

Electrokinetic and Rheological Behaviors of Sepiolite Suspensions in the Presence of Poly(acrylic acid sodium salt)s, Polyacrylamides, and Poly(ethylene glycol)s of Different Molecular Weights

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ABSTRACT: The effects of the molecular weights and concentrations of three polymers, poly(acrylic acid sodium salt) (NaPA), polyacrylamide (PAA), and poly(ethylene glycol) (PEG), on the electrokinetic and rheological properties of sepiolite suspensions were investigated. The ζ -potential values of the sepiolite suspensions were measured at different pH values, and the isoelectric point of sepiolite was determined to be 3.27. The anionic NaPA polymers were much effective in reducing the ζ -potential values of sepiolite than the nonionic polymers PAA and PEG. PAA and PEG of higher molecular weights caused a significant increase in the ζ -potentials of the sepiolite sus-

pensions as their concentrations and molecular weights increased. The suspensions exhibited Bingham flow behavior. The reason for the increase in the plastic viscosity values of the sepiolite/NaPA suspensions was the increase in the polymer concentration in the suspensions; on the other hand, for the sepiolite/PAA or PEG suspensions, the reasons were the increase in the polymer concentration in the suspensions and the sepiolite-polymer interactions. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1850–1860, 2008

Key words: clay; rheology; viscosity

INTRODUCTION

Sepiolite is a hydrous magnesium silicate. The structural formula of sepiolite is $\text{Si}_{12}\text{O}_{30}\text{Mg}_8(\text{OH})_4(\text{OH}_2)_4 \cdot 8\text{H}_2\text{O}$.^{1–3} It has a fibrous structure formed by the alternation of blocks and channels that grow up in the fiber direction.⁴ Each block is composed of two tetrahedral silica sheets and a central octahedral sheet containing Mg. Because of the discontinuity of the external silica sheets, a number of silanol groups exist at the surface of this clay mineral.⁵ The channels of sepiolite are filled by zeolitic water, which forms hydrogen bonds with the oxygen atoms on the tetrahedral sheet or with other water molecules. The terminal Mg^{2+} ions located at the edges of the octahedral sheet complete their octahedral coordination with other water molecules.⁶ Isomorphic substitutions of Si^{4+} in the tetrahedral sheet of the mineral lattice with Al^{3+} form negatively charged sites on the sepiolite surface. These sites are occupied by exchangeable cations that compensate the electrical charge.⁵

Sepiolite is a valuable material for industrial applications because of its fibrous structure, high specific surface area, and high porosity.⁷

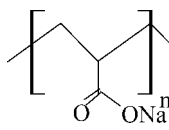
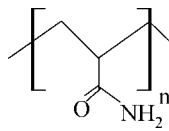
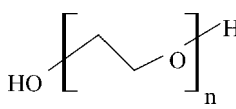
Clay suspensions are commonly used in the production of composite materials, in the preparation of paints, papers, and drilling fluids, and in water purification.⁸ The electrokinetic and rheological properties of clay suspensions are very important for industrial applications because the formulation of commercial products, design and process evaluation, and quality control and storage stability of products depend on these properties.^{9,10}

There are many studies in the literature about the electrokinetic and rheological properties of clay suspensions, especially bentonite and kaolin suspensions. The electrokinetic and/or rheological properties of bentonite suspensions in the presence of polymers, including poly(ethylene glycol) (PEG),^{11,12} poly(vinyl alcohol),¹³ poly(ethylene imine),¹⁴ and anionic polyacrylamide (PAA),^{15,16} have been investigated and published. Sadek et al.¹⁷ studied the effect of poly(styrene sulfonate) on the electrokinetic properties of kaolin. The changes in the ζ -potential and rheological properties of kaolin dispersions after the addition of different polyelectrolyte additives were reported by Marco and Llorens.¹⁸ However, few studies have been published on the electrokinetic properties of sepiolite suspensions. Tekin

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TABLE I
Names, Chemical Structures, Molecular Weights, and Abbreviations of the Polymers

Name	Chemical structure	Molecular weight (g/mol)	Abbreviation
Poly(acrylic acid sodium salt)		1,200	NaPA 1200
		2,100	NaPA 2100
		5,100	NaPA 5100
		8,000	NaPA 8000
Polyacrylamide		1,500	PAA 1500
		10,000	PAA 10,000
Poly(ethylene glycol)		1,500	PEG 1500
		2,000	PEG 2000
		4,600	PEG 4600
		8,000	PEG 8000
		10,000	PEG 10,000

et al.¹⁹ measured the ζ -potentials of sepiolite suspensions in aqueous solutions of NaCl with different cationic PAA concentrations. Moreover, ζ -potential measurements of sepiolite suspensions in the presence of some monovalent, divalent, and trivalent electrolytes have been carried out.^{20–22}

The use of polymers to control the stability and flocculation behavior of colloidal dispersions has great technological importance.¹⁹ Poly(acrylic acid sodium salt) (NaPa), PAA, and PEG are among the polymers most used in the industry. These polymers are widely used in various applications such as soil erosion control, food packing, water treatment, paper manufacturing, adhesives, soil conditioning, and oil recovery. In these applications, the polymers generally react mainly with clay minerals.²³

The aim of this study was to determine the effects of the concentrations and molecular weights of anionic NaPas, nonionic PAAs, and PEGs on the electrokinetic and rheological properties of sepiolite suspensions.

EXPERIMENTAL

Materials

A brown sepiolite sample was obtained from Zafer Mining Co. (Balıkesir, Turkey). NaPas, PAAs, and PEGs with different molecular weight were purchased from Aldrich Chemical Co. (Buchs, Switzerland), except for PEG with a molecular weight of 1500 g/mol, which was supplied by Fluka Chemical Co. (Seelze, Germany). The names, chemical structures, molecular weights, and abbreviations of the polymers used in this study are given in Table I. HCl and NaOH were reagent-grade. Deionized water was used in all experiments.

Methods

Purification of sepiolite

The sepiolite sample was purified before its use in the experiments. The suspension was prepared by the addition of a 100-g sepiolite sample to 1 L of deionized water and was stirred at 960 rpm for 24 h with a Vario-mag Poly magnetic stirrer (München, Germany). Then, the suspension was filtered through filter paper (filter diameter = Φ 25 mm). The purified sepiolite sample was dried at 110°C for 24 h and sieved with a 100- μ m sieve. The particles under 100 μ m were used in further experiments.

Characterization of sepiolite

The sepiolite sample was characterized with several methods, including X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), infrared (IR) spectroscopy, and the determi-

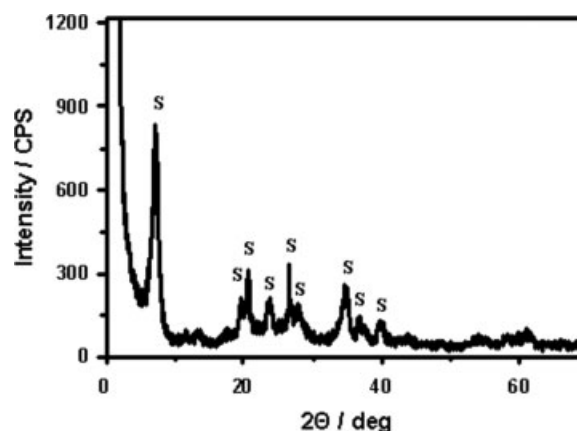


Figure 1 XRD pattern of sepiolite.

TABLE II
Chemical Composition of Sepiolite

Compound	Sepiolite (%)
MgO	24.71
Al ₂ O ₃	2.89
SiO ₂	69.52
K ₂ O	0.69
CaO	0.38
TiO ₂	0.22
Fe ₂ O ₃	1.59

nation of the cation-exchange capacity, density, particle size distribution, and specific surface area.

XRD measurements were performed to determine the type of clay mineral with a Shimadzu (Kyoto, Japan) XRD-6000 diffractometer. The XRD pattern of sepiolite is presented in Figure 1. The observed 2θ values at 7.18, 19.70, 20.58, 23.74, 26.65, 27.98, 34.74, 36.81, and 39.86 indicate that the clay sample used in this study was mainly sepiolite. The chemical composition of sepiolite was analyzed with an XRF spectrometer (Philips PW2404 model, Almelo, Netherlands), and the results are given in Table II. X-ray measurements were carried out by the Scientific and Technological Research Council of Turkey. The purified sepiolite contained essentially Si⁴⁺ and Mg²⁺ (Table II).

A Zeiss Leo 1430 scanning electron microscope (Oberkochen, Germany) was used to observe the morphology of the sepiolite sample. The SEM images of sepiolite obtained at different magnifications are shown in Figure 2. These images show that the sepiolite had a fibrous structure.

The Fourier transform infrared (FTIR) spectrum of sepiolite was recorded with the KBr pellet technique. The KBr pellet was prepared by the mixing of the sepiolite sample with KBr powder (1:100) and the use of a pressure of 10 tons. A Tensor 27 FTIR apparatus (Bruker, Ettlingen, Germany) was used to obtain the IR spectrum of the sample. The FTIR spectrum of the sepiolite sample, recorded in the range of 400–4000 cm⁻¹ at a resolution of 2 cm⁻¹, is shown in Figure 3. The band at 3687 cm⁻¹ is due to the stretching vibrations of Mg—OH. The bands observed at 3565 and 3441 cm⁻¹ indicate the OH stretching bonds of bound water and zeolitic water, respectively. The OH bending peak corresponding to the bound water can be detected at 1661 cm⁻¹. The Si—O—Si bands at 1211 and 1023 cm⁻¹ are due to Si—O vibrations. The small band observed at 788 cm⁻¹ is the OH bending vibration of Mg—Fe—OH. Two peaks at 691 and 647 cm⁻¹ are due to the bending vibration of Mg—OH. The peak at 472 cm⁻¹ is attributable to the Si—O—Si bending vibration.^{24–28}

The cation-exchange capacity and density of sepiolite were determined by the ammonium acetate method and pycnometric method, respectively.

The particle size distribution and specific surface area (according to the Brunauer–Emmett–Teller method) of sepiolite were obtained with a Mastersizer 2000 particle size analyzer (Malvern, UK) and Quantachrome Autosorb-1-C/MS (USA), respectively. These measurements were carried out by the Central Laboratory of Middle East Technical University (Ankara, Turkey). The particle size distribution of sepiolite is shown in Figure 4.

The results obtained for the physicochemical properties of sepiolite are given in Table III.

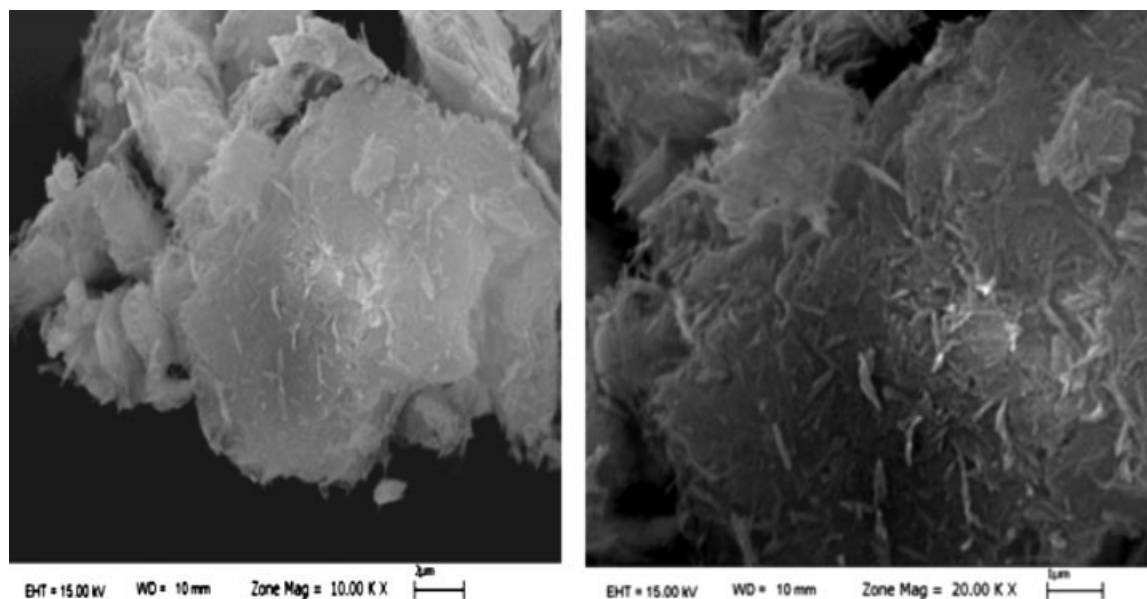


Figure 2 SEM pictures of sepiolite at different magnifications.

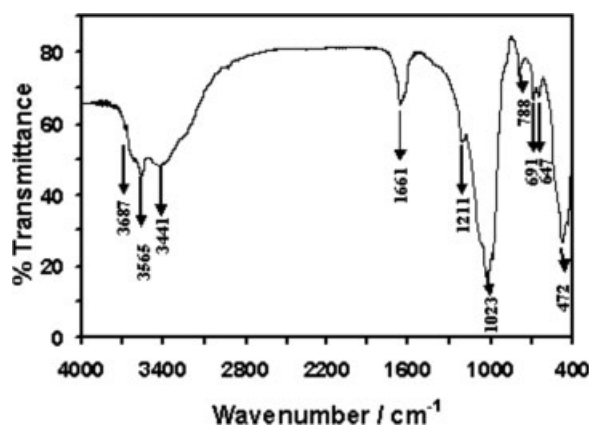


Figure 3 FTIR spectrum of sepiolite.

ζ -potential measurements

ζ -potential measurements were carried out with a Malvern Nano-ZS Zetasizer. This instrument works with the technique of laser Doppler electrophoresis (4-mW He-Ne, 633 nm). Electrophoretic mobilities of particles were measured by the instrument and converted to the ζ -potential with the Smoluchowski equation. The viscosity value of the medium was used for the calculation of the ζ -potential.

ζ -potential measurements were performed to determine the effects of the sepiolite concentration and pH and to estimate the interactions between sepiolite and anionic and nonionic polymers as a function of the molecular weight of the polymer and the polymer concentration.

A sample of 2.0 g of sepiolite in 100 mL of deionized water with the desired polymer concentration was added to an Erlenmeyer flask and then mixed at 400 rpm for 24 h with a Variomag Poly model magnetic stirrer kept in a Sanyo (Osaka, Japan) MIR-250 incubator at $25.0 \pm 0.5^\circ\text{C}$. In the sepiolite/polymer suspensions, the used polymer concentrations were 1×10^{-4} , 5×10^{-4} , 1×10^{-3} , 5×10^{-3} , and $1 \times$

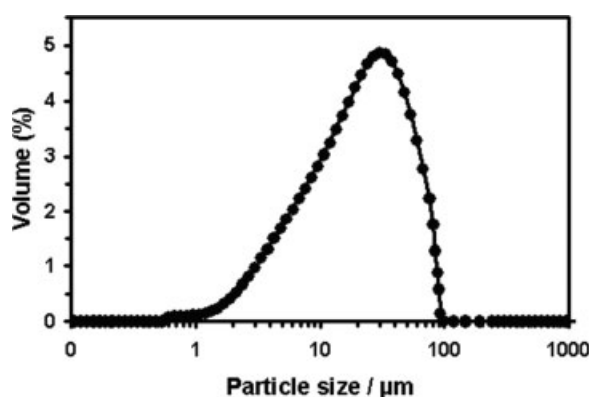


Figure 4 Particle size distribution of sepiolite.

TABLE III
Cation-Exchange Capacity, Density, Average Particle Size, and Specific Surface Area Values of Sepiolite

Physicochemical property	Value
Cation-exchange capacity	9.300 mequiv/100 g of sepiolite
Density	2.048 g/cm ³
Average particle size	22.04 μm
Specific surface area	361.2 m ² /g

10^{-2} M. The equilibrium time was selected to be 24 h for all experiments. The pH was adjusted by the addition of HCl or NaOH solutions and measured with a glass combined electrode. The average of 15 measurements was used to represent the ζ -potential data. The percentage difference in the measured ζ -potential values of the suspensions was, on average, less than 4% of the mean of the 15 values.

Rheological measurements

The rheological measurements of the sepiolite suspensions were carried out with a Brookfield DV-III Ultra programmable rheometer (USA). An ultralow adapter with a sample volume of 16 mL was used in the rheological measurements at $25 \pm 0.5^\circ\text{C}$. All sepiolite/polymer suspensions were mixed at 400 rpm for 24 h by a magnetic stirrer kept in the incubator at $25.0 \pm 0.5^\circ\text{C}$ before the measurements were started, as was done for the ζ -potential measurements. All measurements were performed in duplicate at intervals between shear rates of 1 and 121 s^{-1} . The percentage difference in the measured shear stress values between duplicate samples was, on average, less than 3% of the mean of two values. The average values were used in the determination of the flow properties of the sepiolite/polymer suspensions.

RESULTS AND DISCUSSION

Effect of the sepiolite concentration on the ζ -potential

It is critical to adjust the solid concentration in the suspension because the number of solid particles facilitates the surface charge generation by producing the ionic species at the solid/liquid interface, and this can affect the ζ -potential value of the suspension. An insufficient solid concentration in the suspension can cause errors in the measurement of the ζ -potential. For this reason, before the ζ -potential measurements of the sepiolite/polymer suspensions, sepiolite suspensions having different sepiolite concentrations in water were prepared, and their ζ -potentials were measured.

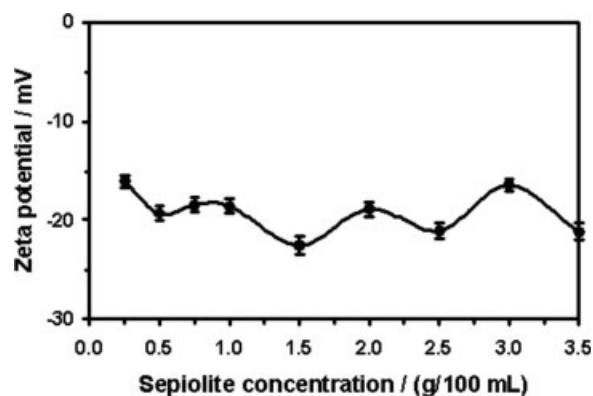


Figure 5 Variation of the ζ -potential of sepiolite as a function of the clay concentration.

The ζ -potential values of the suspensions were plotted as a function of the sepiolite concentration, and they are presented in Figure 5. Figure 5 shows that the ζ -potential values of the sepiolite/water suspensions were not affected by the sepiolite concentration in the studied concentration range of 0.25–3.5 wt %. This means that ionic species produced at the solid/liquid interface did not increase with the sepiolite concentration increasing. Therefore, in the subsequent ζ -potential measurements and viscosity measurements of sepiolite suspensions, the sepiolite-to-liquid ratio was kept constant at 2.0 g/100 mL.

Determination of the isoelectric point of sepiolite

The isoelectric point is a pH value at which the total amount of positive charge on the surface of a solid is equal to the total amount of negative charge on it. The amount of net surface charge of a solid, or the ζ -potential value, is zero at the isoelectric point. The isoelectric point is a characteristic property of solid particles, and that is why it is important to know the isoelectric point of particles for industrial processes.

Sepiolite suspensions (2.0 wt %) with different initial pH values were prepared by the addition of HCl or NaOH solutions, and they were mixed at 400 rpm for 24 h at $25.0 \pm 0.5^\circ\text{C}$. Then, the final pH value and ζ -potential value of each suspension were measured. The measured ζ -potential values for each final pH value of the suspensions are shown in Figure 6. The isoelectric point of sepiolite was determined to be 3.27 because its ζ -potential value was zero at this pH (Fig. 6). An increase in the suspension pH caused negative surface charge on the sepiolite particles.

Effects of the molecular weight and concentration of anionic and nonionic polymers on the ζ -potential of sepiolite

NaPAs of four different molecular weights (NaPA 1200, NaPA 2100, NaPA 5100, and NaPA 8000) were

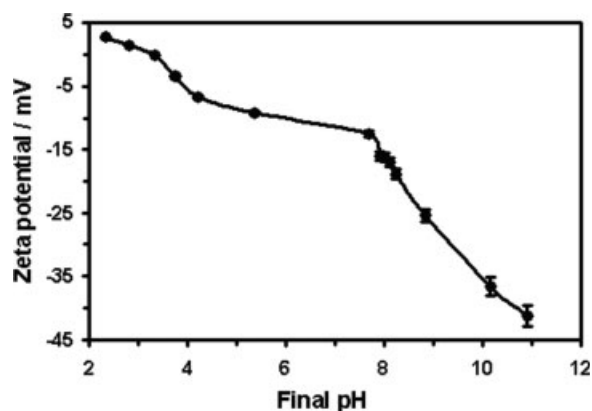


Figure 6 Variation of the ζ -potential of sepiolite as a function of pH.

used to determine the effect of the anionic polymer on the ζ -potential of sepiolite particles. The ζ -potential variation of sepiolite/NaPA suspensions as a function of the NaPA concentration is shown in Figure 7. The measured ζ -potential value of a 2.0 wt % sepiolite/water suspension without any polymer addition was about -20 mV. Figure 7 shows that this value became more negative after the addition of anionic NaPA polymers to the sepiolite particles. This can be explained by the adsorption of anionic polymers onto the sepiolite. In this case, the negativity of the sepiolite particles increased, so the measured ζ -potential values were more negative. This means that electrostatic repulsion between the sepiolite particles increased in the presence of the NaPA polymers.

A decrease in the ζ -potential values of sepiolite was observed with the concentration of NaPA 1200 increasing from 1×10^{-4} to 5×10^{-3} M; after that, an increase occurred. For 1×10^{-4} M NaPA 2100, NaPA 5100, and NaPA 8000, the measured ζ -potential values were -42.4 , -48.2 , and -49.0 mV, respectively. These values became more negative when the

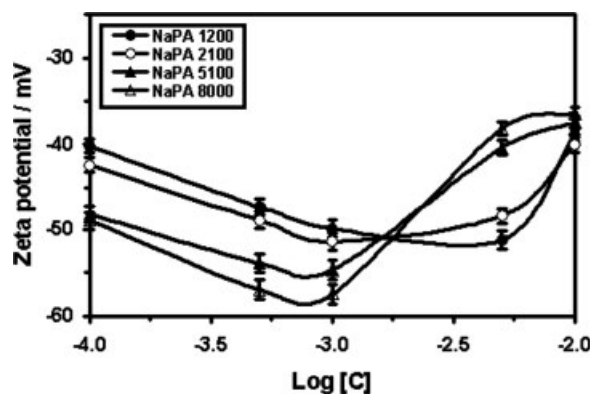


Figure 7 ζ -potential values of sepiolite suspensions as a function of the NaPA concentration (C).

concentrations of these polymers were increased up to 1×10^{-3} M. After this polymer concentration, an increase in these values occurred with increasing polymer concentration. The ζ -potential value of sepiolite decreased with the increase in the chain length or molecular weight of NaPA for each NaPA concentration in the range of 1×10^{-4} to 1×10^{-3} M. The number of negative carboxylate groups in the NaPA polymers increased in the order of NaPA 1200 < NaPA 2100 < NaPA 5100 < NaPA 8000. The NaPA molecules that adsorbed onto particles caused an increase in the negative surface charge of sepiolite. For this reason, the measured ζ -potential values of sepiolite for each polymer suspension in this concentration range showed a parallelism with the chain length of the NaPA polymers.

On the other hand, when the ζ -potential values of sepiolite suspensions were compared at NaPA concentrations of 5×10^{-3} and 1×10^{-2} M, the ζ -potentials increased with the increase in the polymer chain length for each polymer concentration. This result can be explained by the consideration of the available adsorption surface sites of sepiolite. These sites may have been saturated at a NaPA 2100, NaPA 5100, or NaPA 8000 concentration of 1×10^{-3} M. At concentrations higher than 1×10^{-3} M for these NaPA polymers, the excess NaPA molecules caused a screening effect on the sepiolite particles, and thus the ζ -potential values increased with increasing polymer concentration. The decreasing trend in the ζ -potential values of sepiolite finished at the polymer concentration of 1×10^{-3} M for NaPA 2100, NaPA 5100, and NaPA 8000, whereas this trend continued at this concentration for NaPA 1200. This result showed that there were still free adsorption sites on the surface of sepiolite for NaPA 1200 at a 5×10^{-3} M polymer concentration because it had a shorter chain length than the other NaPA polymers.

Similar electrokinetic behaviors were observed for the ζ -potential measurements of bentonite suspensions in the presence of poly(acrylamide sodium salt) (molecular weight = 1,000,000 g/mol) by Mustafa et al.¹⁶ They reported that the ζ -potential values of bentonite suspensions after the addition of 0, 5, 10, 15, 20, and 50 mg/L anionic poly(acrylamide sodium salt) were -32, -50, -55, -47, -40, and -29 mV, respectively. In another study, Sondi et al.²⁹ found that the ζ -potential values of milled ripidolite decreased with the concentration of poly(acrylic acid) (molecular weight = 5000 g/mol) increasing from 0.01 to 10 mg/L.

The pH values of the sepiolite/NaPA suspensions were in the range of 7.9–8.7. This indicated that the NaPA polymers were in an anionic form in the suspensions and that the sepiolite particles carried a net negative charge on their surfaces. In this case, there was electrostatic repulsion between the NaPA mole-

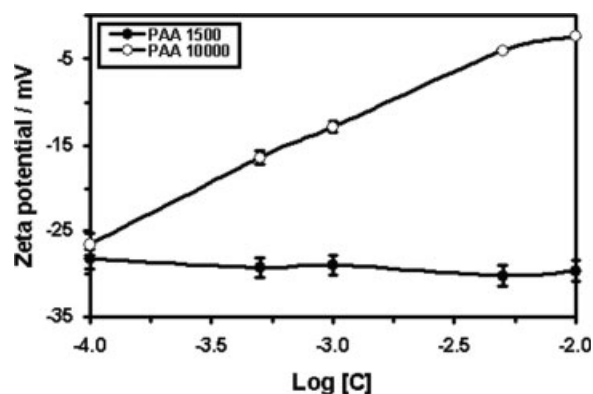


Figure 8 ζ -potential values of sepiolite suspensions as a function of the PAA concentration (C).

cules and sepiolite particles. On the other hand, these anionic polymers could be adsorbed onto the sepiolite particles by hydrogen-bonding formation.

Solutions of two PAAs (PAA 1500 and PAA 10,000) and five PEGs (PEG 1500, PEG 2000, PEG 4600, PEG 8000, and PEG 10,000) as nonionic polymers were used to test their effects on the ζ -potential of sepiolite suspensions. The variation of the ζ -potential of 2.0 wt % sepiolite suspensions with different concentrations of PAA 1500 and PAA 10,000 is shown in Figure 8 as a function of the polymer concentration. Figure 8 shows that the PAA 1500 molecules did not have any significant effect on the ζ -potential of sepiolite, whereas the increase in the concentration for PAA 10,000 led to an increase in the ζ -potential values. The PAA molecules did not interact electrostatically with the negatively charged sepiolite particles because they were nonionic polymers. They could be adsorbed onto the sepiolite by hydrogen bonds that formed between the polymers and sepiolite particles. The chain length of PAA 1500 was shorter than that of PAA 10,000. For this reason, the surface of sepiolite particles was not covered effectively by PAA 1500 molecules even at 1×10^{-2} M. Therefore, the electrostatic repulsion between the negatively charged sepiolite particles was not affected significantly by PAA 1500, and the ζ -potential value maintained its stability in the studied concentration range. On the other hand, for the sepiolite/PAA 10,000 suspensions, there was an increase in the ζ -potential values with the polymer concentration increasing. The adsorption of these polymer molecules onto the sepiolite created a screening effect on the surroundings of negatively charged sepiolite particle surfaces. This effect may have reduced the electrostatic repulsion between the sepiolite particles and may also have increased the ζ -potential value of the system.

The influence of PEG molecules of different molecular weights on the ζ -potential values of sepiolite is shown in Figure 9. Figure 9 shows that the ζ -poten-

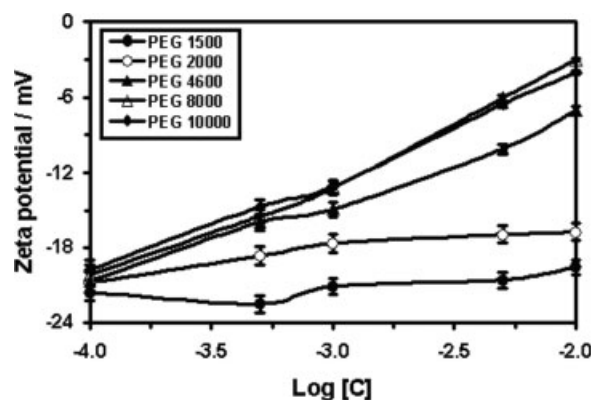


Figure 9 ζ -potential values of sepiolite suspensions as a function of the PEG concentration (C).

tial values of sepiolite did not change significantly with the increase in the PEG 1500 concentration. The difference between the ζ -potential values in the presence of PEGs with different molecular weights was very low at a polymer concentration of 1×10^{-4} M. On the other hand, an increase in the ζ -potential values was observed with an increase in the polymer concentration for PEG 2000, PEG 4600, PEG 8000, and PEG 10,000. The ζ -potential values of 2.0 wt % sepiolite suspensions with 1×10^{-2} M PEG 1500, PEG 2000, PEG 4600, PEG 8000, and PEG 10,000 were measured to be -19.6 , -16.8 , -7.03 , -3.00 , and -4.04 mV, respectively. The variation of the ζ -potential showed a parallelism depending on the chain length or molecular weight of PEG. For each PEG concentration, generally less negative values of the ζ -potential were obtained with the molecular weight of PEG increasing. Similar trends were also observed for the smectite/poly(ethylene oxide) (molecular weight = 2.5×10^6 g/mol) suspensions³⁰ and the bentonite (molecular weight = 3350 g/mol)/PEG (molecular weight = 8000 g/mol) suspensions.¹²

These behaviors observed for the ζ -potential values for sepiolite/PEG suspensions can be explained again by the screening effect on the surface of sepiolite particles. Electrostatic repulsions between sepiolite particles decreased because of the screening of their surfaces by polymer molecules; therefore, an increase in the ζ -potential values was observed.

When the graphs of the ζ -potential versus the polymer concentrations in Figures 7–9 are compared, we can see that the NaPA polymers had a great effect on the decrease in the ζ -potential values of sepiolite because of their anionic structures.

Effects of the molecular weight and concentration of anionic and nonionic polymers on the rheological behaviors of sepiolite

The rheological behaviors of sepiolite suspensions were investigated in the presence of NaPA, PAA,

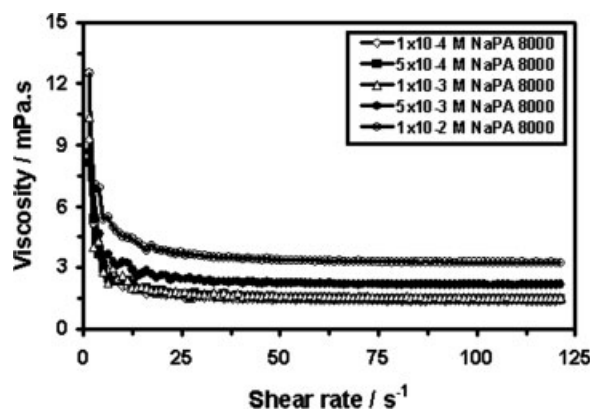


Figure 10 Viscosity versus the shear rate for 2.0% sepiolite with different concentrations of NaPA 8000.

and PEG polymers with different molecular weights and concentrations. Polymer concentrations in the sepiolite suspensions were in the range of 1×10^{-2} to 1×10^{-4} M.

A typical graph of the variation of the apparent viscosity of 2.0 wt % sepiolite suspensions with different concentrations of NaPA 8000 as a function of the shear rate is shown in Figure 10. A sharp decrease can be observed in the viscosity values of sepiolite/NaPA 8000 suspensions at the low shear rate values (Fig. 10). Moreover, as the concentration of NaPA 8000 increased in the sepiolite suspension, the apparent viscosity of the suspension increased, and this increase was much higher for the higher NaPA 8000 concentrations.

A typical graph of the shear stress versus the shear rate is shown in Figure 11 for different concentrations of NaPA 8000. For all sepiolite/polymer suspensions studied, the measured shear stress values with an increasing shear rate were greater than the shear stress values with a decreasing shear rate (Fig. 11). This indicated that the sepiolite/polymer suspensions showed a thixotropic behavior and a hysteresis loop. Thixotropy is a time-dependent

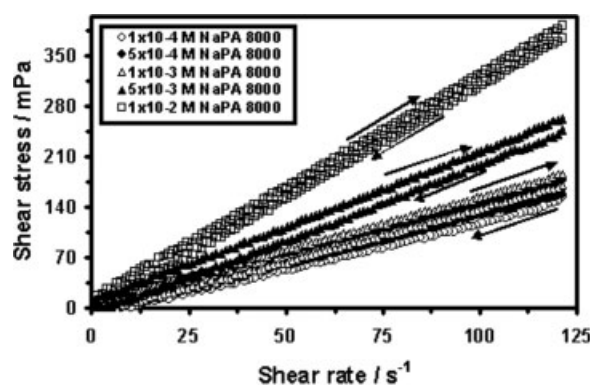


Figure 11 Shear stress versus the shear rate for 2.0% sepiolite with different concentrations of NaPA 8000.

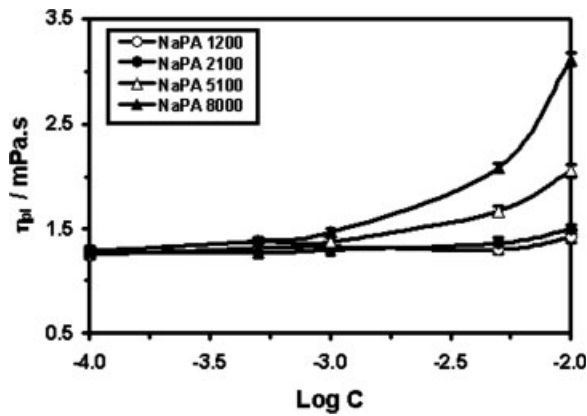


Figure 12 η_{pl} values of 2.0% sepiolite/NaPA suspensions as a function of the NaPA concentration (C).

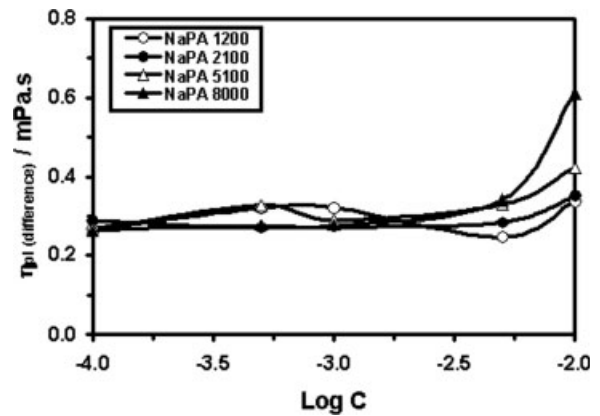


Figure 13 $\eta_{pl(difference)}$ values as a function of the NaPA concentration (C).

decrease in the viscosity. A thixotropic system begins to flow under stirring and thickens again when standing. The network structure can be broken by shear stress, and interparticle bonds tend to reestablish themselves with time. Thixotropy is an important characteristic for industrial applications. For example, drilling fluids and paints must be thixotropic.³¹

A graph of the shear stress versus the shear rate is called a consistency curve, and four different types of curves representing different types of flow behavior of suspensions can be distinguished as Newtonian, pseudoplastic, Bingham plastic, and dilatant. The obtained shear stress and shear rate values fit the Bingham model well (regression coefficient > 0.996 for all studied systems). The equation for the Bingham model is

$$\tau = \tau_{yield} + \eta_{pl} \times \bar{\gamma} \quad (1)$$

where $\bar{\gamma}$ is the shear rate, η_{pl} is the plastic viscosity, τ is the shear stress, and τ_{yield} is the Bingham yield stress.³² The η_{pl} and τ_{yield} values were calculated from the upward flow curve of the graph of the shear stress versus the shear rate.

The η_{pl} values were obtained from the slope of the graph of the shear stress versus the shear rate. Figure 12 shows the variation of η_{pl} values of 2.0 wt % sepiolite/NaPA suspensions as a function of the NaPA concentration. This figure indicates that η_{pl} values for all NaPA polymers generally did not change in the concentration range of 1×10^{-4} to 1×10^{-3} M. On the other hand, at higher anionic polymer concentrations (5×10^{-3} M and 1×10^{-2} M), there was an increase in the η_{pl} values for NaPA 5100 and NaPA 8000, but this behavior could not be observed for NaPA 1200 and NaPA 2100. There may be two reasons for the increase in η_{pl} values. The first one is the interaction between the clay and polymer, and the second one is the increase in the polymer concentration. To understand which one is the

true explanation for this change, the $\eta_{pl(difference)}$ values were calculated by the subtraction of the η_{pl} values of the pure polymers from the η_{pl} values of the sepiolite/polymer suspensions. The $\eta_{pl(difference)}$ values of the sepiolite/NaPA suspensions as a function of the NaPA concentration are shown in Figure 13. Figure 13 shows that the $\eta_{pl(difference)}$ values of the sepiolite/NaPA suspensions did not show any significant change with increasing polymer concentration for all NaPA polymers, except for 1×10^{-2} M NaPA 8000. Therefore, the main reason for the increase in the η_{pl} values was the increase in the polymer concentration. The reason for the increase in the $\eta_{pl(difference)}$ value of the sepiolite/NaPA 8000 suspension at 1×10^{-2} M may be the formation of flocs. Moreover, the electrostatic repulsions between the negative sepiolite particles and the negative NaPA polymers may have prevented larger flocs, and thus the $\eta_{pl(difference)}$ values were not influenced significantly by the increasing molecular weight and concentration of NaPA. It has been proposed that adsorption and flocculation in the presence of anionic polymers occur via hydrogen bonding between the clay surfaces and the polymer molecules.³³

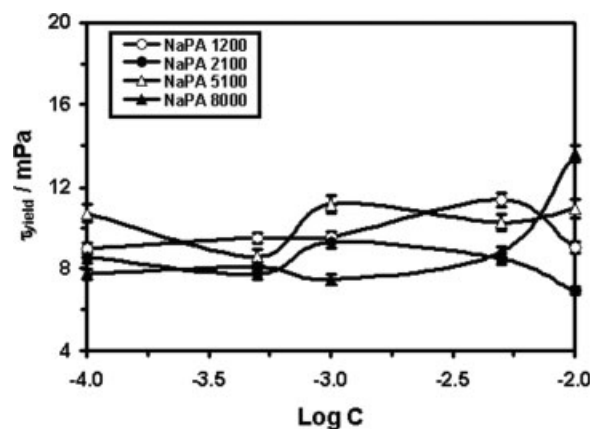


Figure 14 τ_{yield} values as a function of the NaPA concentration (C).

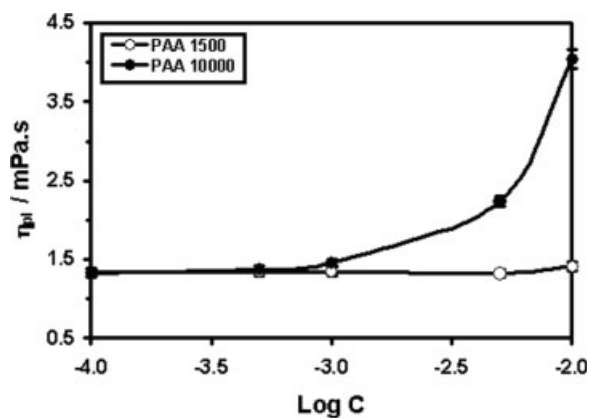


Figure 15 η_{pl} values of 2.0% sepiolite/PAA suspensions as a function of the PAA concentration (C).

The τ_{yield} values obtained from the intercept of the graph of the shear stress versus the shear rate are plotted as a function of the NaPA concentration in Figure 14. There was no regular change in the τ_{yield} values of the sepiolite/NaPA suspensions in the studied concentration range. The τ_{yield} values for these suspensions were between 7.7 and 13.6 mPa.

Figure 15 shows the influence of the PAA 1500 and PAA 10,000 concentrations on the η_{pl} values of the sepiolite/PAA suspensions. The η_{pl} value of the sepiolite/PAA 1500 suspension was approximately the same throughout the studied polymer concentration range, whereas there was an increase in the η_{pl} values of the sepiolite/PAA 10,000 suspension after the addition of of 5×10^{-3} M PAA 10,000. The reason for this increase may be the increase in the PAA 10,000 concentration or sepiolite-polymer interactions. To clarify this state, $\eta_{pl(difference)}$ values of sepiolite/PAA suspensions were obtained as before. A graph of the $\eta_{pl(difference)}$ values versus the PAA concentration is presented in Figure 16. This figure shows that after the subtraction of the η_{pl} values of the pure polymer from the η_{pl} values of the sepiolite/polymer suspensions, there was still an increase in the η_{pl} values of the sepiolite/PAA 10,000 suspension at 5×10^{-3} and 1×10^{-2} M. This indicates that the reasons for the increase in the η_{pl} values of the sepiolite/PAA 10,000 suspension were the increase in the polymer concentration and the sepiolite-polymer interactions. This result can be explained by bridging flocculation. When a polymer chain with a high molecular weight adsorbs onto more than two particles, it causes flocculation in a colloidal suspension. This effect is known as bridging flocculation.³⁴ The bridging flocculation causes the formation of new structures. These structures show much greater mechanical resistance against flowing.³⁵

Figure 17 shows the variation of τ_{yield} values of sepiolite/PAA suspensions as a function of the polymer concentration. The τ_{yield} value of the sepiolite/

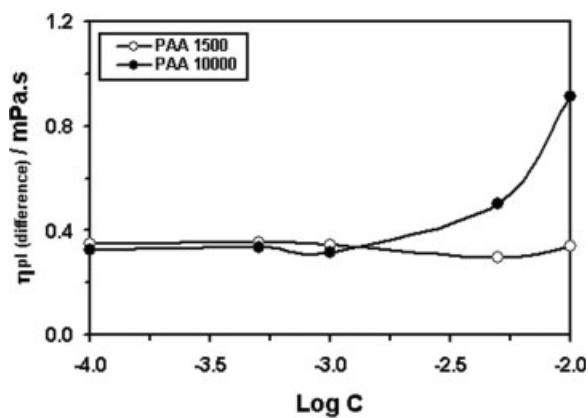


Figure 16 $\eta_{pl(difference)}$ values as a function of the PAA concentration (C).

PAA 1500 suspension did not change significantly with the polymer concentration. However, this value for the sepiolite/PAA 10,000 suspension showed fluctuations in the range of 37.9–17.9 mPa.

The influence of PEG molecules with different molecular weights on the η_{pl} values of sepiolite suspensions is shown in Figure 18. The sepiolite suspensions in the presence of PEG molecules with low molecular weights (PEG 1500 and PEG 2000) had η_{pl} values that were approximately the same, even at higher polymer concentrations. In the polymer concentration range of 1×10^{-4} to 1×10^{-3} M, similar behaviors were also observed for sepiolite/PEG suspensions containing PEG 4600, PEG 8000, and PEG 10,000. However, when the polymer concentration was increased from 1×10^{-3} to 5×10^{-3} M, the η_{pl} values showed approximate increases of 1.34, 1.74, and 2.17 times for PEG 4600, PEG 8000, and PEG 10,000, respectively. This increase continued at 1×10^{-2} M for PEG 4600, PEG 8000, and PEG 10,000.

Figure 19 shows the variation of $\eta_{pl(difference)}$ as a function of the PEG concentration. It can be understood from this figure that the reasons for the increase in the η_{pl} values of the sepiolite suspensions

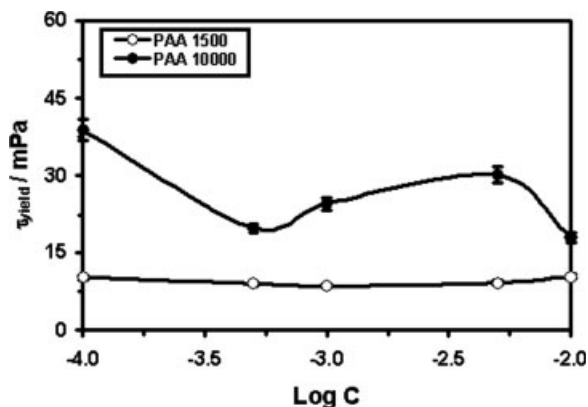


Figure 17 τ_{yield} values as a function of the PAA concentration (C).

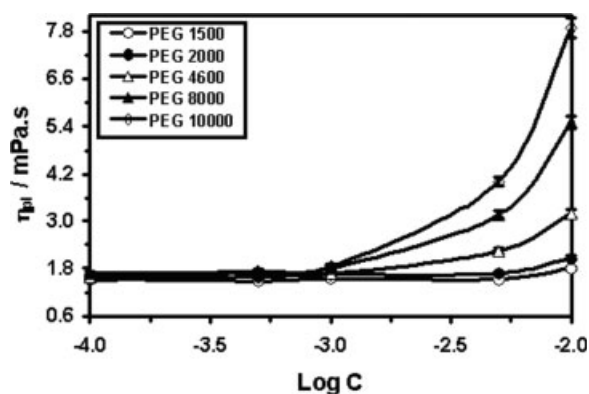


Figure 18 η_{pl} values of 2.0% sepiolite/PEG suspensions as a function of the PEG concentration (C).

in the presence of PEG 4600, PEG 8000, and PEG 10,000 were the increase in the polymer concentration and the sepiolite–polymer interactions. The increase in the molecular weight of PEG led to larger flocs and thus higher η_{pl} values.

A graph of the τ_{yield} values versus the PEG concentration is presented in Figure 20. The τ_{yield} values of the sepiolite/PEG suspensions changed between 16.0 and 41.4 mPa.

CONCLUSIONS

The sepiolite concentrations in the studied range of 0.25–3.5 wt % did not affect the ζ -potential values of sepiolite/water suspensions. The ζ -potential values of sepiolite suspensions were measured at different pH values, and the isoelectric point of sepiolite was determined to be 3.27.

Different molecular weights of anionic polymers (NaPAs) and higher molecular weights of nonionic polymers (PAAs and PEGs) affected the ζ -potential values of sepiolite suspensions in different ways. The ζ -potential values of suspensions became more

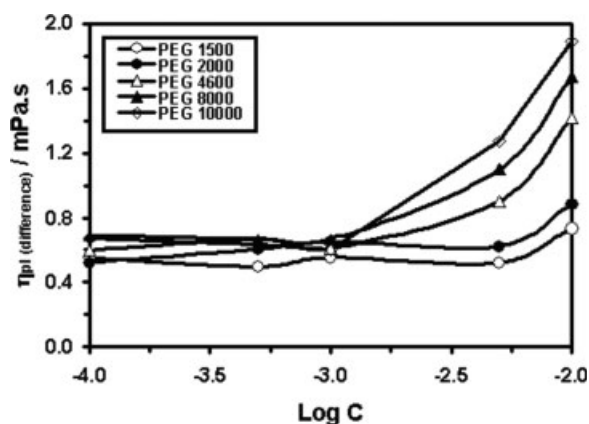


Figure 19 $\eta_{pl(difference)}$ values as a function of the PEG concentration (C).

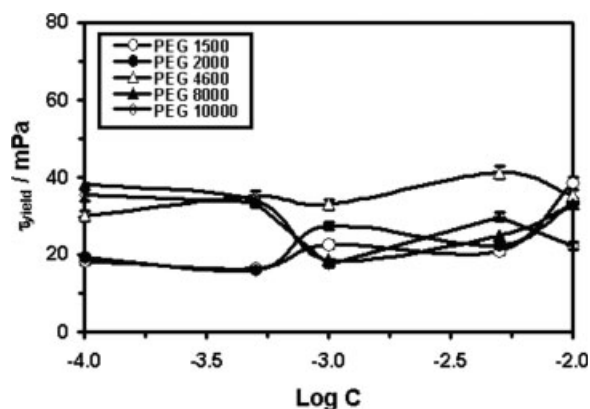


Figure 20 τ_{yield} values as a function of the PEG concentration (C).

negative when the concentrations was increased to 1×10^{-3} M for NaPA 2100, NaPA 5100, and NaPA 8000 and to 5×10^{-3} M for NaPA 1200. After that, a decrease was observed for higher concentrations because of the screening effect of excess NaPA molecules. Low molecular weights of nonionic polymers (PAA 1500 and PEG 1500) did not have any effect on the ζ -potential values, whereas higher molecular weights of nonionic polymers (PAA 10,000, PEG 2000, PEG 4600, PEG 8000, and PEG 10,000) caused a decrease in the ζ -potential values of suspensions. A large decrease in the ζ -potential values of sepiolite suspensions was observed for larger molecular weights at higher concentrations of nonionic polymers.

The effects of the concentrations and molecular weights of the polymers on the $\eta_{pl(difference)}$ values of the sepiolite suspensions were observed only in the presence of polymers of larger molecular weights at higher concentrations. An increase in the $\eta_{pl(difference)}$ values of sepiolite suspensions was determined at 1×10^{-2} M for NaPA 8000, at 5×10^{-3} and 1×10^{-2} M for PAA 10,000, and at 5×10^{-3} and 1×10^{-2} M for PEG 4600, PEG 8000, and PEG 10,000.

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