

# Investigation of Temperature, Thermodynamic Parameters and Dielectrical Properties of Poly(vinylimidazole)–Na–Bentonite Nanocomposite

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Received 26 February 2010; accepted 5 August 2010

DOI 10.1002/app.33168

Published online 5 November 2010 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** The adsorption of poly(vinylimidazole) (PVI) onto Na–Bentonite from aqueous solutions has been investigated as a function of temperature. According to the experimental results, the adsorption of PVI decreases with temperature from 25 to 55°C. The study of temperature effect has been quantified by calculating various thermodynamic parameters such as Gibbs free energy, enthalpy and entropy changes. The electrical and dielectrical properties of PVI–Na–Bentonite composite have been investigated. The current-voltage studies show that conductivity was increased at  $T = 25^\circ\text{C}$ . The dc conductivity was calculated at  $T =$

$25^\circ\text{C}$ . The samples show typical dielectric behavior from capacitive measurements. Depending on maximum interactions at  $25^\circ\text{C}$ , ac conductivity and loss factors are also in high values. Especially, at frequencies over 1.5 kHz, it was seen completely clay behavior. Variation of tangent loss factor-frequency shows decreasing of polarization density in structure in high frequency. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 874–879, 2011

**Key words:** poly(vinylimidazole); adsorption; Na–Bentonite; electrical conductivity; dielectric properties

## INTRODUCTION

Na–Bentonite belongs to smectit group of the clay minerals. These clays are organized as platelets of micrometer size, made of two-dimensional tetrahedral (T) sheet of  $\text{SiO}_4$  units linked by an octahedral (O) sheet  $\text{Al}(\text{O},\text{OH})_6$  units, forming T–O–T layers separated by an interlayer space of varying thickness. On the basal plane of the clay layers, oxygen atoms form a hexagonal network (Fig. 1).<sup>1,2</sup>

The investigations on the adsorption ability of clays for polymers has various applications and modifies the surface properties, rheology and suspensions stability of the clays, which is of great technological importance.<sup>3</sup> The ionic and non-ionic polymers interact with clay particles in different ways. The ionic polymers are adsorbed on the surface of clay particles by electrostatic interactions, while the non-ionic polymers are adsorbed by steric interactions. Polymer concentration, molecular weight and functional groups of polymer, size, shape and surface charge of particles, its concentration in suspen-

sion, and pH and temperature of suspension can affect clay and polymer interactions.<sup>4</sup>

Poly(vinylimidazole) (PVI) is a weak basic polyelectrolyte that is uncharged about pH 9 and above and has been already used as a model polyelectrolyte to study the adsorption properties on various minerals in the literature.<sup>5–9</sup> Due to the tertiary amine groups, PVI is a polybase and its positive charge density depends on pH and also on the concentration and the electrolyte type.<sup>7</sup> The chemical structure of PVI is shown in Figure 2.

Studies on the electrical properties of clay matrixes can be investigated under two groups. The first is the study of conductivity in aquatic surroundings. In this group, the conductivity is mainly reliant upon the proton movement between the clay layers and the polymerization of organics in the structure.<sup>10–14</sup> The second one consists of studies on the conductivity and dielectric properties that are mainly carried out on polycrystal compounds, alloyed thin film, and polymer–clay composites.<sup>14–22</sup> In addition, the electrical conductivity of clay materials has two components: (a) the volume conductivity, (b) the surface conductivity, which is directly related to the cation exchange capacity (CEC).<sup>23</sup>

Investigation of the electrical properties of polymer–clay (nano)composite materials is important in the development of nano electronic devices. Therefore, polymer–clay composite research during the

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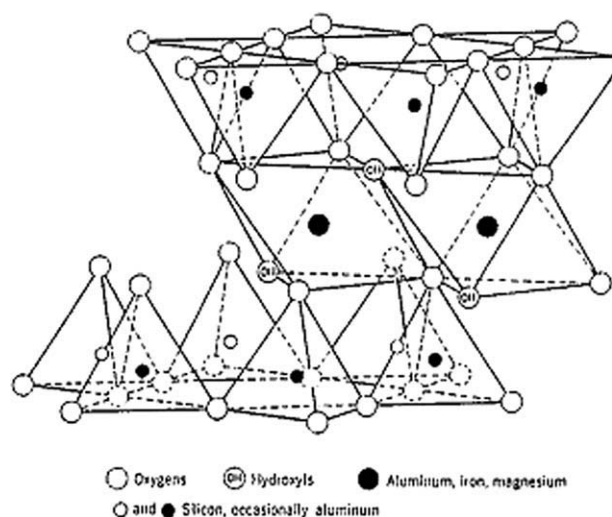


Figure 1 Atomic structure of a layer of Na-Bentonite.1.

past decade has focused on the compounding of different polymer-clay combinations with synthesized different polymers.<sup>19,20</sup>

PVI is an important cationic model polyelectrolyte and therefore the objective of the present study was to determine the factors controlling the adsorption of PVI onto Na-Bentonite. The effects of temperature on PVI adsorption have been evaluated.<sup>5,6</sup>

In addition, in this paper dc conductivity and dielectrical properties have been investigated in PVI-Na-Bentonite composite.

## EXPERIMENTAL

The Na-Bentonite sample was obtained from Zafer Mining (Balıkesir, Turkey). The chemical constituents of Na-Bentonite were analyzed by XRF as shown in Table I. The CEC of Na-Bentonite was determined as 75 meq 100 g<sup>-1</sup> by the ammonium acetate method, and the density as 2.68 g ml<sup>-1</sup> using a pycnometer.<sup>8,24</sup>

The polymer was synthesized by free-radical polymerization in benzene using azobisisobutyronitrile as an initiator, following a reported method.<sup>8,25</sup> The molecular weight was controlled using CCl<sub>4</sub> as a chain transfer agent. The mean molar mass and the polymericity index were  $M_w = 70,000$  g mol<sup>-1</sup> (viscosi-

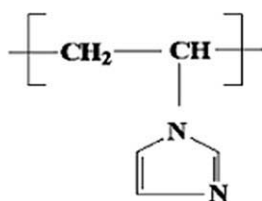


Figure 2 The chemical structure of PVI.

metric measurements) and  $M_w/M_n = 1.8$  (aqueous size-exclusion chromatography), respectively.

Adsorption studies were performed by the batch technique to obtain equilibrium data. The batch technique was selected because of its simplicity. Adsorption experiments were carried out by shaking 0.05 g Na-Bentonite samples with a 50 ml aqueous solution in a series of 250 ml polyethylene flasks. Each polyethylene flask was filled with 50 ml of a PVI solution of 250 ppm and adjusted to the desired pH 8.50 and 25–55°C. At the end of the adsorption period, the solution was centrifuged for 15 min at 5000 rpm and then the concentrations of the residual PVI, Ce, were determined with the aid of a Shimadzu UV-2450 UV-Vis spectrophotometer. The maximum wavelength of Brilliant Yellow from Acros (C<sub>26</sub>H<sub>18</sub>N<sub>4</sub>O<sub>8</sub>S<sub>2</sub>Na<sub>2</sub>, (C.A.S.: 3051-11-4)) is 400 nm and the maximum wavelength of PVI-Brilliant Yellow complex is 494 nm; therefore the measurements were made at the wavelength  $\lambda = 494$  nm. Blanks containing no PVI were used for each series of experiments.

The adsorption studies were also carried out at different temperatures, 25, 35, 45, and 55°C, to determine the effect of temperature and to evaluate the sorption thermodynamic parameters. A thermostated shaker bath was used to keep the temperature constant. The amounts of PVI adsorbed were calculated from the concentrations in solutions before and after adsorption.<sup>26</sup> The amount of PVI adsorbed (mg/g) ( $q_e$ ), onto Na-Bentonite was calculated from the mass balance equation as;<sup>27</sup>

$$q_e = (C_0 - C_e) \frac{V}{W} \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium liquid-phase concentrations of PVI (ppm), respectively,  $V$  the volume of PVI solution (L), and  $W$  the mass of Na-Bentonite sample used (g).

Polymer-clay composite samples were formed as discs (pellets) with a diameter of 13 mm under an

TABLE I  
Chemical Composition of Na-Bentonite

Constituent	Percentage present (%)
SiO <sub>2</sub>	62.66
MgO	2.48
CaO	0.22
K <sub>2</sub> O	0.72
Al <sub>2</sub> O <sub>3</sub>	19.31
Fe <sub>2</sub> O <sub>3</sub>	6.10
MnO	0.01
Na <sub>2</sub> O	2.36
TiO <sub>2</sub>	0.78
P <sub>2</sub> O <sub>5</sub>	0.04
LoI	5.32

LoI, Loss of Ignition.

TABLE II  
Isotherm Constants for PVI Adsorption onto Na-Bentonite

Adsorption temperature (°C)	I (M)	pH	Langmuir isotherm			Freundlich isotherm		
			$q_m$ (mg g <sup>-1</sup> )	$K \times 10^2$ (L mg <sup>-1</sup> )	$R^2$	$n$	$K_F$	$R^2$
25	0	8.5	56.82	3.85	0.9961	2.77	7.21	0.9220
25	0.001	8.5	50.25	2.56	0.9877	2.76	5.79	0.9648
25	0.01	8.5	46.29	2.24	0.9907	2.54	4.42	0.9673
25	0.1	8.5	42.55	1.60	0.9883	2.32	3.04	0.9883
25	0	9.5	65.36	3.37	0.9934	2.61	7.21	0.9178
25	0	10.5	75.19	4.24	0.9954	2.60	8.70	0.8886
25	0	11.5	82.64	6.82	0.9938	3.72	18.47	0.7974
35	0	8.5	53.19	2.64	0.9962	2.39	4.65	0.9477
45	0	8.5	46.51	1.72	0.9917	2.28	3.04	0.9988
55	0	8.5	42.55	1.59	0.9907	2.22	2.52	0.9974

hydraulic press. Contacts were taken in a vacuum with Univex 300 Leybold vacuum apparatus using an evaporation technique on bulk contacts taken from both surfaces of the samples. The dc conductivity was measured using a Keitley 4687 Picoammeter/voltage source. The capacitive parameters (i.e. capacitance, reel, and complex permittivities, tangent loss factor) were measured with a computer-controlled HP Agilent 4284 A (20 Hz–1 MHz) LCR meter at a 1 V<sub>rms</sub> potential.

## RESULT AND DISCUSSION

### Adsorption isotherms

The analysis of the isotherm data is important to develop an equation that accurately represents the results and that could be used for design purposes. The adsorption curves were applied to both the Langmuir and Freundlich equations.<sup>28,29</sup>

Parameters of the Langmuir and Freundlich isotherms were computed as shown in Table II. As also seen in Table II, Langmuir isotherm fits quite well with the experimental data (correlation coefficient  $R^2 > 0.99$ ), whereas the low correlation coefficients ( $R^2 < 0.98$ ) show poor agreement of the Freundlich isotherm with the experimental data. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogeneous distribution of active sites on the Na-Bentonite surface, since the Langmuir equation assumes that the surface is homogeneous.<sup>30,31</sup>

### Effect of temperature of adsorption

The effect of temperature on adsorption is important not only because it affects the rate and extent of adsorption but also due to the fact that temperature dependence of adsorption provides information about possible adsorbate-adsorbent interaction. A study of the temperature dependence of adsorption

gives valuable information about the enthalpy change during adsorption. The effect of temperature on the adsorption isotherm was studied by carrying out a series of isotherms at 25, 35, 45, and 55°C for the Na-Bentonite. Results shown in Figure 3 indicate that adsorption capacity of Na-Bentonite for adsorption of PVI decreases with increasing temperature.

The equilibrium adsorption capacity of PVI onto Na-Bentonite decreases with increasing temperature (Fig. 3), which indicates that adsorption of PVI is controlled by an exothermic and physical adsorption process due to a weakening of the attractive forces between PVI and Na-Bentonite sites. The decrease in amount of adsorbed PVI at 25–55°C temperature range can also be understood by the effect that as the temperature of adsorption system increases, the intermolecular hydrogen bonds operative between the PVI and organic matter of Na-Bentonite get

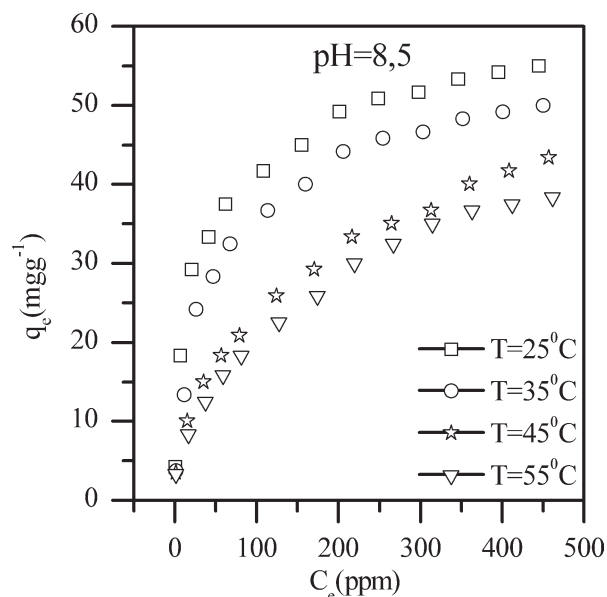
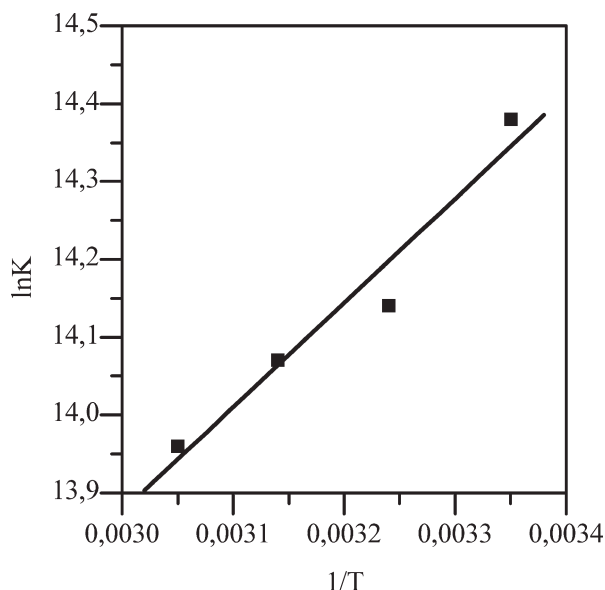


Figure 3 The effect of temperature on the adsorption of PVI onto Na-Bentonite.



**Figure 4** Plot of  $\ln K$  versus  $1/T$  for PVI adsorption onto Na-Bentonite.

weaken and, therefore, PVI chain desorb into the bulk solution and adsorption decreases.<sup>32</sup>

The isosteric enthalpy ( $\Delta H^0$ ), entropy change ( $\Delta G^0$ ), and Gibbs free energy ( $\Delta G^0$ ) of the adsorption process have been calculated from the line in Figure 4.<sup>27,33,34</sup>

A plot of  $\ln K$  against  $1/T$  should be a straight line. Figure 4 shows typical isosteres and reveals an approximately linear relationship. The value of  $\Delta H^0$  has been calculated to be  $-11.14 \text{ kJ mol}^{-1}$  obviously; the negative value of  $\Delta H^0$  indicates the exothermic nature of adsorption process. The entropy change of the adsorption process  $\Delta S^0$  has been calculated from the intercept of the line in Figure 4. Gibbs free energy of adsorption ( $\Delta G^0$ ) can be found from;

$$\Delta G^0 = \Delta H^0 - T\Delta S^0. \quad (2)$$

The change of free energy for physisorption is usually between  $-20$  and  $0 \text{ kJ mol}^{-1}$ , whereas for chemisorption it ranges from  $-80$  to  $-400 \text{ kJ mol}^{-1}$ .<sup>35</sup> The values of  $\Delta G^0$  and  $\Delta S^0$  were calculated as  $-35.57 \text{ kJ mol}^{-1}$  and  $81.94 \text{ J mol}^{-1} \text{ K}^{-1}$  at  $25^\circ\text{C}$ , respectively. A negative  $\Delta G^0$  value indicates that the nature of adsorption process or PVI is spontaneous. This value was in the middle of physisorption and chemisorption. In conclusion, this is interpreted a physical adsorption enhanced by a chemical effect.<sup>36</sup> The reorientation or restructuring of water around non-polar solutes or surfaces is very unfavorable in terms of entropy, since it disturbs the existing water structure and imposes a new and less ordered structure on the surrounding water molecules. As a result of adsorption of PVI onto Na-Bentonite surface, the number of the water molecules surrounding PVI

molecules decrease and thus the degree of the freedom of the water molecules increases. Therefore, the positive values of  $\Delta S^0$  suggest increased randomness at the solid-solution interface during the adsorption of PVI on Na-Bentonite.<sup>33,37</sup>

### ELECTRICAL CONDUCTIVITY MEASUREMENTS

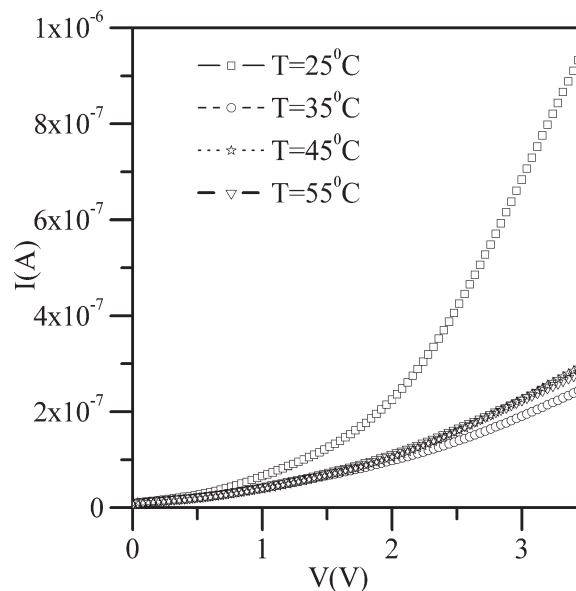
The dc conductivity ( $\sigma_{dc}$ ) was calculated for  $25^\circ\text{C}$  sample using the following equation:

$$\sigma_{dc} = \frac{d \Delta I}{A \Delta V} \quad (3)$$

where  $d$  is the distance between electrodes (bulk thickness),  $A$  is the area of pellet as a unit-section (cross-sectional area),  $V$  is applied voltage, and  $I$  is measured current. From eq. (3), dc conductivity of this sample was calculated as  $\sigma_{dc} = 1.3559 \times 10^{-7} \text{ A/Vm}$ .

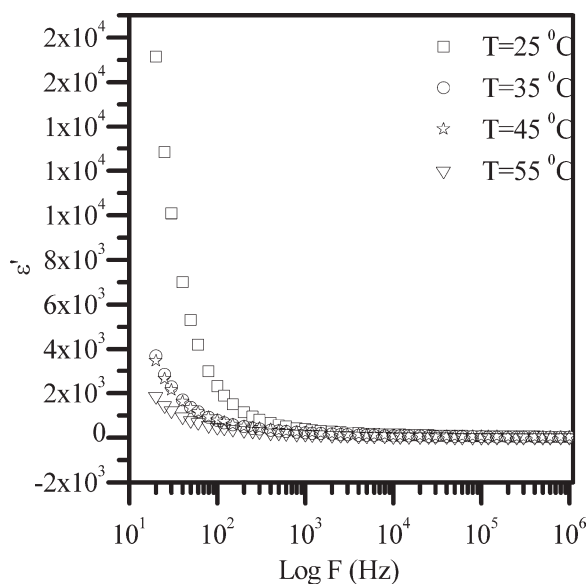
From the current-voltage plot (Fig. 5), it is seen that conductivity is increased at  $T = 25^\circ\text{C}$ , but at other adsorption temperatures, increments of conductivities are not as high as at  $T = 25^\circ\text{C}$ . At low temperatures, interactions of PVI-Na-Bentonite are maximized and exchangeable cations in clay structures have role actively. Thus in interaction at  $25^\circ\text{C}$ , conductivity which depends on ionic conductivity increase significantly. Due to moving of water between layers with increasing temperature and repulsion of OH groups to each others, conductivity can be decreased.

On the other hand, the formation of Na-Bentonite-PVI interactions from the nitrogen atoms causes



**Figure 5** Current versus voltage for Na-Bentonite-PVI at different temperatures.





**Figure 6** Variation of real part of dielectric permittivity of samples as a function of frequency.

a variation of the nitrogen orbitals hybridization. Therefore a little electronic conduction occurred due to the  $\pi$ -electron clouds and it can be enhanced by doping.<sup>12</sup>

### Dielectrical behavior

Dielectric permittivities ( $\epsilon'$ ,  $\epsilon''$ ) and tangent loss factor ( $\tan \delta$ ) calculated by using dielectric equations are

$$\epsilon' = C/C_0 \quad \epsilon'' = \frac{G}{\omega C_0}, \quad C_0 = \epsilon_0 \frac{A}{d} \quad (4)$$

and

$$\tan \delta = \epsilon''/\epsilon'$$

where  $C_0$  is vacuum capacitance,  $C$  is capacitance,  $\omega$  is angular frequency and  $G$  is conductance.

Figures 6 and 7 show the variations of real permittivity and tangent loss factor with frequency. It is seen that samples show typical dielectric behavior. Depending on maximum interactions at 25°, ac conductivity values are higher than the values of samples prepared at high temperatures. The tangent loss exchange shown in Figure 7 indicates that the polymer is responsible for the dielectric loss at low frequencies. In the literature, in studies about plasticized polymer–clay nanocomposites similar changes were observed and it is emphasized that at lower frequencies some electrode polarization and interfacial polarization occur.<sup>20,21</sup> This situation can be interpreted that the effect of polymer is dominant because of weak molecular mobility between the

clay layers in the low frequencies relaxation.<sup>38</sup> At high frequency dielectric relaxation should be affected due to dipolar orientation of the water molecules in the clay structure.

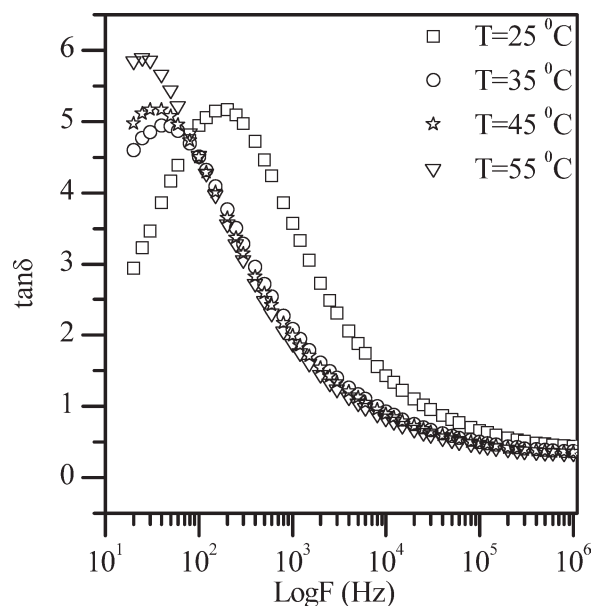
Thus, the tangent loss peaks shift toward the high frequency side.<sup>21</sup> At the same time, at frequencies over 1,5 kHz, clay behaviour was seen completely.

Electrical and dielectric results are compatible with values of increasing temperature and concentration of PVI adsorbed onto Na–Bentonite.

### CONCLUSIONS

The present work provided an important contribution to the understanding of the adsorption mechanism of PVI onto Na–Bentonite. According to the results, the adsorption process becomes more favorable with decreasing temperature which indicates that adsorption of PVI is controlled by an exothermic and physical adsorption process due to weakening of the attractive forces between PVI and Na–Bentonite sites. As the temperature of adsorption system increases, the intermolecular hydrogen bonds operative between the PVI and organic matter of Na–Bentonite get weaken and, therefore, PVI chain desorbs into the bulk solution and adsorption decreases.

The Langmuir isotherm model appears to fit the isotherm data better than the Freundlich isotherm model. Adsorption equilibrium correlated reasonably well by Langmuir isotherm. The data obtained from adsorption isotherms at different temperatures were used to calculate thermodynamic quantities such as Gibbs free energy, enthalpy and entropy of adsorption. The value of  $\Delta H^0$  has been calculated to



**Figure 7** Variation of dielectric loss ( $\tan \delta$ ) of samples as a function of frequency.

be  $-11.14 \text{ kJ mol}^{-1}$  obviously; the negative value of  $\Delta H^0$  indicates the exothermic nature of adsorption process. The values of  $\Delta G^0$  and  $\Delta S^0$  were calculated as  $-35.57 \text{ kJ mol}^{-1}$  and  $81.94 \text{ J mol}^{-1} \text{ K}^{-1}$  at  $25^\circ\text{C}$ , respectively. A negative  $\Delta G^0$  value indicates that the nature of adsorption process or PVI is spontaneous. This value was in the middle of physisorption and chemisorption. It may be concluded that physical adsorption is enhanced by a chemical effect.

Depending on the properties of polymer, this type of clay-polymer structures can have wide application areas at low temperatures and concentrations. It can be recommended that the investigation of the different concentrations and different temperatures dielectric behaviors will provide important knowledge to understand the dielectric loss and the relaxation mechanisms.

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