

Examination of the surface properties of kaolinites by inverse gas chromatography: Acid-base properties

Young Cheol Yang[†] and Pyoung Ran Yoon

Department of Mineral Resources & Energy Eng., Chonbuk National Univ., Jeonju 561-756, Korea

(Received 13 November 2006 • accepted 19 January 2007)

Abstract—The specific component of the free energy of adsorption, $-\Delta G_A^{SP}$, of untreated kaolinite and kaolinites surface-treated with isopropyl triisostearoyl titanate (ITT) and isopropyl tri(dioctylpyrophosphato) titanate (ITDT) was estimated, using the adsorption of several polar and non-polar probes on these surfaces at various measuring temperatures, by the inverse gas chromatography (IGC) method. The acid-base properties of the untreated kaolinite and surface-treated kaolinites were quantified by K_A and K_D parameters, reflecting the ability of the surface to act as an electron acceptor and donor, respectively. In the result, all kaolinite surfaces were amphoteric and were able to function as both an electron acceptor and an electron donor.

Key words: Inverse Gas Chromatography (IGC), Specific Component of the Free Energy of Adsorption (ΔG_A^{SP}), Enthalpy of Specific Adsorption (ΔH_A^{SP}), Surface Acid-base Characteristics

GENERAL

1. Introduction

In the first paper of this series we described the surface properties of untreated kaolinite and kaolinites surface-treated with titanate coupling agents by dispersive force parameters, as determined by inverse gas chromatography (IGC).

However, it is clear that the full description of the surface properties can only be achieved with the use of acid-base interaction parameters. Acid-base interactions are important components of polar forces and play a significant role in the adhesion of inorganic fillers to organic polymers. This paper investigates the acid-base characteristics of the same samples to complete the previously defined characterization of their surface properties.

Finally, we calculate the values of various parameters- the specific component of the free energy of adsorption (ΔG_A^{SP}), the enthalpy of specific adsorption (ΔH_A^{SP}), electron acceptor index (K_A), electron donor index (K_D) and S_C (K_D/K_A)- to examine the eventual differences in the acid-base properties of untreated and treated kaolinites with titanate coupling agents.

2. Theory of Inverse Gas Chromatography (IGC)

For a test substance, the free energy of adsorption, ΔG_A , is the sum of the energies of adsorption attributable to dispersive and specific interactions. Adsorption of non-polar probes such as n-alkanes occurs through dispersive interaction, whereas for polar probes both London and acid-base interactions contribute to ΔG_A . In this study, we used the model of Donnet et al. because the injected probe is a gas state [1]. In this model, ΔG_A is given by the following expressions:

$$[-\Delta G_A] = [-\Delta G_A^D] + [-\Delta G_A^{SP}] \quad (1)$$

$$= [RT \ln V_N + C] \quad (2)$$

$$= [K \cdot (h \nu_s)^{1/2} \cdot \alpha_{0S} \cdot (h \nu_L)^{1/2} \cdot \alpha_{0L}] + [-\Delta G_A^{SP}] \quad (3)$$

where ΔG_A^D and ΔG_A^{SP} are the dispersive and specific components of the free energy of adsorption, respectively. The value of the constant, C, in expression (2) depends on the arbitrarily chosen reference state of the adsorbed molecule. In expression (3), K is a constant, $h \nu_s$ and $h \nu_L$ are the ionization potentials of the interacting materials, and α_0 is the deformation polarizability of the molecules. Subscripts S and L refer to solid and liquid, respectively. In the case of n-alkanes, ΔG_A is equal to the free energy of adsorption corresponding to dispersive interactions ΔG_A^D only, i.e., $[-\Delta G_A^{SP}] = 0$ in expression (3). The term $[K \cdot (h \nu_s)^{1/2} \cdot \alpha_{0S}]$ is characteristic of a given solid surface and is related to ΔG_A^D . Consequently, $[RT \ln V_N + C]$, between adsorbate-adsorbent, appears as a linear equation of the parameter $[(h \nu_L)^{1/2} \cdot \alpha_{0L}]$, while $[K \cdot (h \nu_s)^{1/2} \cdot \alpha_{0S}]$ becomes the slope of the linear equation. The polar testing probes [Lewis acids and bases, e.g. chloroform (CHCl_3) and tetrahydrofuran (THF)] have their corresponding $[-\Delta G_A]$ values above the reference line. The vertical distance between the n-alkane plot and the data for the polar probe of interest produces the $[-\Delta G_A^{SP}]$ value.

Examination of the temperature dependence of ΔG_A^{SP} enables the determination of the enthalpy of specific adsorptions ΔH_A^{SP} [2]:

$$\Delta H_A^{SP} = \frac{\partial(\Delta G_A^{SP}/T)}{\partial(1/T)} \quad (4)$$

The enthalpy of specific adsorptions between the examined surface and the test solutes may be correlated with the acid-base properties of both species by using Drago's equation or through the following equation [2]:

$$-\Delta H_A^{SP} = K_D \times AN + K_A \times DN \quad (5)$$

where AN and DN are the electron acceptor and donor numbers of test solute, respectively, and denote the number in Gutmann [3], AN, which indicates its ability to attract electrons (acidity), and DN, which quantifies its ability to release electrons (basicity), respectively. Parameters K_A and K_D reflect the ability of the examined surface to act as electron acceptor and donor, respectively, and the ratio K_D/K_A (S_C) describes the character of the surface (acidic or basic).

[†]To whom correspondence should be addressed.

E-mail: yang072@chonbuk.ac.kr

K_D and K_A determined according to the method using Gutmann's AN values in Eq. (5) are expressed in different units, i.e., to obtain both sides of Eq. (5) in the same units K_D must be in $\text{kJ}\cdot\text{mol}^{-1}$ while K_A has to be dimensionless. Therefore, evaluation of conclusions from their ratio must be treated with caution since the value of K_D/K_A remains unclear. Further discussion will be based only on K_D , K_A and S_C values determined according to the method using Ridle-Fowkes AN^{*} [4] values in Eq. (5).

The procedure described above has been used in the characterization of silicas, modified silicas, oxides, various minerals and solid polymers [5-14].

EXPERIMENTAL

1. Materials

The natural kaolinite used in this work was sourced from Indonesia. The titanate coupling agents used in the adsorption experiment were isopropyl triisostearoyl titanate (ITT) and isopropyl tri(dioctylpyrophosphato) titanate (ITDT). In order to modify the kaolinite surface, ITT and ITDT were dissolved in hexane (C_6H_{14}) and methyl ethyl ketone (2-butanone, $\text{C}_2\text{H}_5\text{COCH}_3$), respectively.

We used a homologous series of n-alkanes-hexane(C_6H_{14}), heptane(C_7H_{16}), octane(C_8H_{18}), nonane(C_9H_{20})- as non-polar probes, and acetone(CH_3COCH_3), carbon tetrachloride(CCl_4), chloroform(CHCl_3), benzene(C_6H_6), and THF($\text{C}_4\text{H}_8\text{O}$) as polar probes for the IGC experiment.

2. Adsorption Experiment

The experiment to modify the kaolinite surface was performed as follows: Solvent (100 ml), titanate coupling agents (2.0 g) and kaolinite (20 g) were stirred by magnetic bar stirrer for an hour and then separated into solid and liquid components by a centrifugal separator. The separated kaolinites were then dried for 6 hours at 105°C . Three types of samples were prepared in this way for IGC study at infinite dilution: untreated, ITT-treated and ITDT-treated kaolinites.

3. IGC Experiment Conditions

Since the kaolinite particle size was too small to allow the manufacture of chromatographic supports, kaolinite disks were prepared by compression of the powders in an IR die, under a pressure of 10^8 Pa. The disks were then hand-crushed and sieved to select the fraction of particles having diameters between 250 and $425\ \mu\text{m}$. Particles of the correct size were introduced into a stainless steel column, 50 cm long and 3.17 mm in diameter. Approximately 1 g of each sample was used as the chromatographic column filling. Each column, filled with sample, was conditioned at 200°C for 24 hours to remove any impurities in the column. IGC measurements were made with a Hewlett Packard 6890 GC System, equipped with a highly sensitive flame ionization detector (FID). The carrier gas was nitrogen (N_2) and the flow rate was 20 ml/min. The temperature of IGC measurement was varied from 110 to 210°C . Very small probe amounts were injected using the following stratagem: 1 to $5\ \mu\text{l}$ of probe was introduced via a septum in a 1 L flask, which was flushed with N_2 , after which 0.05 ml of the diluted probe was injected in the GC System. We referred to the CRC Handbook [15] for the physical and chemical properties of the probes.

RESULTS AND DISCUSSION

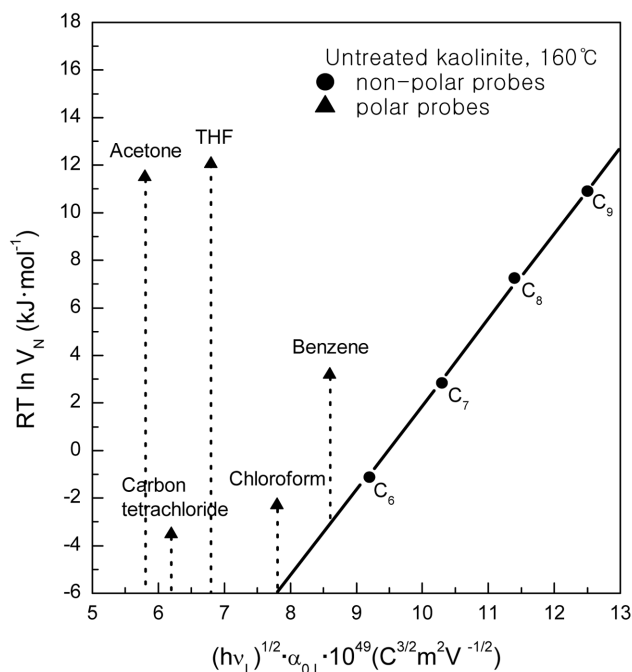


Fig. 1. Variation of $[RT \ln V_N]$ for all probes as a function of $[(h\nu_L)^{1/2} \cdot \alpha_{0L}]$ on the untreated kaolinite.

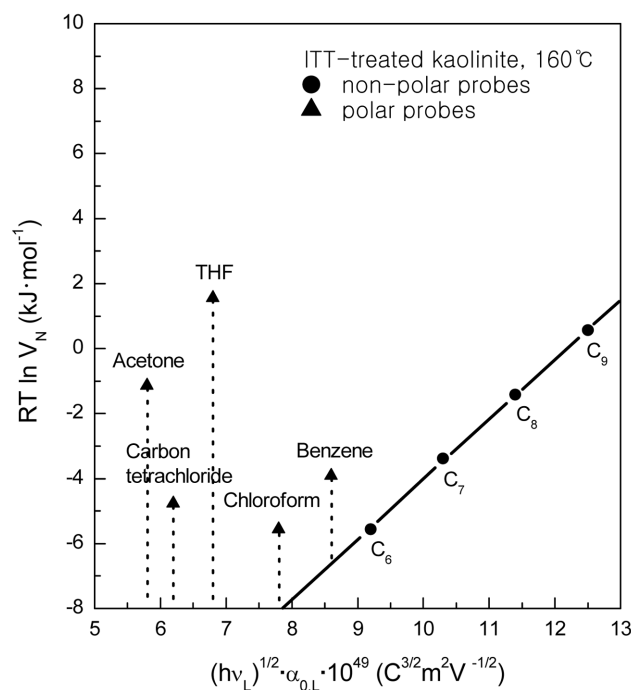


Fig. 2. Variation of $[RT \ln V_N]$ for all probes as a function of $[(h\nu_L)^{1/2} \cdot \alpha_{0L}]$ on the ITT-surface-treated kaolinite.

We evaluated $-\Delta G_d^{sp}$ values for the three types of kaolinite by the well-established IGC method. Figs. 1, 2 and 3 display the variation of $[RT \ln V_N]$ vs. a characteristic of $[(h\nu_L)^{1/2} \cdot \alpha_{0L}]$ of each probe used to evaluate $-\Delta G_d^{sp}$ of the untreated kaolinite and ITT- and ITDT-surface-treated kaolinites by expression (3), respectively. The $[RT \ln V_N]$ values of the n-alkanes used as nonpolar probe varies linearly with their characteristic $[(h\nu_L)^{1/2} \cdot \alpha_{0L}]$ and the $[RT \ln V_N]$ values for the po-

lar probes of interest are above the reference line, as shown in these figures. The vertical distance between the n-alkane plot and the $[RT \ln V_N]$

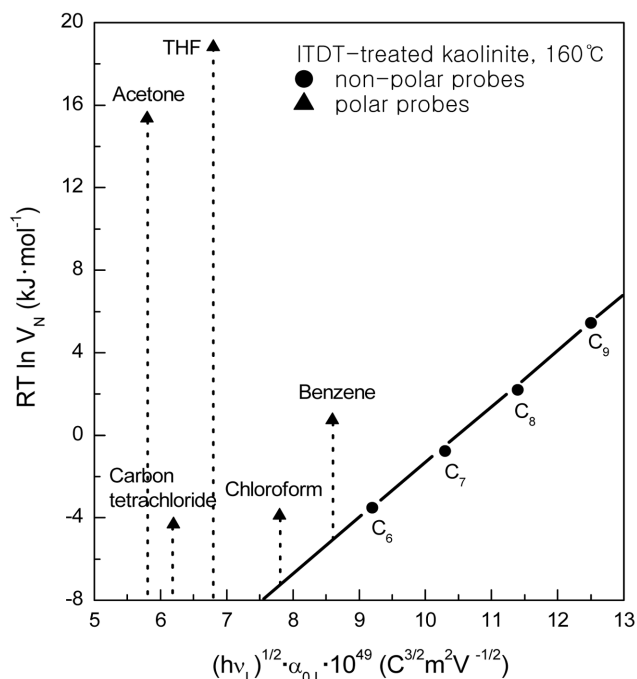


Fig. 3. Variation of $[RT \ln V_N]$ for all probes as a function of $[(h \nu_L)^{1/2} \cdot \alpha_{0,L}]$ on the ITDT-surface-treated kaolinite.

$\ln V_N]$ for the polar probe is the $-\Delta G_A^{SP}$ value. The $-\Delta G_A^{SP}$ values of the three types of kaolinite were computed at various measuring temperatures between 110 and 210 °C.

The calculated values of $-\Delta G_A^{SP}$ are presented in Table 1. The values of $-\Delta G_A^{SP}$ decreased with increasing measuring temperature for all the samples except a few cases where $-\Delta G_A^{SP}$ increased slightly. In addition, the range of IGC measuring temperature differs according to the type of kaolinite, i.e., the range of suitable temperature to measure their surface characteristic differs because their surface characteristics are not same. However, this difference of measuring temperature didn't affect the values of K_A and K_D because they didn't affect the computation of their acid-base surface characteristics using the K_A and K_D parameters.

The $-\Delta G_A^{SP}$ values decreased in order of untreated kaolinite, ITDT-surface-treated kaolinite and ITT-surface-treated kaolinite for acid probes like benzene, chloroform, and carbon tetrachloride, while the $-\Delta G_A^{SP}$ values of ITDT-surface-treated kaolinite were greater than those of the untreated kaolinite in the case of basic probes like THF and acetone, as shown in the $-\Delta G_A^{SP}$ values of 160 °C in the Table 1. This indicated that the surface characteristic of surface-treated kaolinites changed very slightly to acidic.

Figs. 4, 5 and 6 display the variation of $[-\Delta G_A^{SP}/T]$ with the inverse of measuring absolute temperature. In these figures, $-\Delta H_A^{SP}$ is the slope of the line from expression (4). The values of $-\Delta H_A^{SP}$ calculated in accordance with the above method are presented in Table 2. The K_A and K_D parameters were calculated using these $-\Delta H_A^{SP}$ values.

Table 1. The specific component of free energy of adsorption, $-\Delta G_A^{SP}$, of polar probes on the untreated and surface-treated kaolinites

Untreated kaolinite, $-\Delta G_A^{SP}$ (kJ·mol ⁻¹)						
Probe \ Tem.	160 °C	170 °C	180 °C	190 °C	200 °C	210 °C
Benzene	6.5850	6.5045	6.0716	5.5403	5.3974	4.8226
Chloroform	4.1230	4.1508	3.8076	3.4012	3.2865	3.0198
Carbon tetrachloride	8.9872	8.6165	8.1763	7.8424	7.2043	6.7790
THF	22.2646	21.7679	19.5676	22.4136	18.2888	17.4650
Acetone	25.5152	24.2728	24.9231	23.9855	22.4365	20.7056
ITT-surface-treated kaolinite, $-\Delta G_A^{SP}$ (kJ·mol ⁻¹)						
Probe \ Tem.	110 °C	120 °C	130 °C	140 °C	150 °C	160 °C
Benzene	3.3873	2.9135	2.8490	2.7615	2.5937	2.5214
Chloroform	3.5028	3.1240	2.9164	2.7995	2.6452	2.3038
Carbon tetrachloride	7.5327	6.9734	6.6927	6.5116	6.2046	5.9807
THF	15.7705	14.0519	13.3918	12.0158	12.1706	11.2277
Acetone	15.3366	12.4344	12.8168	11.6656	11.1592	10.3151
ITDT-surface-treated kaolinite, $-\Delta G_A^{SP}$ (kJ·mol ⁻¹)						
Probe \ Tem.	160 °C	170 °C	180 °C	190 °C	200 °C	
Benzene	6.0709	5.7260	5.4978	5.3535	4.8996	
Chloroform	3.6051	3.5450	3.4207	3.3203	2.4987	
Carbon tetrachloride	7.4948	7.3425	7.0021	7.1197	5.9545	
THF	29.0189	27.4467	27.3115	25.2189	24.8001	
Acetone	28.2546	27.6789	27.1293	27.1323	24.6079	

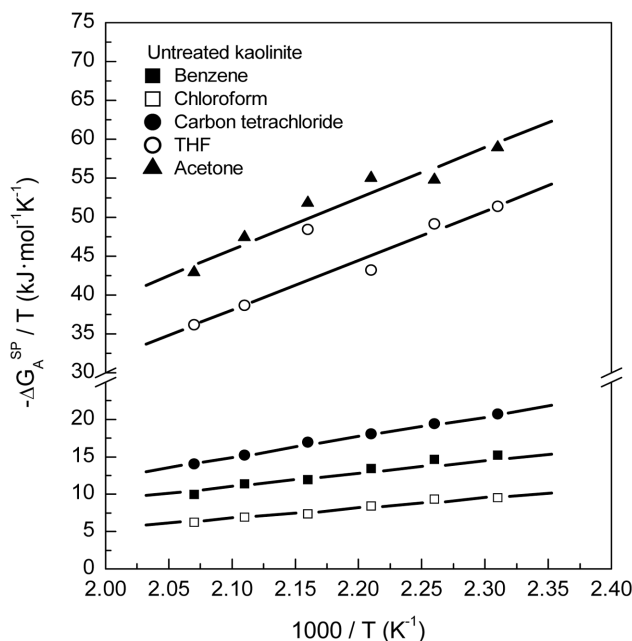


Fig. 4. Variation of $[-\Delta G_A^{SP}/T]$ with the inverse of temperature for polar probes on the untreated kaolinite.

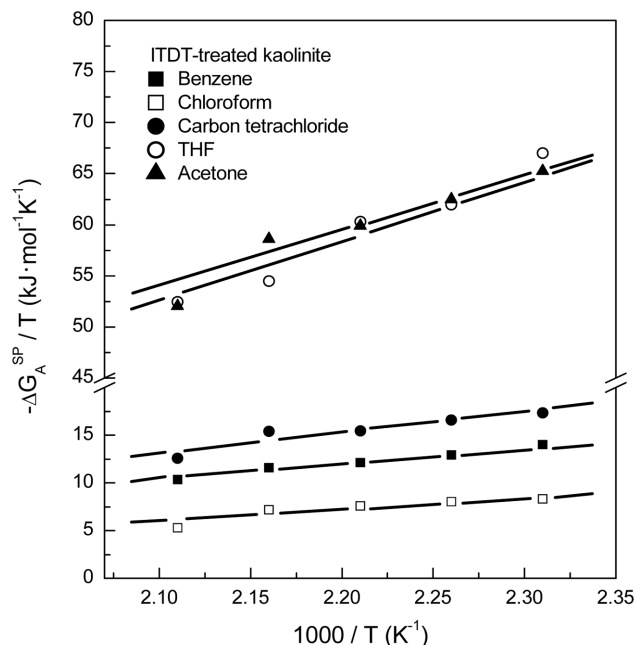


Fig. 6. Variation of $[-\Delta G_A^{SP}/T]$ with the inverse of temperature for polar probes on the ITDT-surface-treated kaolinite.

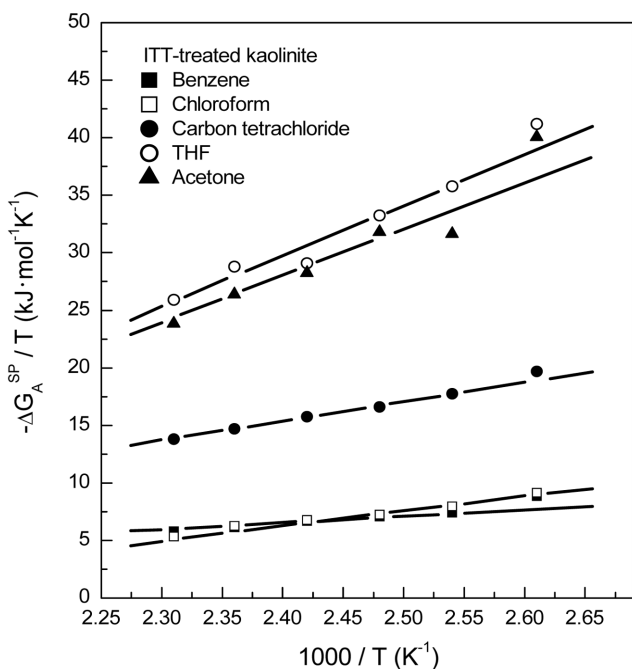


Fig. 5. Variation of $[-\Delta G_A^{SP}/T]$ with the inverse of temperature for polar probes on the ITT-surface-treated kaolinite.

Gutmann's AN, DN [3] and Riddle-Fowkes AN^* [4] numbers of the interested polar probes, as well as their acid-base characteristics, are reported in Table 3. We have chosen Riddle-Fowkes AN^* with the units of $\text{kcal}\cdot\text{mol}^{-1}$ instead of Gutmann's AN.

Expression (5) becomes

$$-\frac{\Delta H_A^{SP}}{AN^*} = K_A \frac{DN}{AN^*} + K_D \quad (6)$$

Table 2. The specific components of the enthalpy of adsorption, $-\Delta H_A^{SP}$, of polar probes on the untreated and surface-treated kaolinites

Probe	$(\text{kJ}\cdot\text{mol}^{-1})$		
	Untreated kaolinite	ITT-surface-treated kaolinite	ITDT-surface-treated kaolinite
Benzene	19.0	7.4	11.0
Chloroform	16.5	8.3	8.3
Carbon tetrachloride	27.5	17.0	22.2
THF	65.0	43.0	60.0
Acetone	64.4	40.3	53.6

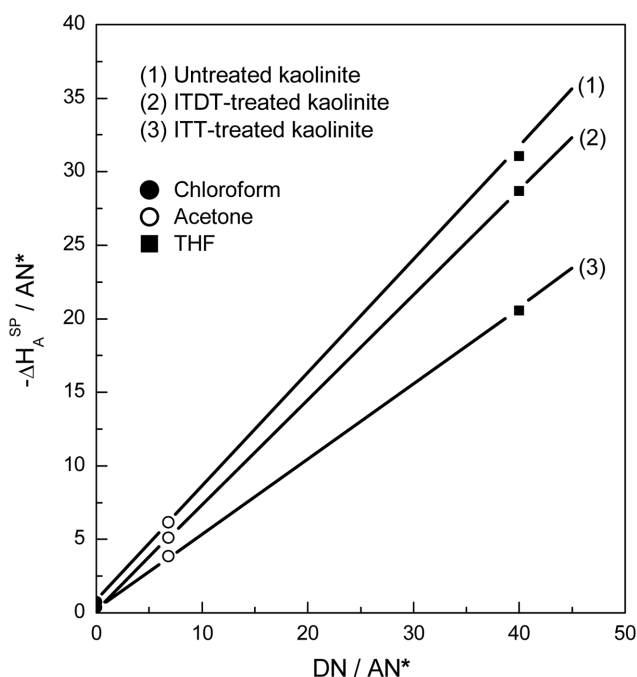
where $[-\Delta H_A^{SP}/AN^*]$ values of the polar probes varied linearly with their $[DN/AN^*]$ values. Fig. 7 displays the variation of $[-\Delta H_A^{SP}/AN^*]$ vs. $[DN/AN^*]$ of the polar probes on the three types of kaolinite. The slopes of each line become K_A values, and the intercept values of the Y-axis become K_D values from Fig. 7. The values of K_A and K_D evaluated in accordance with the above method are presented in Table 4.

In this paper, we excluded benzene and carbon tetrachloride in the reference line to evaluate K_A and K_D parameters, as shown in Fig. 7, because their calculated values from expression (6) deviated from the reference line. The causes cannot be explained by enthalpic effects, but are attributable to a particular behavior of their molecules. Similar observations like negative values of $-\Delta G_A^{SP}$ for benzene and carbon tetrachloride have been reported in other studies [16,17]. Hence we evaluated K_A and K_D parameters using only the values of chloroform, THF and acetone without those of benzene and carbon tetrachloride.

It has already been proved that kaolinite is amphoteric [18]. Our

Table 3. Acid-base characteristics of polar probes

Probe	AN (%)	AN* (kcal·mol ⁻¹)	DN (kcal·mol ⁻¹)	DN/AN*	Specific character
Benzene	8.2	0.17	0.1	0.5882	amphoteric
Chloroform	23.1	5.4	0	0	acid
Carbon tetrachloride	8.6	0.7	0	0	acid
THF	8.0	0.5	20.0	40	base
Acetone	12.5	2.5	17.0	6.8	base

**Fig. 7. Variation of $[-\Delta H_A^{SP} / AN^*]$ vs. $[DN/AN^*]$ of the polar probes on the untreated and surface-treated kaolinites.****Table 4. Acid-base characteristics of the untreated and surface-treated kaolinite surfaces**

Sample	K_A	K_D	$S_C = K_D/K_A$
Untreated kaolinite	0.76	0.73	0.961
ITT-surface-treated kaolinite	0.50	0.37	0.74
ITDT-surface-treated kaolinite	0.71	0.37	0.521

results suggested that untreated kaolinite is also amphoteric and able to function as both an electron acceptor and an electron donor, as shown in Table 4. While the ratio K_D/K_A of kaolinites surface-treated with ITT and ITDT was changed into slightly acidic, as shown in Table 4, their acid-base properties were considered to be still amphoteric. That is, all three of the kaolinite types were considered amphoteric and suitable for both of acid and basic polymers.

CONCLUSIONS

In this work, we have used the well-established IGC method to evaluate the acid-base properties of untreated kaolinite and kaolinites surface-treated with ITT and ITDT. By using n-alkanes and po-

lar solutes as probes, the $-\Delta G_A^{SP}$ values were determined from plots of $[RT \ln V_N]$ vs. $[(h\nu_L)^{1/2} \cdot \alpha_{0L}]$ of the solutes. The values of $-\Delta H_A^{SP}$ were determined from the temperature dependence of $-\Delta G_A^{SP}$. These values were found to correlate with Gutmann's donor numbers, DN, and the new acceptor numbers, AN*, introduced by Riddle-Fowkes in units of kcal·mol⁻¹, i.e., in the same units as the donor numbers. The present study produced the following conclusions:

1. The values of $-\Delta G_A^{SP}$ decreased with increasing measuring temperature for all the samples except a few cases where $-\Delta G_A^{SP}$ increased slightly.
2. The acid-base properties of untreated kaolinite and kaolinites surface-treated with ITT and ITDT were characterized by means of two parameters describing its acidity (K_A) and basicity (K_D) in consistent units. It was shown that the untreated kaolinite is amphoteric and that kaolinites surface-treated with ITT and ITDT, while predominantly acidic, retain subordinate donor properties and are more accurately described as amphoteric. To summarize, all three of the kaolinite types are able to function as both an electron donor and an electron acceptor, and can be considered suitable for both acidic and basic polymers.

REFERENCES

1. J. B. Donnet, S. J. Park and M. Balard, *Chromatographia*, **31**(9/10), 434 (1991).
2. M. Nardin, H. Balard and E. Papirer, *Carbon*, **28**(1), 43 (1990).
3. V. Gutman, *The donor-acceptor approach to molecular interactions*, Plenum Press, New York, 1 (1978).
4. F. L. Riddle and F. M. Fowkes, *J. Am. Chem. Soc.*, **112**(9), 3259 (1990).
5. H. Balad, M. Sidqi, E. Papirer, J. B. Donnet, A. Tuel, H. Hommel and A. P. Legrand, *Chromatographia*, **25**(8), 712 (1988).
6. E. Papirer, H. Balad and Y. Rahmani, *Chromatographia*, **23**(9), 639 (1987).
7. E. Papirer, J. Perrin, B. Siffert and G. Philipponneau, *J. Colloid Interface Sci.*, **144**(1), 263 (1991).
8. M. Sidqi, H. Balard and E. Papirer, *Chromatographia*, **27**(7/8), 311 (1989).
9. M. Sidqi, G. Ligner, J. Jagiello, H. Balard and E. Papirer, *Chromatographia*, **28**(11/12), 588 (1989).
10. M. M. Chehimi and E. Pigois-Landureau, *J. Mater. Chem.*, **4**(5), 741 (1994).
11. U. Panzer and H. Schreiber, *Macromolecules*, **25**, 3633 (1992).
12. P. Mukhopadhyay and H. P. Schreiber, *Colloids surfaces A: Physicochem. Eng. Aspects* 100, Elsevier, 47 (1995).
13. A. Voekel, E. Andrzejewska, R. Maga and M. Andrzejewski, *Poly-*

- mer*, **33**, 3109 (1993).
14. A. Voekel and A. Krysztafkiewicz, *Powder technology* 95, Elsevier, 103 (1998).
 15. *CRC Handbook of chemistry and physics*, 69ed, CRC Press, Inc. (1989).
 16. H. Hadjar, H. Balard and E. Papirer, in *Colloids surfaces A: Physicochem. Eng. Aspects* 99, Elsevier, 45 (1995).
 17. A. Saada, E. Papirer, H. Balard and B. Siffert, *J. Colloid Interface Sci.*, **175**, 212 (1995).
 18. D. H. Solomon and D. G. Hawthorne, *Chemistry of pigments and fillers*, John Wiley & Sons, New York, 32 (1983).