

EFFECT OF POLYVINYLPIRROLIDONE ON FLOCCULATION OF KAOLINITE AND MONTMORILLONITE

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ABSTRACT

Two different clays (kaolinite and montmorillonite) were treated with polyvinyl pyrrolidone (PVP). The effect of PVP on flocculation of the clay particles was investigated using infrared spectroscopy, x-ray diffraction and zeta potentials. The zeta potential of the two clays decreases with increasing the adsorbed amount of PVP on the clay surface. The results show that the flocculation of montmorillonite in presence of PVP is more easier than in the case of kaolinite.

Keywords: Infrared, x-ray, zeta potential, polyvinyl pyrrolidone, kaolinite, montmorillonite.

INTRODUCTION

High molecular weight polymers used as flocculants play an important role in many industrial processes such as mineral processing, water treatment and solid-liquid separation, etc., (for treatment of ultrafine particles in aqueous solutions). [1,2].

The adsorption and conformation of polymers on clay surfaces are important in the control of the stability behavior of clay suspension. The important chemical and physico-chemical properties of adsorption of polymer molecules by clay colloids include the nature of the functional groups in the molecule, and its shape, molecular weight, conformation, and polarity. These properties in turn determine the polymers abilities to bind by hydrogen bonding or by ionic, covalent or chelate structures. [3-7] The aim of this work is to study the effect of polyvinyl pyrrolidone on the flocculation of two different clays (kaolinite and montmorillonite) using infrared spectroscopy, x-ray diffraction and zeta potentials.

EXPERIMENTAL

Materials

Two different clays were used. The first one was kaolinite (Merck, Germany), {particles of flat shape, x-ray diffraction pattern for (001)=7.2 Å°, surface area=23 m²/g, surface charge density = 3.469X10⁴e.s.u/cm², unit cell weight = 516}, to

represent the 1:1 non swelled clay type minerals. While the second one was montmorillonite (Union Carbide, U.S.A), {particles of needle shape, x-ray diffraction pattern for (001)=9.3 Å°, surface area=120 m²/g, surface charge density = 1.339X10⁴e.s.u/cm², unit cell weight = 720} as a 2:1 dioctahedral swelled clay mineral.

Polyvinyl pyrrolidone (BDH) of molecular weight 50,000 was used.

METHODS

Clay Separation and Saturation

Fine particles, less than 1 micron in effective diameter, were separated after suspending about 1 Kg of each clay in 10 liters of water and decanting the particles that are suspended above the depth of 10 cm after 16 hours using Stokes law for sedimentation. The fine particles collected by this method were about 300 g.

The clay was stirred in 8L of 0.5 N CaCl₂ solution for 30 minutes and then left to settle for some days. The supernatant liquid was decanted and the above mentioned steps were repeated for many times until the supernatant and the added solution has the same composition. Excess salts were then removed by repeated washing with distilled water until the free electrolyte level becomes of the order of 0.1 x 10⁻⁵ N. The clays, free from electrolytes, were dried at 40°C, ground in porcelain mortar and kept.

The cation exchange capacity (C.E.C.) was determined using ammonium acetate (1N) as described by Black. [8] The cation content was determined by Pye Unicam SP 1900 atomic absorption spectrometer. The obtained values of C.E.C. for clay saturated with calcium cations, were 6.4 ± 0.15 meq/100g and 91.5 meq/100g for kaolinite and montmorillonite respectively.

The clay moisture content was determined at 110°C for 24 hours. All calculations were done on dry weight basis.

The specific surface area was determined by Lawrie's method. [9] The surface area of clay was calculated from the amount of O-phenanthroline adsorbed. The specific surface area was 23 and 120 m²/g for kaolinite and montmorillonite respectively.

Construction of Polymer Adsorption Isotherms

The polymer adsorption measurements were performed in duplicates by equilibrating known amounts of Ca-clay (0.5 g) together with aliquots of polyvinyl pyrrolidone (PVP) solution (10 g/l) to give the following initial concentrations (10, 6, 4, 2, 1, 0.8, 0.6, 0.4, 0.2, 0.1 mg/ml). The experiments were carried out at $30 \pm 1^\circ\text{C}$ and the systems were allowed to equilibrate for four days on a reciprocation shaker, then centrifuged at 10,000 r.p.m for 30 min. A sample of the supernatant was then extracted and the amount of polymer adsorbed on the clay was calculated from the change in the concentration of the polymer solution. The residual concentration of PVP was determined employing the intense ultra violet (UV) absorption of the polymer at 196 nm. Absorbance measurements were carried out using a Shimadzu 240 double beam spectrophotometer.

Infrared Spectroscopy

Spectra were recorded using a Model 1430 Perkin-Elmer infrared spectrophotometer in the infrared region between 4000 and 200 cm⁻¹.

Samples were dried at 65°C and ground to fine particles. The powdered sample of weight (1mg) was added to finely ground KBr powder (300 mg) and thoroughly mixed and then pressed into a disc.

X-Ray Diffraction

X-ray diffraction analysis of the clay-polymer complexes was performed using a "Shimadzu-XD-3" diffractometer. Nickel filtered copper radiation was used.

Zeta Potentials

The zeta potentials of the Ca-clay suspensions in presence and absence of polymer were determined by measuring the electrophoretic mobility using a micro-electrophoresis apparatus (zeta meter Inc. New York, U.S.A.).

The zeta potential (ζ), in millivolts, is obtained from the equation:

$$\zeta = \frac{1.131 \times 10^6 V_E \eta}{\epsilon}$$

Where :

V_E = the measured mobility in $\mu/\text{sec}/\text{V}/\text{cm}$

η = the viscosity of the medium (water)

ϵ = the dielectric constant of the medium (water)

RESULTS AND DISCUSSION

Infrared Spectra

In this study, infrared spectroscopy was used to confirm the adsorption of polyvinyl pyrrolidone (PVP) on clay surfaces. The IR spectrum of PVP shows a band at 3435 cm⁻¹ due to NH stretch and two bands at 2927 and 2829 cm⁻¹ due to CH stretch. Also the spectrum shows absorption bands at 1679 cm⁻¹ due to C=O stretch, at 1455 cm⁻¹ due to CH₂ bend, at 1338 cm⁻¹ due to C-N stretch and at 1031 cm⁻¹ due to N-H deformation [10,11].

The spectrum of kaolinite shows absorption bands at 3624 and 3447 cm⁻¹ and are attributed to OH stretch of adsorbed water on clay surface and to bonded OH in octahedral sheet respectively. A band at 1664 cm⁻¹ is due to OH bend of adsorbed water [12,13]. The low frequency region of the spectrum showed absorption bands at 1110 and 1006 cm⁻¹ due to Si-O stretch in tetrahedral sheet. A band at 916 cm⁻¹ is due to Al-OH vibration in octahedral sheet. Also absorption bands at 791 and 756 cm⁻¹ were attributed to Si-O-Si stretch. The band characteristic of Al-O-Si stretch is observed at 469 cm⁻¹ and the

Si-O bend occurred at 424 cm^{-1} . Spectrum of kaolinite treated with PVP shows the same characteristic bands of kaolinite in addition to new bands at $2927, 2820, 1679, 1455$ and 1383 cm^{-1} which are assigned to the presence of PVP on kaolinite surface.

IR spectrum of montmorillonite shows bands at $3637, 3439\text{ cm}^{-1}$ due to OH stretch of adsorbed water on clay surface and bonded OH in octahedral sheet respectively. A band at 1640 cm^{-1} is due to OH bend of adsorbed water. The low frequency region of the spectrum (like kaolinite) showed absorption bands at 1047 cm^{-1} due to Si-O stretch in tetrahedral sheet, at 918 cm^{-1} due to Al-OH bend in octahedral sheet, at 799 cm^{-1} due to Si-O-Si stretch and at 526 cm^{-1} due to Si-O bend [14]. The infrared spectrum of montmorillonite treated with PVP shows the same bands of montmorillonite in addition to new bands which are characteristic to PVP.

X-ray Diffraction

To obtain a comprehensive study of the effect of PVP adsorption on clay surface, X-ray technique was applied. Two important aspects were studied using this technique; the extent of penetration of the interlamellar region by PVP, and the orientation of PVP in these regions.

Figure (1) shows the X-ray diffraction patterns of Ca-kaolinite. Spacing characteristic of 7.2 \AA is observed. In the case of kaolinite treated with PVP the spacing value is not changed (Figure 1). This indicates that adsorption of PVP on kaolinite occurs only on the external surface of unit layer particles. This is because the nature of kaolinite clay aggregates is built in domains. [15]

Figure (2) shows the x-ray diffraction patterns of montmorillonite in which spacing characteristic of 14 \AA was observed (where montmorillonite sample was partially air dried). When montmorillonite is treated with PVP, the C-spacing deviates to 21.4 \AA . The C-spacing of fully dried montmorillonite sample was found to be 9.3 \AA . [16,17] By subtracting the C-spacing of the fully dried sample from the C-spacing of the partially air dried clay sample ($14-9.3$), the thickness of the adsorbed water layer can be estimated (4.7 \AA).

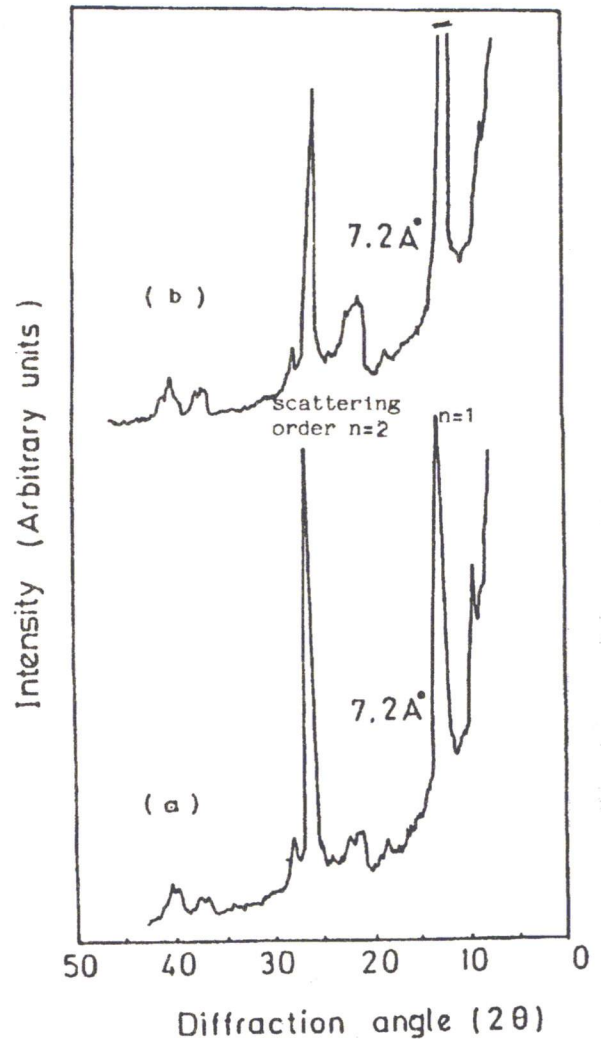


Figure 1. X-ray diffraction patterns of (a) kaolinite, (b) PVP-kaolinite complex, at 25°C .

This is corresponding to two molecular layers of water adsorbed between every two unit layers of clay. Also when the C-spacing of fully dried sample is subtracted from C-spacing of the sample treated with PVP ($21.4-9.3$), the thickness of the interlayer polymer can be obtained (12.1). As the value of the coil dimension for PVP is about 6 \AA , [18] the value of (12.1) is corresponding to two monolayers of PVP penetrated between the interlayer of montmorillonite surface (one layer adsorbed to each surface interlayers).

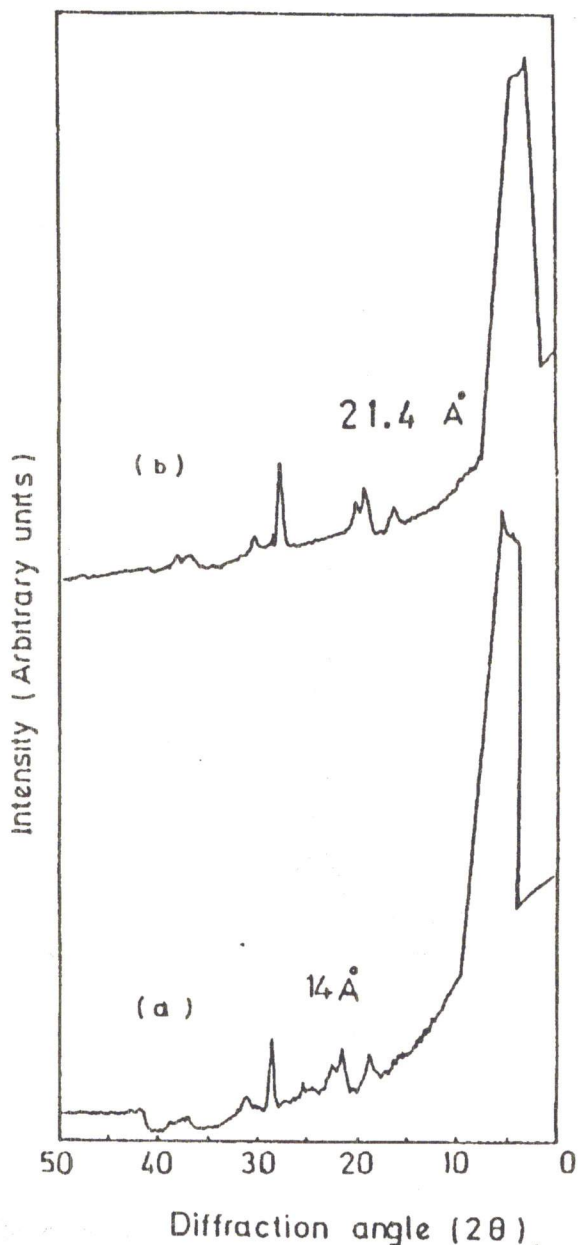


Figure 2. X-ray diffraction patterns of a) montmorillonite, and b) PVP-montmorillonite complex at 25°C .

Polymer Adsorption Isotherms

Figure (3) shows the adsorption isotherms of PVP on kaolinite and montmorillonite at 30°C . The adsorption maxima are $0.425 \text{ g PVP/g kaolinite}$ and $0.47 \text{ g PVP/g montmorillonite}$ respectively (Table 1).

This result is due to the difference in the surface area and structure of kaolinite and montmorillonite clays. Figure (4) shows that the adsorption isotherms obey Freundlich's equation. [19] The adsorption isotherms show one form (L. shape). This indicates the similar mechanism of PVP adsorption on these clays surfaces. To resolve the adsorption isotherms of Figure (3) the hypothesis of multilayer adsorption with different chain species can be suggested. To test this, for example, the adsorption maximum of PVP on kaolinite per surface was 18.5 mg/m^2 ($0.425 \text{ g polymer/g clay}$) while for montmorillonite was 3.9 mg/m^2 ($0.47 \text{ g polymer / g clay}$). These values are considerably greater than 0.135 mg/m^2 which is the amount of PVP needed to be accommodated in the form of a close monolayer on these surfaces. From the above considerations, it would be concluded that multilayer adsorption takes place around/or at the maximum polymer adsorption [20].

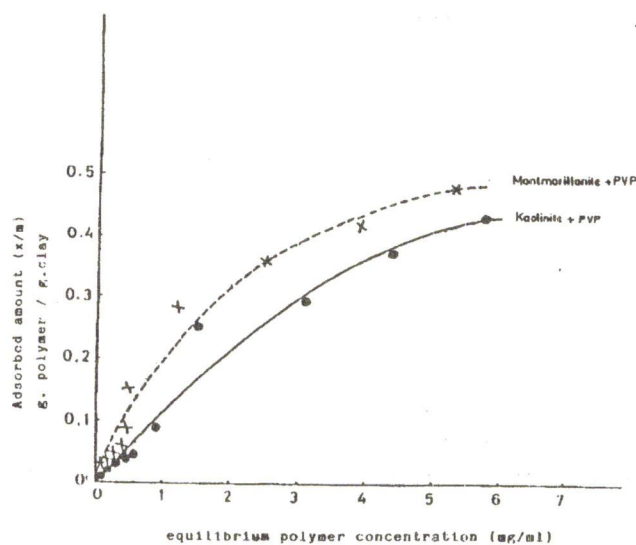


Figure 3. Adsorption isotherms of PVP on Ca-kaolinite and montmorillonite at 30°C .

To be sure of the irreversibility of polymer adsorption, attempts were made to desorb PVP from the clay surface. The clay treated with PVP was stirred in water for a long time. No PVP was detected in water. It means that, PVP molecules are strongly attached to the clay surface. Therefore PVP is considered as a good stabilizer for clay suspension than electrolytes which are mostly reversible adsorbed materials.

Table 1. Adsorbed amount (x/m) of PVP on Ca-kaolinite and montmorillonite surfaces at 30°C.

Initial PVP concentration mg/ml	Ca-kaolinite		Ca-montmorillonite	
	Eq.conc mg/ml	(x/m) g.polymer/ g.clay	Eq.conc. mg/ml	(x/m) g.polymer/ g.clay
0.2	0.07	0.013	0.050	0.015
0.4	0.12	0.027	0.100	0.030
0.6	0.30	0.030	0.250	0.035
0.8	0.45	0.035	0.330	0.045
1.0	0.55	0.045	0.400	0.060
2.0	0.65	0.130	0.500	0.150
4.0	1.50	0.250	1.200	0.280
6.0	3.10	0.290	2.500	0.350
8.0	4.40	0.360	3.900	0.410
10.0	5.75	0.425	5.300	0.470

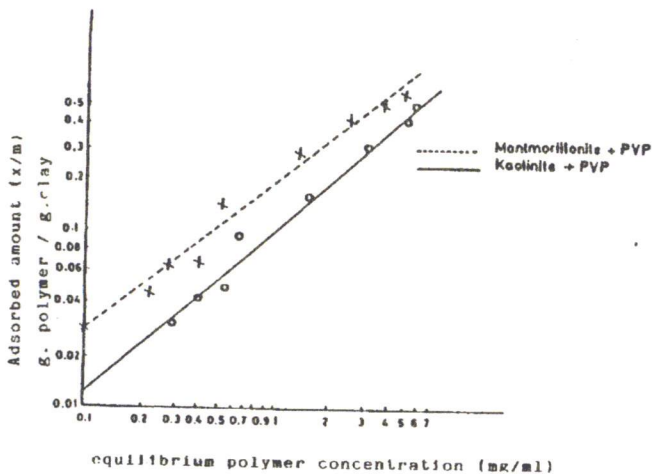


Figure 4. Freundlich adsorption isotherms for PVP on Ca-Kaolinite and montmorillonite.

Zeta Potentials

Figure (5) shows the zeta potential values of kaolinite and montmorillonite at different adsorbed amounts (x/m) of PVP. The zeta potential of kaolinite and montmorillonite decreased rapidly at low adsorbed amount of PVP and with the increase of PVP adsorbed, the decrease in zeta potential becomes insignificant. It has been shown that this reduction of zeta potential in the presence of the adsorbed PVP is not a consequence of change in the

ionic distribution within the electrical double layer but is due to a physical displacement of the plane of shear with respect to its position in the absence of the adsorbed polymer [21,22]. The distance at which the shear plane is displaced represents the thickness, Δ , of the adsorbed polymer layer since the outermost extensions of the adsorbed polymer molecules will be free draining with respect to the solvent (water).

In presence of adsorbed PVP, the results show that the decrease in zeta potential of montmorillonite is more than that observed in the case of kaolinite. This is due to that montmorillonite has two available surfaces for polymer adsorption (inter and outer surface) while kaolinite has only one surface.

Interactions Energy Profile

The interaction energies of the double layer around the clay particles were calculated using the zeta potential values. Figure (6) shows the potential energy profiles for kaolinite. The repulsion energy (V_R) and attraction energy (V_A) between the surface of two kaolinite particles were calculated as a function of distance from the clay surface. By adding these components V_A and V_R the total interaction free energy, V_T is obtained. As the zeta potential of kaolinite is high (about 53 mV), the repulsion between clay particles is very high and clay particles are separated from each other.

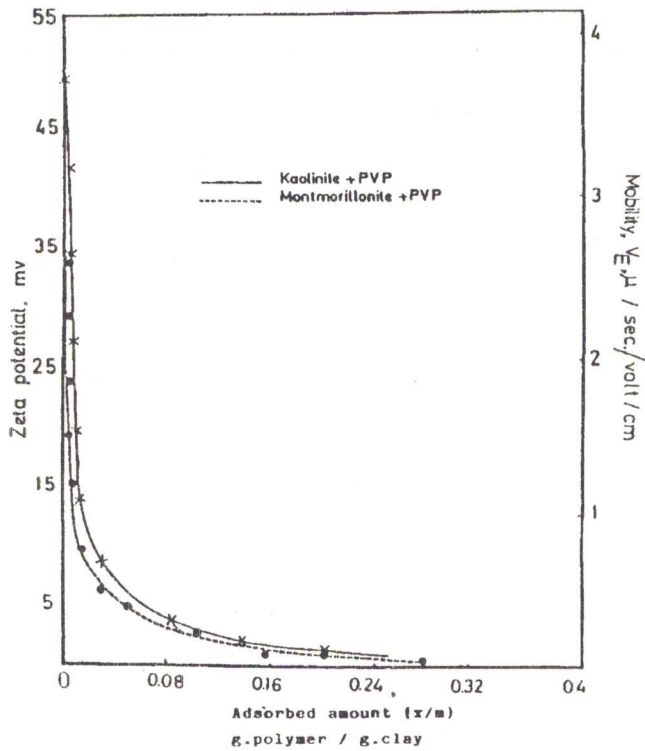


Figure 5. Electrophoretic mobility and zeta potential of Ca-Kaolinite and montmorillonite as a function of adsorbed amount of PVP.

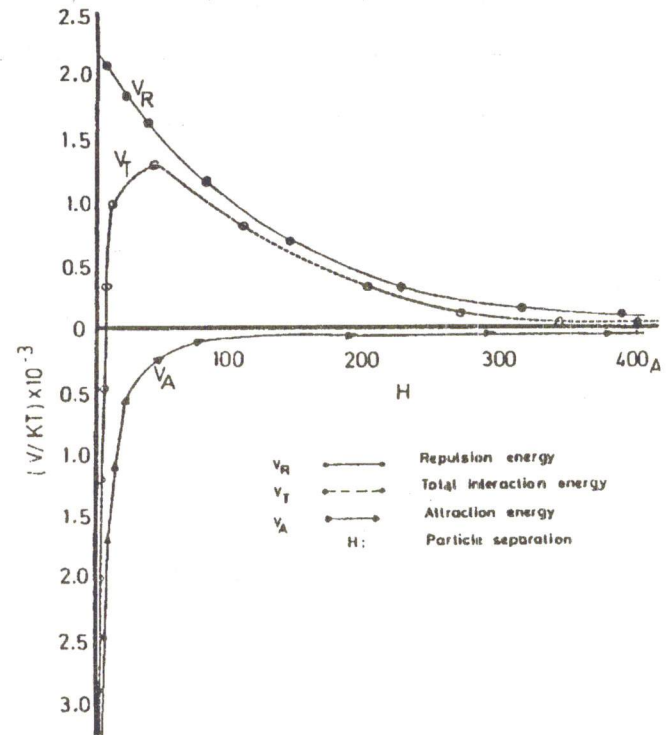


Figure 6. Potential energy profiles of Ca-kaolinite.

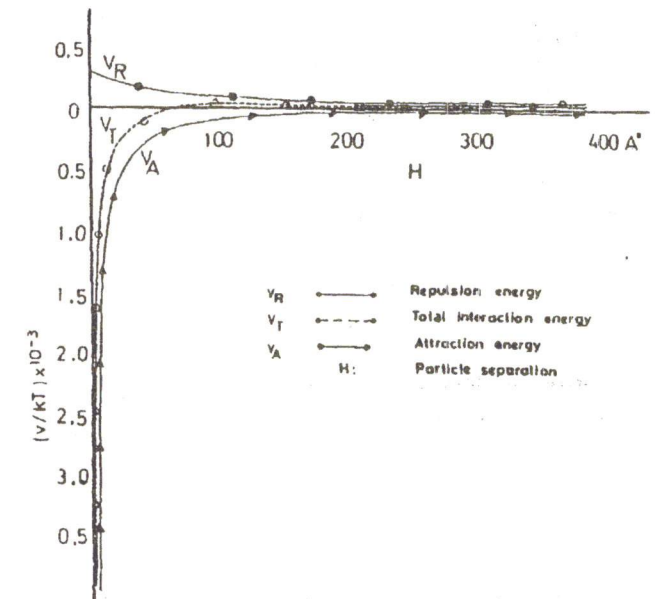


Figure 7. Potential energy profiles of Ca-kaolinite in presence of 0.1 mg/ml of PVP.

Figure (8) shows the potential energy profiles of montmorillonite. The potential energy barrier of the untreated clay was about 650 KT. This value is less than the corresponding value of kaolinite and is attributed to the zeta potential of montmorillonite

(35 mV) which is lower 20 mV unit than kaolinite.

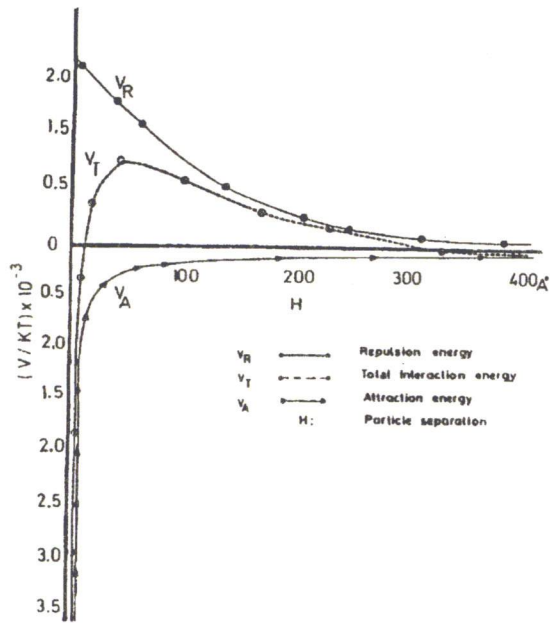


Figure 8. Potential energy profiles of Ca-montmorillonite.

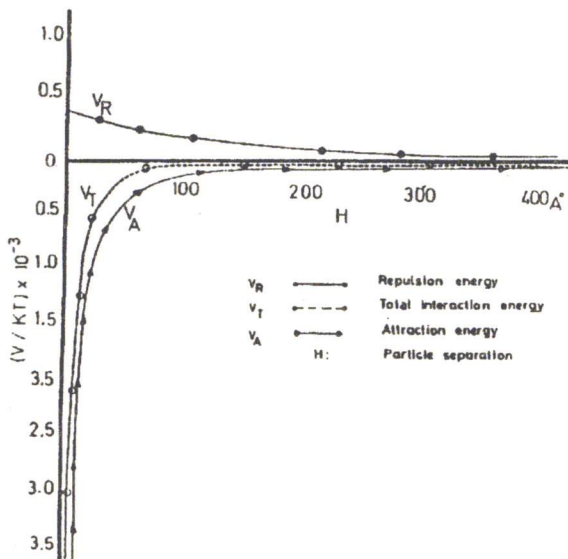


Figure 9. Potential energy profiles of Ca-montmorillonite in presence of 0.1 mg/ml of PVP.

Figure (9) shows that the energy barrier decreases from 650 KT for the untreated clay to zero KT for montmorillonite treated with 0.1 mg PVP/ml. These results indicate that montmorillonite exhibits smaller energy barrier than that observed in the case of

kaolinite treated with PVP of the same concentration. So, the flocculation of montmorillonite in presence of PVP is more easier than in the case of kaolinite. This is attributed to the difference in surface nature of these two clays.

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