.
- Morales E., Dabrio M.V., Herrero C.R., Acosta J.L., 1991. Acid/base characterization of sepiolite by inverse gas chromatography, *Chromatographia*, 31(7/8), 357-361.
- Mravcakova M., Boukerma K., Omastova M., Chehimi MM., 2006. Montmorillonite/polypyrrole nanocomposites. The effect of organic modification of clay on the chemical and electrical properties. *Mater Sci Eng, C*, 26, 306–13.
- Murray, H., 2002. Industrial Clays Case Study. *Int Inst Environ Dev (IIED)* 64, 1–9.
- Nagendrappa G., 2011. Organic synthesis using clay and clay-supported catalysts. *Applied Clay Science*, 53, 106–38.

- Önal, M., 2007. Examination of some commercial sorptive organo bentonites, *Turkish Journal of Chemistry*, 31, 579-588.
- Paluszkiewicz, C., Holtzer, M., Bobrowski, A., 2008. FTIR analysis of bentonite in moulding sands, *Journal of Molecular Structure*, 880, 109-114.
- Price, G. J., Ansari, D. M., 2003. An Inverse Gas Chromatography Study of Calcination and Surface Modification of Kaolinite Clay. *Physical Chemistry Chemical Physics*, 5, 5552-5557.
- Ray SS, Okamoto M., 2003. Polymer/layered silicate nanocomposites: a review from preparation to processing. *Prog Polym Sci* 28, 1539–641.
- Rodriguez, M.A., Rubio, J., Rubio, F., Liso, M.J., Oteo, J.L., 1997. Application of Inverse Gas Chromatography to the Study of the Surface Properties of Slates, Clays Clay Minerals, 45, 670-680.
- Saada, A., Papirer, E., Balard, H., Siffert, B., 1995. Determination of the Surface Properties of Illites and Kaolinites by Inverse Gas Chromatography. *Journal of Colloid and Interface Science*, 175(1), 212-218.
- Santos JMRCA and Guthrie J.T., 2005. Analysis of interactions in multicomponent polymeric systems: the key-role of inverse gas chromatography. *Materials Science and Engineering: R: Reports*, 50(3), 79-107.
- Santos, JMRCA, Fagelman, K., Guthrie J.T., 2002. Characterization of the surface Lewis acid–base properties of poly(butylene terephthalate) by inverse gas chromatography. *Journal of Chromatography A*, 969(1-2), 111-118.
- Shi B., Wang Y., Jia L., 2011. Comparison of Dorris–Gray and Schultz methods for the calculation of surface dispersive free energy by inverse gas chromatography, *J.Chromatography A*, 1218, 860-862.
- Thielmann F., 2004. Introduction into the characterization of porous materials by inverse gas chromatography. *Journal of Chromatography A*, 1037(1-2), 115-123.
- Vidal, A., Papirer, E., Jiao, W.M., Donnet, J.B., 1987. Modification of silica surfaces by grafting of alkyl chains. 1-Characterization of silica surfaces by inverse gas-solid chromatography at zero surface coverage. *Chromatographia*, 23, 121–128.
- Ylä-Mäihäniemi P.P., Heng J.Y.Y., Thielmann F., Williams D.R., 2008. Inverse gas chromatographic method for measuring the dispersive surface energy distribution for particulates, *Langmuir*, 24, 9551-9557.