Eng. & Tech. Journal, Vol.27, No.4, 2009

# Study the Influence of Poly Vinyl Acetate on Flow Behavior of Bentonite Dispersions in Water

Saad R. Sultan*

Received on:15/7/2008
Accepted on:15/3/2009

**Abstract**

The present investigation is concerned to study the influence of poly vinyl acetate (PVAc.) on flow behavior of bentonite dispersions in water, poly vinyl acetate was added to the bentonite dispersion in different concentration (5, 7.5, 10, 12.5, 15, 17.5 and 20) gm/l. after that, the flow properties of these samples was measured and that included (viscosity, shear stress, shear rate and Bingham yield value), The results show thixotropy flow by a hysteresis loop of the flow curves for bentonite dispersion with and without poly vinyl acetate, but with (PVAc.) give higher fluidity flow.

Also the morphology of bentonite dispersions was analyzed before and after adding poly vinyl acetate by scanning electron micrograph (SEM), it is show that a weak association between (PVAc.) and bentonite dispersions.

**Keywords:** Bentonite, Poly vinyl acetate, Rheology, Thixotropy flow

## دراسة تأثير البولي فنيل اسيتت على سلوكية جريان البنتونايت المشتت في الماء

**الخلاصة**

يتناول البحث دراسة تأثير البولي فنيل اسيتت (.PVAc) على سلوكية الجريان البنتونايت المشتت في الماء , حيث تم أظافة البولي فنيل اسيتت الى البنتونايت بتراكيز مختلفة هي ( 5 , 7.5 , 10 , 12.5 , 15 , 17.5 و 20 ) غرام/لتر , بعد ذلك جرت دراسة الخواص الأنسيابية لتلك النماذج والتي تضمنت الزوجة وأجهاد القص , لقد أظهرت النتائج سلوك Thixotropy flow للبنتونايت المشتت قبل وبعد أضافة البولي فنيل اسيتت ولكن مع أضافة (.PVAc) اعطى أنسيابية جريان اعلى.

كذلك تم دراسة التشكيل Morphology للبنتونايت قبل وبعد أضافة البولي فنيل اسيتت بواسطة فحص (Scanning electron micrograph) وقد أوضحت النتائج ضعف الترابط بين جزيئات البنتونايت و (.PVAc) .

## Introduction

Clay is a natural raw material that has been used for various purposes since ages**,** it's defined as material with particle size below 2 µm, outstanding properties of this material in particular flow behavior and plasticity, would be inconceivable if the particle size were the only decisive parameter, the properties of clays are brought about by the content of clay minerals, besides the small size of the particles several other parameters determine the rheological properties: shape of particles, layer charge, exchangeability of cations, structure of particle edges and edge charge density, a further strong point is that the shape of smectite particles can change with environmental or experimental conditions and can never be considered as invariable, [1].

Bentonite is a softly clay substance composed essentially of clay mineral of the smectite group minerals (Ca-

*** Chemical Engineering Department, University of Technology/Baghdad**



https://doi.org/10.30684/etj.27.4.16
2412-0758/University of Technology-Iraq, Baghdad, Iraq

montmorillonite) and formed in –situ chemical weathering of volcanic materials such as tuft of glass, volcanic ash, other igneous rocks or from rocks of sedimentary origin, the natural of the weathering environment and the original composition of the volcanic material will generally determine the type of bentonite that forms ; the color of bentonite ranges from white to light olive agreen, yellow, earthy red and times some sky when fresh by yellowing rapidly exposure to air, [2].

Bentonite has many uses due to its high plasticity and getting property its ability to take up large quantities of water and its capacity to swell to many times its dry volume, [3].

Nowadays, many different industrial branches such as ceramics, paper, rubber; clarification of water, wine, soaps and cleaning and polishing of compounds, drug industry are using these materials, dispersions of solids in liquids find application in wide variety of industries and have been extensively in scientific studies of colloidal phenomena and fundamental properties of matter, [4].

Bentonite group minerals show a colloidal structure in water due to their internal structure and small particle size. They have large adsorption capacity for polymer compounds and surfactants due to their unique crystal structure, [5].

Rheology is the study of deformation or flow behavior exhibited by materials; rheologists are concerned with both the measurement of deformation of the fluid with stress and formulation of relations between deformation rates and stress, these relations called rheological models or constitutive equation, can be used in the momentum balance equation to compute a given laminar flow situation velocity profiles and volumetric flow rates. The determination of rheological properties of clay-water systems is very important for its characterization, clay dispersions have colloid structure. The control of the rheological properties of these systems is not only important from a technological but also from a scientific point of view, [6].

The rheological behavior of the system is determined by a mutual effect of attractive and repulsive forces between clay particles, which interact with each other through Coulombic and Van der Waals forces. As a result of these interactions edge–to–edge (EE), edge–to–face (EF) and face–to–face (FF) combinations may be obtained. These simple modes of the particle interactions were found to be rather practical in understanding the stability and the rheological behavior, [7].

The rheological parameters (viscosity, shear stress, Bingham yield value) of clay dispersion can be used to characterize particle–particle interactions. The polymers that have been added to the bentonite dispersions interact with the clay particles, according to their ionic or non-ionic character, the ionic polymers induce electrostatic interactions, but the non-ionic polymers are adsorbed on the surface by steric interactions, polymer concentration, molecular weight, hydrolysis degree of polymer, functional groups of polymer, clay particle’s size, shape, and surface charge, clay concentration in dispersion, clay’s pH, and temperature are effective factors when clay particles interact with the polymers.

These interactions can be changed to gain the desired properties with the addition of various electrolytes, polymers, surfactants, and organic matters. There are numerous studies related to these topics.

A. Alemidar and N. Oztekin studied the influence of cationic polymer, polyethyleneimine (PEI) adsorption on flow behavior of bentonite suspensions (2%, w/w), they have notice the PEI molecules adsorbed strongly on the surface of the clay minerals, [8].

Gungor N. investigated the effect of poly (vinyl alcohol) addition on rheological behavior of bentonite clay; they have clearly found the degree of interaction between polymer molecules and clay particles depended on the polymer concentration in the dispersion, [5].

Finally, Brandenburg and Lagaly G. studied the effect of PH on the viscosity of bentonite dispersion, they have notice the viscosity is strongly PH dependent, [1].

In this study, changes in flow properties under the influence of poly (vinyl acetate) (PVAc.) polymer additions at different quantities were investigated, the data were interpreted taking into account the interactions of the colloidal clay particles, the interactions between bentonite and PVAc. were also studied by using Scanning electron micrographs (SEM).

## Experimental Work

### Materials

Bentonite clay used in this study was supplied by National Company for Geological and Mining. It has a good strength stiffness and able to absorb moisture and available at low cost. Bentonite chemical composition is shown in table (1), poly vinyl acetate (PVAc.) is a synthetic polymer produced by the emulsion polymerization of acetate groups [–$(CH_2CHOH)$*n*_+2$CHOCOCH_3$)*m*–], the commercial Poly (vinyl acetate) consist of (29%) solid content with PH (4-7) and the average molecular weight was calculated from a single point viscosity value and was found to be ~ 60,000 is an available in Al- Gihad factories, That-Al-Sawary Company. Baghdad –Iraq, [9].

### Samples preparation

(2% w/w) of the bentonite particles were dispersed in water with continuous mixing for (6) hours. These dispersions were mixed with different concentrations of poly (vinyl acetate) [5, 7.5, 10, 12.5, 15, 17.5 and 20] gm/l. Then the dispersions were stirring for another (6) hours, and their rheological properties were determined with Coaxial – Cylinder Rheometer type (VEB MLW fgerate –Wark) Company as show in fig. (1).

### Characterization & Measurements

Bentonite sample was identified as Ca-montmorillonite clay minerals using FTIR analysis methods which are available in Iraq National Company for Geological and Mining.

FTIR analyses (400–4000 $cm^{-1}$) were performed using Jasco Model 5300 FTIR spectrophotometer on KBr pellets with a concentration of 0.1%. Spectral outputs were recorded either in absorbance or transmittance mode as a function of wave number.

Coaxial – Cylinder Rheometer type (VEB MLW fgerate –Wark) Company was used to measure viscosity, this apparatus has four rotational speeds (16, 37, 77, & 150) rpm an electrical motor drives the rotor, the shear stress (scale reading) is determined as a function of shear rate from the rotational speed, this instrument consists of two cylinders, first the inner is moved and second the outer is fixed as shown in fig. (1), the rheometer has dimensions as follows, [10].

$r_i$=radius of inner cylinder = 11.5 mm
$r_o$= radius of outer cylinder = 19 mm

$$\omega = (2\Pi N) / 60 \qquad (1)$$

Where:
$\omega$ = angular frequency ($S^{-1}$)
N = rotational speed (rpm)

The sample placed in fixed cylinder under suitable temperature and the instrument will be read the factor (α) it is proportional with shear stress, and then will be read shear stress. While the shear rate is a function of rotational speed as follows, [10]

$$\tau = z \cdot \alpha \qquad (2)$$

Where:
$\tau$ = shear stress (dyne / $cm^2$)
z = constant
$\alpha$ = scale reading

$$\gamma = (\omega * r_o^2) / (r_o^2 - r_i^2) \ldots\ldots (3)$$

Where:
$\gamma$ = shear rate ($s^{-1}$)
Then

$$\eta = (\tau / \gamma) \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where:
$\eta$ = Viscosity

Scanning electron micrographs (SEM) were taken using a microscope with special digital camera which is available in ministry of science and technology ,suited plates were chosen of microscope examination , they were put on a glass holder were covered with a glass slide and were watched at 100 fold magnification.

**Results and Discussion**

The flow behavior of any material may be characterized by a consistency curve or flow curve, a diagram relating the shear rate ($\gamma$) and the shear stress ($\tau$). In ideal case (Newtonian liquid) the fluid begins to flow appreciably as soon as a shear stress is applied. The shear stress ($\tau$) is proportional to the rate of shear [$\tau=\eta*\gamma$], the proportionality constant is the shear viscosity.

Very diluted clay dispersions exhibit Newtonian flow, at higher concentration ($\tau$) is no longer proportional to ($\gamma$) and flow is plastic, plastic flow can exhibit a yield stress. The dispersion begins to yield to the applied stress only above a finite stress. Plasticity occurs when a particular network is formed throughout the system, which can resist to the mechanical deformation as long as the force remains below a critical value. If the flow curve is a linear at higher rates of shear (Bingham flow), the extrapolated shear stress is called Bingham yield stress ($\tau_B$).

A system behaves thixotropic when the apparent viscosity decreases continuously with time under shear and is subsequently recovered when the flow is discontinued. A thixotropic system (clay dispersions, paints, drilling fluid, tomato catch-up) begins to flow under stirring or vibrating and solidifies at rest; thixotropic is detected by a hysteresis loop of the flow curve.

The shear stress vs. shear rate curve for bentonite clay dispersion shown in figure (2), from this figure it is clearly that the curve is typical of Bingham pseudoplastic system, showing a thixotropic loop and the sample dispersion exhibit Bingham plastic behaviour. It can be seen that Bingham yield value showed little variation, the graph obtained indicated that the sample had yield point, and was consistent with the Bingham flow model, a Bingham model was applied,[1].

$$\tau = \tau_B + \eta_{PL}\, \gamma \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

From equation (5) the yield value ($\tau_B$) was obtained by extrapolation of the linear portion of the shear stress – shear rate curve to ($\gamma$ =0), and the plastic viscosity ($\eta_{PL}$) from the slop of the linear portion of the curve, the Bingham yield value was (2.05 mPa) for bentonite – water system.

On other hand figure (3) show the changing of apparent viscosity of bentonite clay dispersion as a function of shear rate, the curve showed a sudden decrease at small shear rates indicating thixotropic properties of the sample.

Poly (vinyl acetate) is a polymer with non-ionic structure, which is swells and softens on prolonged immersion in water. Non-ionic polymer dose not interact electro statically with charged clay particles, the polymer molecules can attach or anchor on the particle surfaces and into the interlayer. Adsorption of the polymer on charged surface of the clay particles leads to significant modification of the charge distribution in the electrical double layer.

In figure (4), the Bingham yield value of bentonite dispersions was plotted as a function of increasing poly (vinyl acetate) concentration. Theory and practice indicated that Bingham yield value was a criterion of the particle-particle interactions. When (PVAc.) was added to the dispersions a decrease in initial yield value was observed, showing an interaction between polymer molecule and clay particle, this caused a decrease in electro viscous effect and yield values of dispersions decreased to minimum (6) g/l polymer concentration. The groups existing before the addition has been dispersing and the environment can display less resistance against the flow, [4].

An increase was observed after addition of (7) g/l poly (vinyl acetate), the reason was that the bridge flocculation made by two clay particles with their surrounding polymer extensions when they approached each other, the entanglement of adsorbed polymer chains may also occur and result in high system viscosity. The increase of yield value was an indicator of a net structure formed in the dispersions. Further increase in polymer concentration resulted in a reduction in this gelation. This decrease was related to the steric push that occurred between (PVAc.) covered clay particles, the Bingham yield value of clay – water – PVAc. , was (1.17) mPa, the adsorption phenomena of (PVAc.) on bentonite particles as a function of concentration of the polymer is schematically presented in figure (5).

Figure (6) show the hesteresis effect was observed for the bentonite dispersion, these results suggested that bentonite dispersion were thixotropic. The results indicated that a gradual increase in gelation on addition of (PVAc.) polymer reached a maximum at (10) g/l polymer concentration, this gel – like – dispersion showed pronounced thixotopy. Further increase in polymer concentration resulted in reduction in this gelation. These results were in good agreement with Bingham yield value behaviour of bentonite dispersion, [1].

Scanning electron microscopic (SEM) picture of the samples were used for characterization of the bentonite dispersions with different (PVAc.) concentration show in figure (7). Direct evidence of intercalated bentonite dispersion can be found in (SEM) examination of the cross – section of montmorillonite /(PVAc.). In figure (7a), forming different aggregates (heaps) of clay particles with each other could be seen in 2% clay dispersion. Face –face interaction were in great number in (10)g/l (PVAc.) dispersion (figure 7b), polymer coated particles exhibited appearance of layers with one on top of the other. In (20g/l PVAc.) dispersion we could see that the stacked structure was scattering (figure 7c). SEM images were in consistency with the rheological data which were showing decrease of the yield value with decrease in (PVAc.) concentration.

**Conclusions**

Based on the results presented and discussed, the main conclusions are:

- Addition of (PVAc.) polymer greatly changed the rheological properties of bentonite dispersion. The degree of interaction between polymer molecules and clay particles depended on the polymer concentration in the dispersion.
- Thixotropy was observed in bentonite dispersions with & without polymer. As it is known, thixotropy is an important characteristic for industrial applications. For example, drilling fluids and paints must be thixotropic. Thixotropy effect results were in good agreement with the behaviour of bentonite dispersion’s yield value.
- SEM analysis showed a weak association between (PVAc.) and bentonite, probably coming from the hydrophobic modification of the clay surface.
- Iraqi bentonite samples have been used in applications for decolorizing or moisture absorption purpose. The (PVAc.) with bentonite dispersion has

a higher fluidity than bentonite dispersion. The presence of (PVAc.) did not prevent extensive swelling of bentonite and they have also led to uses without destroying the applications. In the applications, ease of flow is desired and this (PVAc.) bentonite dispersion can be used.

**References**

[1] Lagaly, G. "Effect of poly ethylene imine adsorption on rheology of bentonite", Appl. Clay Sci., Vol.4, No.105, 1989

[2] Grim, R.E. "Applied Clay Mineralogy" Mc. Graw. Hill, INC.New York, 1962

[3] Taylor, J. R.and Bull, A.C. "Ceramic Clay Technology" Pregham Press, 1986

[4] Tadros, T.F. " Solid - Liquid Dispersions", New York Academic Press, 1987

[5] Gungor, N. & Unlu, C. "Rheology and structure of bentonite with poly vinyl alcohol", Indian Academy of Sciences", Vol.29, No.5, PP.449-456, 2006

[6] Vinogradov G.V. and Yamalkin, A. "Rheology of Polymer" mir publisher, 1980

[7] Olphen H. "Clay Colloid Chemistry" New York Wiley, 1977

[8] Alemdar, A. Oztekin, N. "Effect of sodium dodecyl sulfate on flow electro kinetic properties" Indian Academy of Sciences, Vol.28,No.3, 2005

[9] Lindemann, M. K. "Encyclopedia of polymer science and technology", HF Mark et.al New York Wiley, Vol.14, P.168, 1971

[10] Jwad, A."Study the Effect of Carbon Black on Physical Properties of Polymer Blend PP/PC", M.Sc. Thesis, ChemicalE ngineering Department University of Technology, 2007

**Table (1): Chemical composition (%) of Iraqi Bentonite Clay**

| $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $Na_2O$ | $K_2O$ | $P_2O$ | $SO_2$ | Cl | $LiO_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 56.77 | 15.67 | 5.12 | 4.48 | 3.42 | 1.11 | 0.60 | 0.65 | 0.59 | 0.57 | 9.49 |

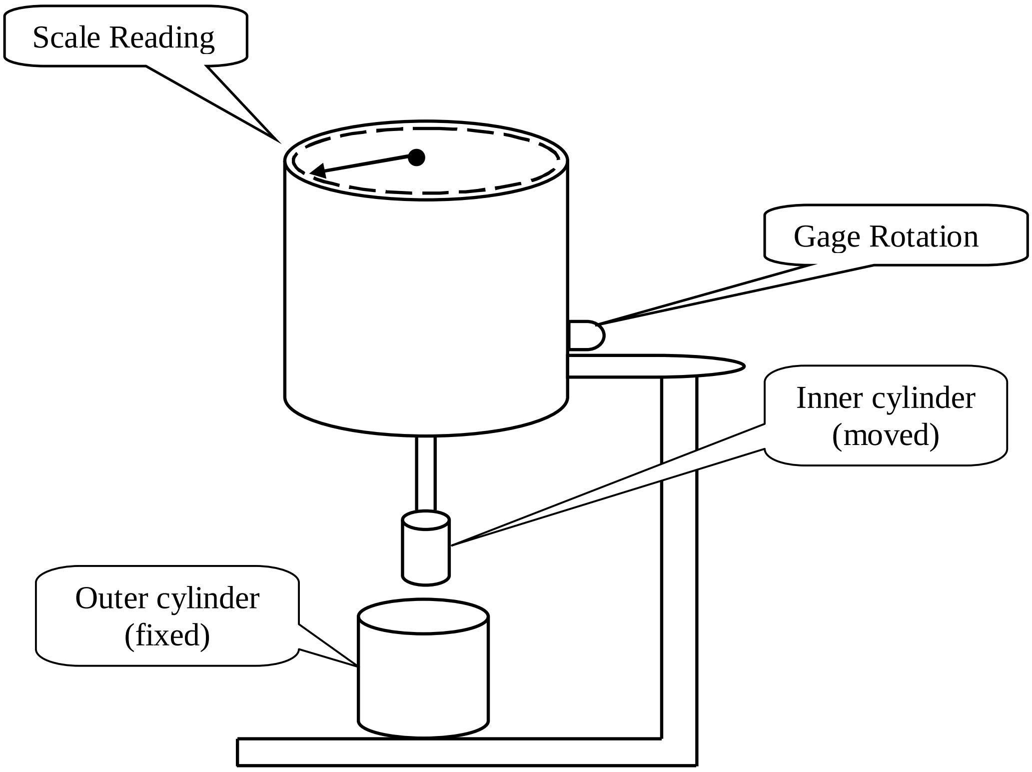


**Figure. (1) Coaxial – Cylinder Rheometer**

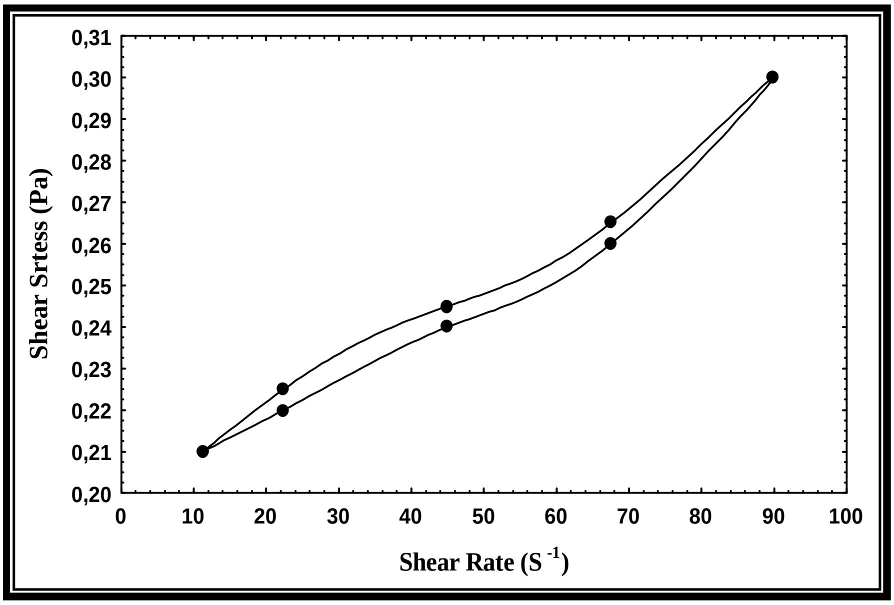


**Figure (2): The flow curve of 2% dispersion of Iraqi bentonite clay**

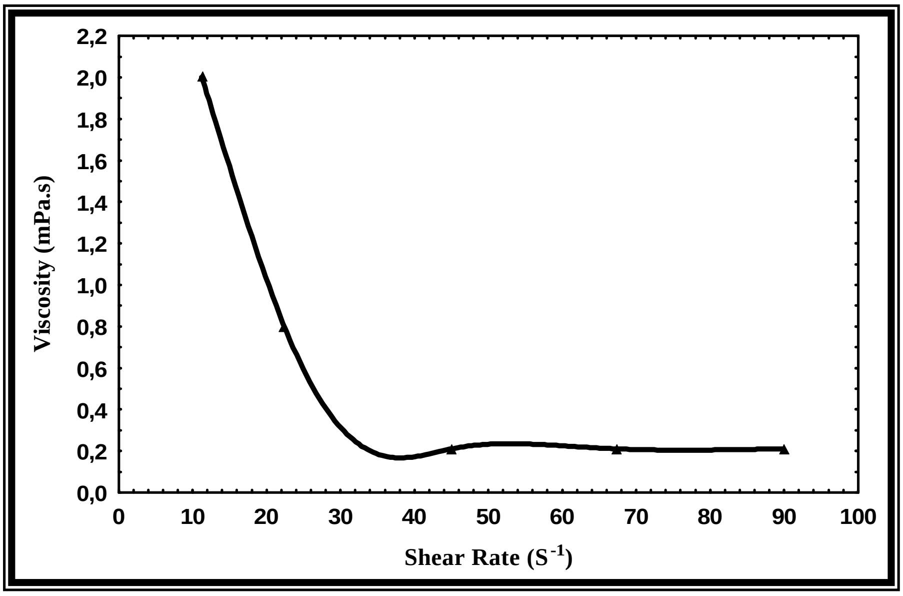


**Figure (3): Viscosity – Shear rate curve of 2% dispersion of Iraqi bentonite clay**

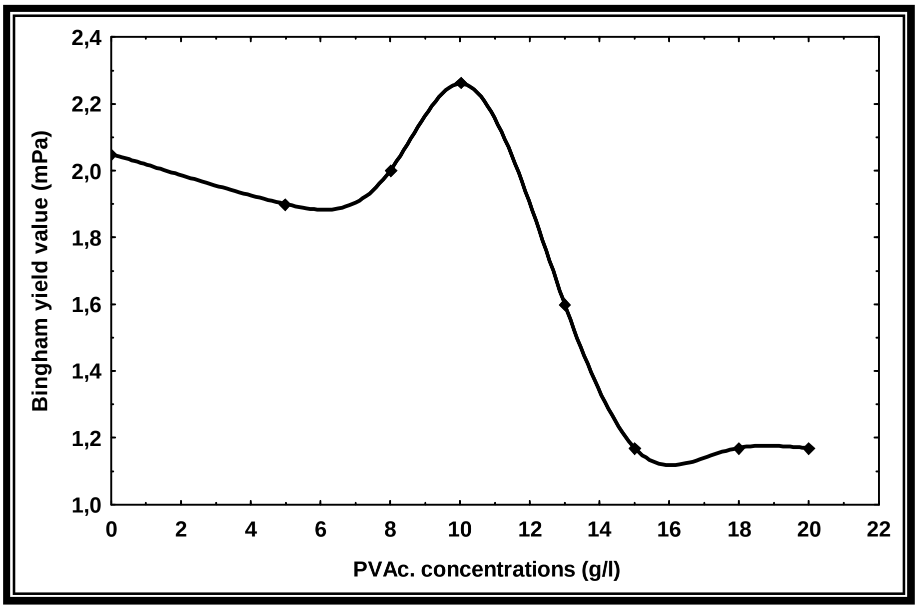


**Figure (4): The influence of poly (vinyl acetate) on the Bingham yield value of 2% bentonite –water system**

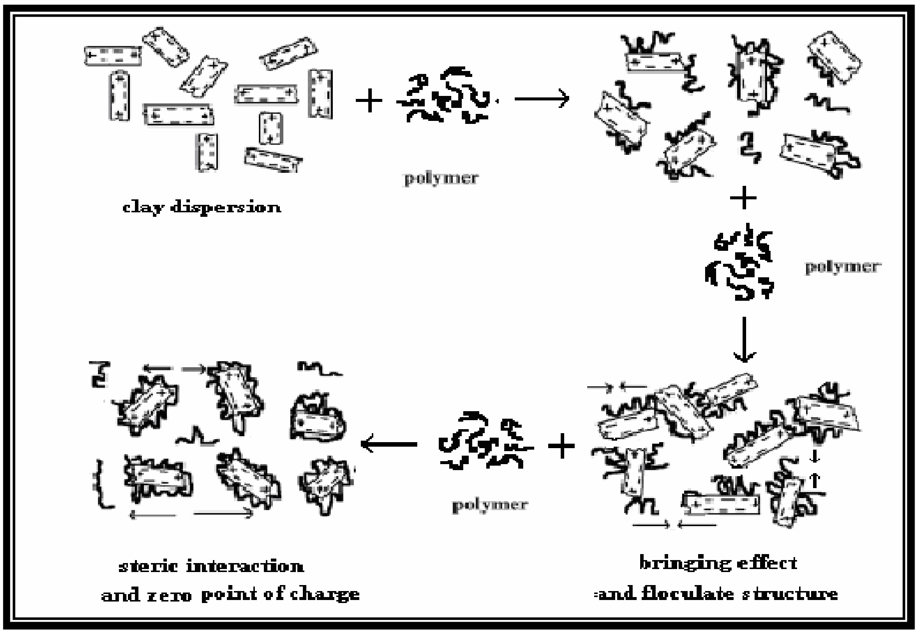


**Figure (5): Schematic representation of adsorption of (PVAc.) polymer on bentonite particles as a function of concentration of polymer.**

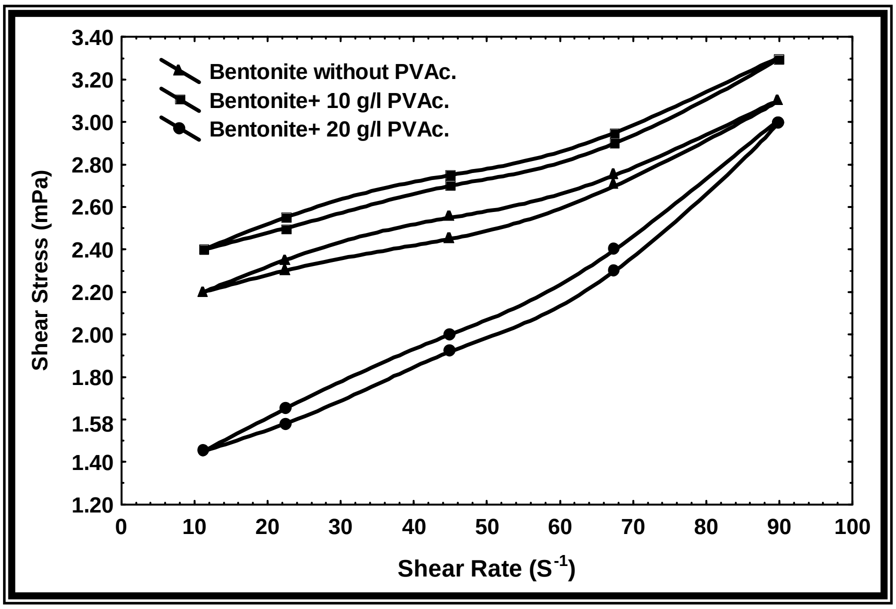


**Figure (6): The flow behaviour of bentonite dispersion with and without poly (vinyl acetate)**

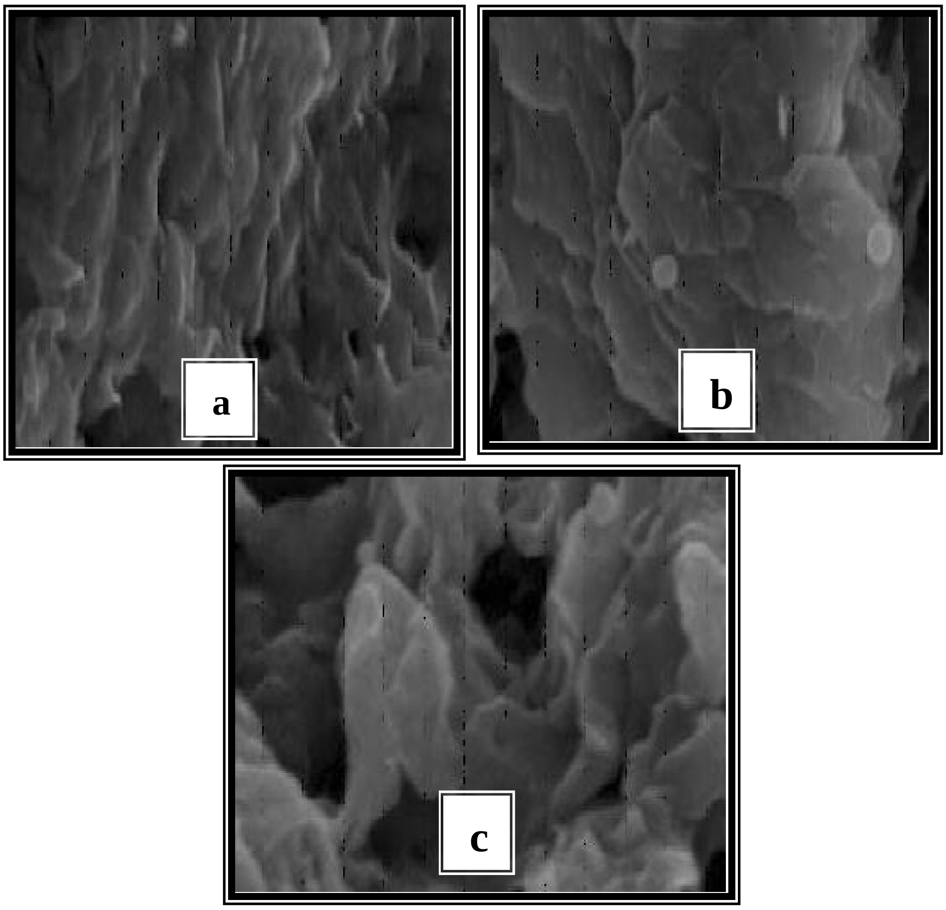


**Figure (7): SEM micrograph of (a): bentonite without (PVAc.), (b): bentonite with (10g/l PVAc.), (c): bentonite with (20g/l PVAc.),**