

## ARAŞTIRMA MAKALESİ/RESEARCH ARTICLE

# THE EFFECT OF POLYVINYL ALCOHOL (PVA) ON RHEOLOGICAL AND DIELECTRIC PROPERTIES OF KAOLINITE DISPERSION

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### ABSTRACT

The purpose of this study is to investigate the effect of polyvinyl alcohol (PVA) on rheological and dielectric properties of suspension in the different concentration of PVA prepared by using kaolinite 0.1 %. The viscosity values of suspension have been measured and the dependence of viscosity on temperature and concentration have been investigated. The specific viscosity and activation energy have been calculated by using the measured viscosity values. It has been observed that the values of viscosity increase exponentially with the concentration of PVA and decrease with increasing temperature. Dielectric constants of suspensions prepared by using PVA-deionized water and PVA-water-kaolinite have been measured in the temperature range from 0°C to 15°C, and its dependence on concentration and temperature also investigated. It has been observed that dielectric constant slightly increases with PVA concentration, but decreases with increasing temperature.

**Key Words:** Viscosity, Dielectric constant, Kaolinite, Polyvinyl alcohol.

## KAOLİN DİSPERSİYONUNUN REOLOJİK ve DİELEKTRİK ÖZELLİKLERİ ÜZERİNDE POLİVİNİL ALKOL (PVA) ETKİSİ

### ÖZ

Bu çalışmanın amacı % 1 kaolin kullanarak değişik PVA konsantrasyonlarında hazırlanmış süspansiyonun reolojik ve dielektrik özellikleri üzerinde polivinil alkol(PVA)ün etkisini araştırmaktır. Süspansiyonun viskozite değerleri ölçülmüş ve viskozitenin sıcaklık ile konsantrasyona bağlılığı incelenmiştir. Ölçülen viskozite değerleri kullanılarak spesifik viskozite ve aktivasyon enerjisi hesaplanmıştır. Viskozite değerlerinin PVA konsantrasyonu ile eksponansiyel olarak arttığı ve artan sıcaklıkla azaldığı gözlenmiştir. PVA-deiyonize su karışımlarının dielektrik sabitleri ve PVA-su-kaolin ile hazırlanan karışımların dielektrik sabitleri 0°C-15°C sıcaklık aralığında ölçülmüş, sıcaklık ve konsantrasyon bağlılıkları incelenmiştir. Dielektrik sabitinin PVA konsantrasyonu ile yavaş artış gösterdiği ve artan sıcaklıkla azaldığı gözlenmiştir.

**Anahtar Kelimeler:** Viskozite, Dielektrik sabiti, Kaolin, Polivinil alkol.

## 1. INTRODUCTION

The viscosimetric method exhibits many advantages due to its simplicity and inexpensive equipment. Moreover, the method allows the characterisation of macromolecules in the dispersed state and is determined by knowing the properties of rheological and dielectric of that dispersion.

Viscosity is of importance in the establishment of intermolecular interactions. In system dominated by attractive interactions, the viscosity increases and the other hand in the repulsive interactions the viscosity decreases. Therefore they are important factor since the nature of the system component (ionic-ionic, ionic-non-ionic and nonionic-nonionic) and its electrical charge determine the viscosity.

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Hsu and Lin (1996), Jenkins and Snowden (1996) proposed a theoretical method useful in characterisation of the polymers' system in dilute aqueous solution. They proposed a theoretical relation to calculate the depletion interactions between the two polymers.

M'Bareck et al. (1996) applied a theoretical relation of the polyvinyl alcohol and poly(styrenesulfonic acid) aqueous solution to proposed theories. They also investigated the dependence of molecular weight of PVA on the polymer mixture, hydrolysis degree and total mixture concentration.

To some extent there are rather sparse literature on the clay but is a negligible literature concerning effect of PVA on kaolinite, which consist of charged particles, and its dielectric properties.

Adsorption of PVA by sodium, calcium and cesium montmorillonites has been studied by Greenland (1963). It is pointed out that PVA is strongly and reversibly adsorbed by montmorillonite and bonding between surface oxygens of clay and hydroxyl groups of polymer is supplied by hydrogen bonds.

Colloidal stabilization of BaTiO<sub>3</sub> with polyvinyl alcohol in water has been studied by de Laet and Derks (1993) and several types of polyvinyl alcohol in their study have been tested with respect to their ability to provide sterically stabilized BaTiO<sub>3</sub> dispersions.

Frost et al. (1996) studied different properties of kaolinite, discit, nacrit and halloysite as a microscopically. The spectra of different crystal orientations have been obtained for kaolinite, discit, nacrit and halloysit.

Zhang et al. (1996) studied the effect of PVA adsorption on segregation using by a model experiment of one dimension drying and simulated it by a mathematical model. It was shown that the adsorption of PVA on alumina was a slow process, and the adsorbed binder was not desorbed at higher temperatures.

Frost (1997) examined the structure of kaolinite minerals taking into consideration the condition of hydroxyl groups.

The dependence of separation properties on flocculation dynamics of kaolinite suspension has been examined by Sengupta et al (1997). The best separation properties are obtained from the flocs which can withstand shear for a long time.

PVA is also used in medicine. J. Broadwall et al. (1997) conducted a comparative study of polyacrylic acid (PAA) liquid gel versus PVA in the treatment of dry eyes.

Dielectric properties of the matter are quite important in terms of the structure of matter and the interactions of compound each other.

Permien and Lagaly (1994a) and Yılmaz et al. (1999) calculated dielectric constants at the different concentrations for sodium montmorillonite and kaolinite in water-alcohol mixtures respectively.

The dc field rheological properties and frequency dependent dielectric properties of a set of electrorheological (ER) fluids composed of oxidized polyacrylonitrile or aluminasilicate materials dispersed in silicone oil were examined by Hao et al. (1997). In this paper dielectric constants, dielectric loss tangent and conductivities were employed.

Kaolins are one of the most important clay minerals. They are utilized in a large variety of applications in the ceramic industry.

The rheological behaviour of colloidal ceramic dispersions are very important in the ceramic production industries. Casting processing is still the main large-scale production method and understanding the mechanism of particle interactions is necessary for process optimisation and best desing of the initial formulations.

Binder and a dispersant are used in the casting slip to enhance processibility. These additives affect the rheological and electrical behaviour of their amount in the initial formulation.

Flocculation of clay minerals, which is aluminosilicate, is needed in the filtration operation. On the other hand, a uniform dispersion should be performed in the production of ceramic materials obtained by slip casting. For this reason, different polymers are used. In order to examine this kind of properties of polymers the rheological properties should be known. Therefore in this study, the rheological properties of PVA-water-kaolinite mixture have been examined and also measured its dielectric properties in order to understand rheological properties of such systems.

## 2. MATERIAL AND METHOD

Kaolinite particles (size < 0,2 µm) are isolated by using sedimentation and residual iron is removed Yılmaz et al. (1999), Permien and Lagaly (1994b). PVA (Riedel-de Haen) solutions at different concentrations with deionize water which is purified from organic materials have been prepared and kaolinite 0.1 % are added to the solutions. The mixture was stirred for about 4h in order to obtain a suspension.

Their viscosities of suspensions and the PVA-water mixtures were measured at the different temperatures by using Reo [VEB MLW PRÜFGERATE-WERK MEDİNGEN] and Oswald viscosimetries respectively.

The measurements of dielectric constants by using cell MFL3 ( $21 < \epsilon < 90$ ) were conducted using Decameter DK03 [Weissenhaftlich-Technische-Werkstätten (WTW)] at the constant frequency (1.8MHz). The instrument operates on the resonance principle. The sample forms the dielectric of a condenser (measuring cell) joined parallel to the oscillating circuit. An alteration of the dielectric constant causes a change of the capacitance of the measuring cell, which in turn effects mis-tuning of the oscillator against the indicator circuit. This mis-tuning is compensated by the adjustment of the tuning condenser of the oscillator circuit. The mis-tuning expressed in terms of dial divisions corresponds to the dielectric constant of the substance. The cell used in this study is 50 ml and all measurements have been done between 0 and 15°C. The cell is calibrated using pure liquids such as ethanol ( $\epsilon=24.30$  at 25°C), methanol ( $\epsilon=32.63$  at 25°C), acetone ( $\epsilon=20.70$  at 25°C), n-propanol ( $\epsilon=20.10$  at 25°C) and deionized water ( $\epsilon=78.54$  at 25°C) Lide (1994), Yılmaz and Güler (1998), Kirak et al. (1999). The dielectric constants of the mixture are found from the calibration curve.

### 3. RESULTS AND DISCUSSION

Figure 1 shows the variation of viscosity values with temperature at the different concentrations of the PVA-water mixtures. For the PVA-water-kaolinite suspensions, the variations of viscosity values with temperature at the same concentrations are given in Figure 2. As can be seen from the figures, it has been observed that the viscosity does not change significantly with the temperature at low concentrations but the viscosity decreases exponentially at high concentrations as the temperature increases. The viscosity increases with the concentration as the interaction of molecules is accelerated. The viscosity values of the PVA-water-kaolinite suspensions are higher than that of the PVA-water mixtures. Viscosity of the suspension containing kaolinite increases since intermolecular friction is increased by kaolinite particles in the suspension and the structure to be formed by the PVA molecules which are bounded with hydrogen bonds.

The viscosity of the PVA-water mixtures in the temperature range from 27°C to 47°C decreases with the temperature. For example, the viscosity value of 27°C of the PVA-water mixtures, which has concentration of 100.000 ppm, is about 17.7 mPa.s but this value drops to 9.8 mPa.s at 47°C. While the temperature increases from 27°C to 47°C in the kaolinite suspension with the same concentration, the viscosity value falls from 19.3 mPa.s to 9.9 mPa.s. As the PVA concentration increases the adsorption increases. As a result of this, decreasing in the viscosity value at high concentrations is higher than that of low concentration.

The variations of specific viscosity values ( $\eta_{sp}$ ) with the concentration are given Figures 3 and 4. As can be seen from the figures, the variation of specific viscosity values with the concentration exhibits similar behaviour in the variations of viscosity-concentrations. Specific viscosity values of the PVA-water-kaolinite are always the higher than that of the PVA-water mixtures at all temperatures and concentrations.

Activation energy ( $\Delta G$ ) concerning the viscosity can be calculated using the slope of the line  $\ln\eta$  versus  $1/T$  Smyth (1955). Figure 5 shows the variation of  $\ln\eta$  with  $1/T$  for the PVA-water-kaolinite suspension and the PVA-water mixtures. The variation of the activation energy calculated from the slope of lines in Figure 5 with the concentration are shown in Figure 6. The activation energy of the PVA-water-kaolinite suspensions is the higher than that of the PVA-water mixtures. Viscosity increases due to presence of the kaolinite in the suspension. Therefore, their rotational and transitional motions of the molecules in the suspension will be difficult and increase the friction between molecule layers. Therefore, the activation energy of PVA-water and PVA-water-kaolinite suspension increases with the concentration. In addition to this, the activation energy of kaolinite suspension due to the same effect is higher than PVA-water mixture.

The variation of dielectric constant  $\epsilon$  with concentration for the PVA-water mixtures and the PVA-water-kaolinite suspensions at the temperature range from 0°C to 15°C are shown in Figure 7. Although the variation of dielectric constant with the concentration is very little, the dielectric constant decreases significantly as the temperature increases. The value of dielectric constant of the PVA-water in the temperature from 0°C to 15°C decreases from about 88 to 82. The decreasing for the PVA-water-kaolinite suspensions is from about 89 to 84. In order to determine the effect of kaolinite on the dielectric constant, the PVA concentration (5000 ppm) which can be taken as a common measurement at all temperatures, has been taken into consideration. In this case, the value of  $\epsilon$  of the PVA-water mixtures at 0°C is increased from 87.61 to 88.68 by adding kaolinite and so the difference between them is 1.07 unit. Besides, the measurements done for 5°C, 10°C and 15°C are found to be 1.11, 1.22, 2.04 unit respectively. These differences are decreased the increasing with PVA concentration and the temperature, because of the adsorption of PVA on the kaolinite increases with the increasing concentration and temperature.

Since the suspensions of the PVA-water and the PVA-water-kaolinite containing less than of PVA of 500 ppm are frozen at 0°C, we could not take the measurements at this temperature.

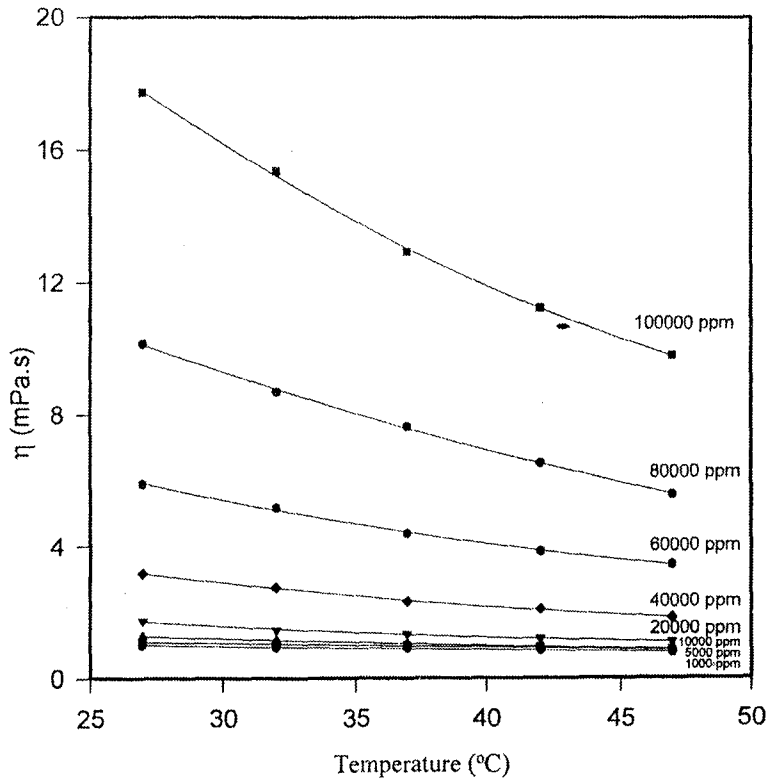


Figure 1. The Variation of Viscosity With The Temperature For PVA-Water Mixtures at Different Concentrations Which are Prepared From 5000 ppm to 100000 ppm.

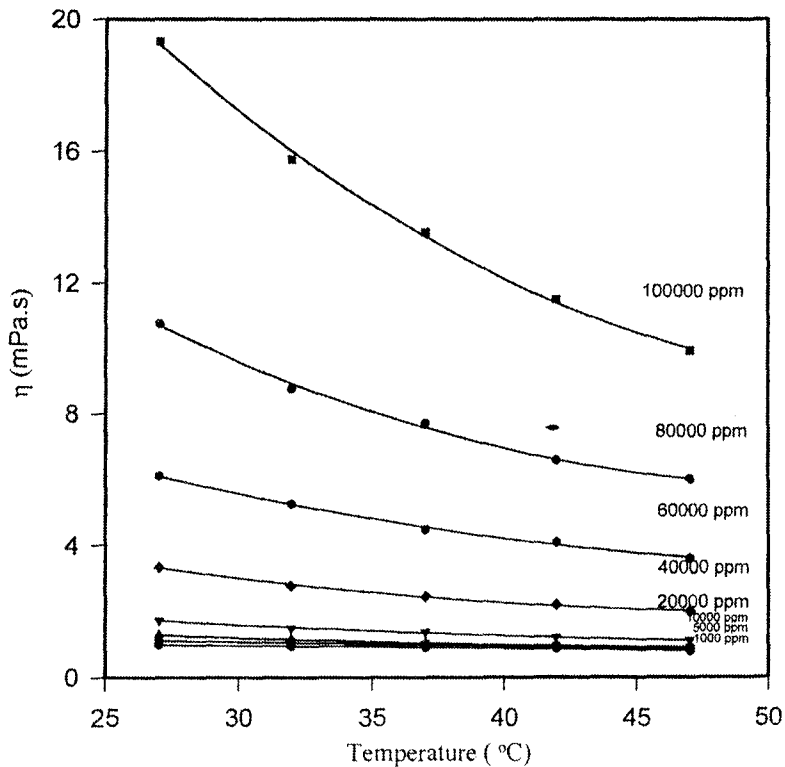


Figure 2. The Variation of Viscosity With The Temperature For PVA-Water Kaolinite Suspensions at Different Concentrations Which are Prepared From 5000 ppm to 100000 ppm.

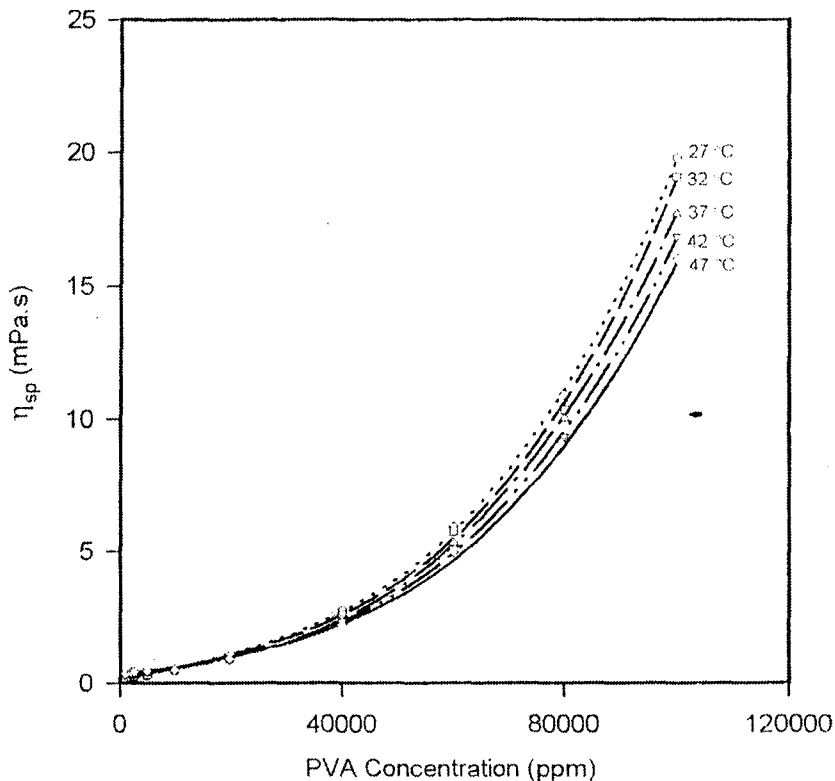


Figure 3. The Variation of Specific Viscosity With Concentration at Different Temperatures for PVA-Water Mixtures.

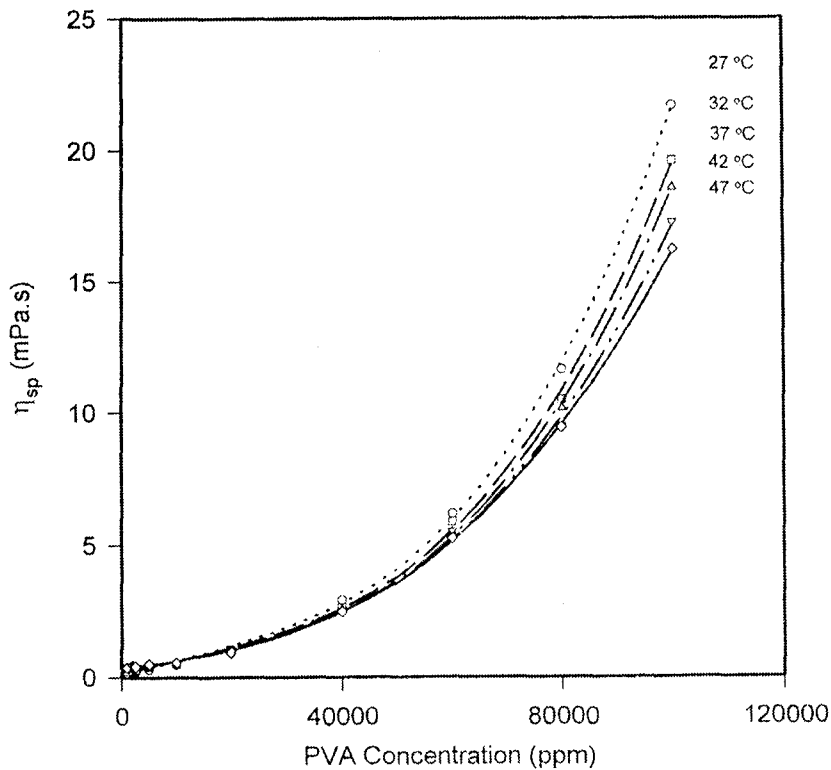


Figure 4. The Variation of Specific Viscosity With Concentration at Different Temperatures for PVA-Water-Kaolinite Mixtures.

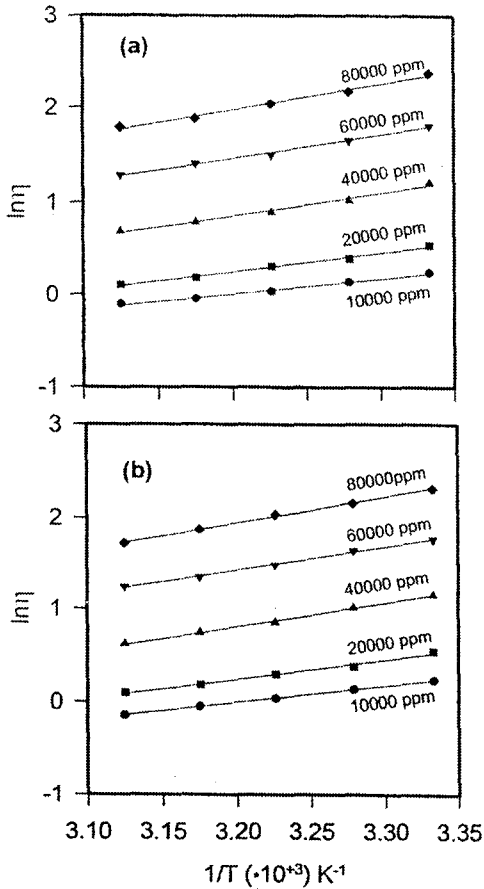


Figure 5. The Variation of  $\ln \eta$  Versus  $1/T$  for the Different Concentrations: (a) and (b) Show the Data for PVA-Water Mixtures and PVA-Water-Kaolinite Suspensions Respectively.

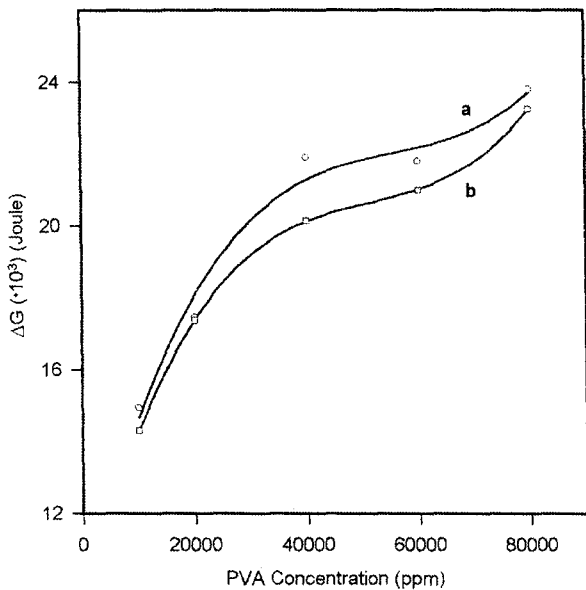


Figure 6. The Variation of Activation Energy  $\Delta G$  With Pva Concentration: (a) and (b) Show the Data for PVA-Water Kaolinite and PVA-Water Mixtures Respectively.

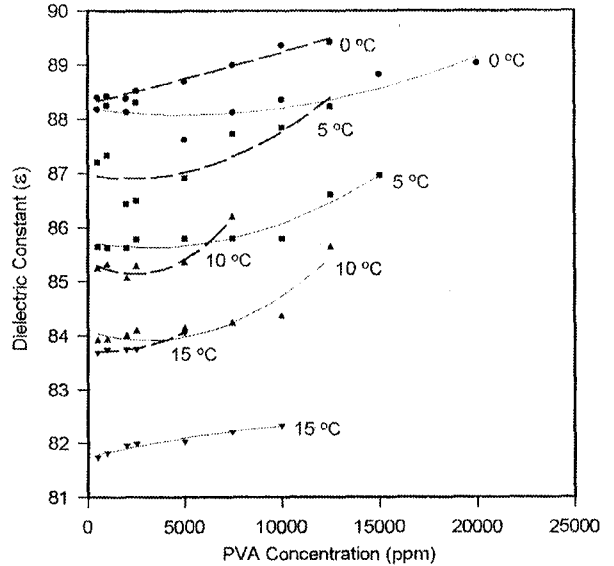


Figure 7. The Variation of Dielectric Constant With PVA Concentration. Dashed and Solid Lines Denote for the PVA-Water-Kaolinite Suspensions and PVA-Water Mixtures Respectively.

The viscosity values of the PVA-water mixtures and the PVA-water-kaolinite suspensions decrease with increasing temperature but increase with increasing concentration. The viscosity values of suspension are higher than that of the mixture.

A stable suspension is formed by the PVA-water-kaolinite suspensions until PVA concentration (2500 ppm). Flocculation process is carried out above this concentration and then a stable suspension is formed starting from 80.000 ppm PVA concentration. This is because, according to the bridge mechanism Hunter (1993) of the low concentrations, bonding of clay particles each other is possible after a certain concentration. At high concentration, the PVA molecules surround clay particles and then bonding of the particles is prevented. Therefore a stable dispersion is formed by the particles.

Dielectric constant,  $\epsilon$ , of the PVA solution does not change significantly as the concentration increases but it decreases significantly since interaction of the PVA-water increases with increasing temperature. Dielectric constants of the PVA-water-kaolinite suspension are higher than that of the PVA-water mixtures.

#### 4. CONCLUSION

The results presented here show that viscosity of the suspension is increased by adding PVA to the system of the water-kaolinite. However, viscosity of the PVA-water and the PVA-water-kaolinite system decreases with the temperature.

Dielectric constant of the water-kaolinite system slightly increases with the concentration but decreases with increased temperature.

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