Competitive Adsorption of Water-Soluble Polymers on Attapulgite Clay

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SYNOPSIS

The individual, competitive, and displacement adsorption of polyvinyl alcohol (PVOH), hydroxyethyl cellulose (HEC), and hydroxypropylmethyl cellulose (HPMC) in aqueous solution onto an attapulgite clay has been systematically studied. For the individual adsorption experiments, the amount of polymer adsorbed at equilibrium decreased in the order PVOH, HEC, HPMC. In the competitive adsorption experiments, the adsorption level of each polymer is diminished by the presence of a competing polymeric species. Binary mixtures of a cellulosic polymer (HEC or HPMC) with PVOH result in a substantial reduction in the amount of cellulosic polymer adsorbed. In the displacement adsorption studies, the sequential addition of HEC or HPMC is not able to displace previously adsorbed PVOH molecules to any appreciable extent. However, the addition of PVOH to previously equilibrated HEC/clay or HPMC/clay suspensions results in a large amount of the adsorbed cellulosic polymer being displaced by PVOH, especially under conditions of high surface coverage. These results indicate that PVOH is preferentially adsorbed on the clay surface and the strength of attachment to the surface is greater for PVOH than for either cellulosic polymer.

INTRODUCTION

The importance of polymer adsorption in various industrial applications, such as coatings, cosmetics, wastewater treatment, petroleum recovery processes, and so forth, is widely recognized. Extensive studies have been conducted with regard to the adsorption of individual polymeric species onto the surfaces of various substrates. However, data involving the competitive or displacement adsorption of different polymeric structures are extremely limited.

Synergistic effects have been reported by Csempesz et al.[1,2] with regard to the flocculation of binary mixtures of methylcellulose and polyvinyl pyrrolidone on silver iodide and arsenic trisulfide sols. These effects were attributed to the irregularly extended adsorption layers formed by the competitive adsorption of the polymeric species. The conformation of the weakly adsorbed polymer appears to be distorted at the solid–liquid interface by the preferentially adsorbed polymer.

Displacement adsorption has also been studied in aqueous solutions of various binary mixtures including methylcellulose, polyvinyl pyrrolidone, and polyvinyl alcohol on silver iodide sol,[1] and binary mixtures of poly(ethylene oxide) and poly(4-vinyl-N-n-propylpyridinium bromide) on a nonporous silica.[3] In these systems, it was observed that the polymer with the higher affinity for the solid surface could not be displaced by the subsequent addition of a second polymer of lower affinity. On the other hand, a polymer possessing a lower affinity can be desorbed from the solid surface by the addition of a polymer of greater affinity.

The objective of the present article is to investigate systematically the individual and competitive binary adsorption behavior of polyvinyl alcohol (PVOH), hydroxyethyl cellulose (HEC), and hydroxypropylmethyl cellulose (HPMC) in aqueous solution onto an attapulgite clay. Preferential affinity is studied by means of displacement adsorption behavior in which the polymeric species constituting the binary pair are added sequentially to the mixture.

EXPERIMENTAL

Materials

Three water-soluble polymers were used in this study. Polyvinyl alcohol (PVOH) was supplied by Air Products and Chemicals, Inc. (Airvol 540S, MW = 108,000). Hydroxyethyl cellulose (HEC) was obtained from the Aqualon Company (Natrosol 250 LR, MW = 90,000). Hydroxypropylmethyl cellulose (HPMC) was obtained from Dow Chemical Company (Methocel K15M, MW = 100,000). These materials were chosen to have the same approximate molecular weights.

The clay used in the study was an attapulgite clay supplied by the Gold Bond Building Products Division of National Gypsum. This clay is a porous, fibrous mineral, having a high adsorptive capacity because of the extensive convoluted external surface area and internal pore surface (structural channels). It possesses a submicroscopic needle-like morphology, having widths of between 100 and 300 Å, thicknesses of between 50 and 100 Å, and lengths ranging from 0.2 to 10 μm. Estimated values for the external and internal surface areas of Georgia attapulgite are 300 m^2 g^{-1} and 600 m^2 g^{-1}, respectively. The channel cross-sectional area is approximately 6.4×3.7 Å^2.[4]

Attapulgite clay plays an important role in products such as joint treatment or wallboard compounds. It provides thickening properties and thixotropic characteristics, which provide sag resistance, viscosity control, spreadability, and excellent feathering capability.

Procedure

Adsorption Studies of Individual Polymeric Components

The adsorption studies of individual polymeric species were conducted by placing 2 g of dry clay into the polymer solution under investigation in order to form a 200 mL suspension. These suspensions were contained in 250 mL Erlenmeyer flasks and were maintained in a well-dispersed state with the aid of a magnetic stirrer. The flasks were continuously swirled on a shaker table at a speed of 200 RPM in a room at constant temperature maintained at 25°C.

At various time intervals samples were withdrawn from the flasks and centrifuged at a speed of 5500 RPM for 30 min. The polymer concentration in the supernatant was determined spectrophotometrically using a GCA/McPherson double-beam UV/Visible spectrophotometer. The procedure for determining the concentration of PVOH followed the protocol

suggested by Zwick.[5] The colorimetric determination of the concentration of the cellulosic polymers followed the procedures according to Kanzaki and Berger.[6] Unknown sample concentrations were then readily determined from previously constructed calibration curves of polymer concentration as a function of absorbance.

The amount of polymer adsorbed is expressed as grams of polymer adsorbed per 100 grams of clay and is obtained by calculating the difference in concentration between the initial polymer solution and that measured in the supernatant after the attainment of equilibrium.

Competitive Adsorption Studies

The competitive adsorption studies were conducted by preparing a 200 mL aqueous solution containing equal weight fractions of PVOH and HEC or PVOH and HPMC. Two grams of dry clay were mixed into the polymer solution and were allowed to equilibrate. The concentration of each individual polymer species was determined by using the same colorimetric techniques as employed for the individual polymer adsorption studies.

Displacement Adsorption Studies

The displacement adsorption of PVOH by HEC was conducted by first adsorbing PVOH onto 2 g of the attapulgite clay. A series of experiments was conducted using 200 mL aqueous solutions of PVOH containing various weight fractions of the polymer. After equilibrium conditions were achieved, the same weight fraction of HEC was added to the suspension. The system was allowed to reestablish equilibrium and the concentrations of both polymers were determined using the previously described techniques. All experimental measurements were conducted at 25°C. These same procedures were followed for the displacement adsorption of HEC by PVOH, PVOH by HPMC, and HPMC by PVOH.

RESULTS AND DISCUSSION

Adsorption Studies of Individual Polymeric Components

Figure 1 gives the amount of polymer adsorbed on the attapulgite clay for various initial polymer concentrations. All of these individual adsorption isotherms are of a high affinity type, which means that the polymer is completely adsorbed on the clay surface at lower concentrations. The data points at c
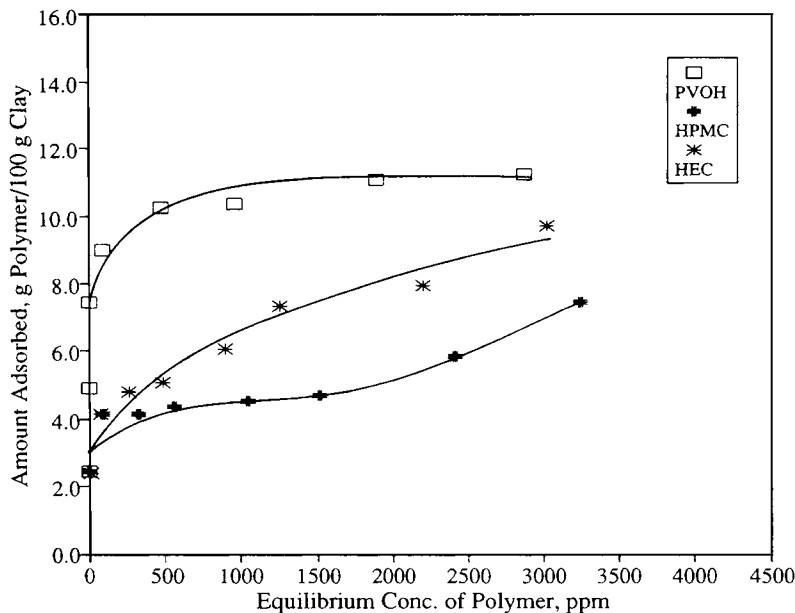
Figure 1 Adsorption isotherms for PVOH, HEC, and HPMC.

= 0 correspond to all of the polymer molecules being adsorbed onto the clay surface with no remaining free polymer present in solution.

The adsorption isotherm of PVOH is very steep in the low concentration regime and reaches a plateau level at an equilibrium concentration of approximately 500 ppm. The adsorption isotherms of HEC and HPMC do not reach a plateau level until an initial concentration of at least 4000 ppm is reached. Beyond this point, the effect of depletion flocculation sets in, which decreases the total accessible area of clay. Thus the adsorption measurements made under these conditions can not be meaningfully compared with measurements made at the lower initial concentrations.

The amount of polymer adsorbed at various initial polymer concentrations decreased in the order PVOH, HEC, HPMC.

Competitive Adsorption Studies

In order to demonstrate how the mode of adsorption affects the adsorption characteristics of the polymer, the adsorption isotherms of the individual components, along with the results for the simultaneous adsorption from binary mixtures composed of equal weight fractions, are plotted together as shown in Figures 2 and 3. Figures 2 and 3 indicate that a significant difference exists between the adsorption characteristics of individual polymeric components and the adsorption that occurs during their simul-

taneous competitive adsorption. The adsorption of each polymer is reduced by the presence of a competing polymer.

Mixtures of PVOH and HEC or PVOH and HPMC result in a considerable decrease in the amount of cellulosic polymer adsorbed. The relative decrease is somewhat less at high surface coverage than at moderately low surface coverage. This can be explained by the molecular conformation of the PVOH molecules upon adsorption. As indicated by Greenland,[7] the PVOH molecule tends to collapse upon adsorption to the clay surface and is not attached at only a few "anchor points." Thus, it is very likely that the HEC or HPMC molecules that have arrived at the surface early may be entangled or confined by the adsorption and subsequent collapse of the PVOH molecules. This phenomenon may be more prevalent at high initial concentrations as compared to moderately low initial concentrations. At high polymer concentrations, the vicinity of the solid surface will be relatively crowded by polymer molecules and there will be a greater tendency for HEC or HPMC molecules to become entrapped by the collapsing PVOH molecules.

Displacement Adsorption Studies

In order to determine whether the preferential adsorption of PVOH onto attapulgite clay is a result of stronger attachment to the clay surface, as compared to the cellulosic polymers, displacement ad-
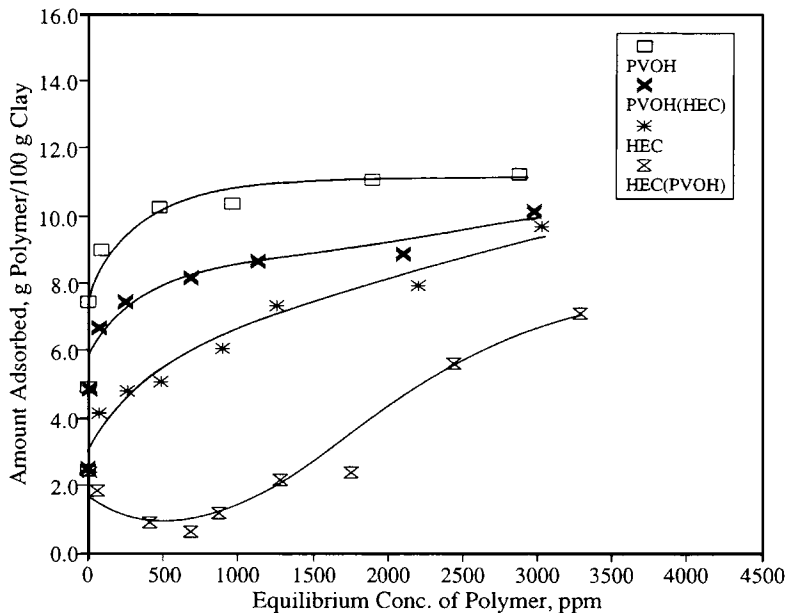
Figure 2   Competitive adsorption of PVOH/HEC on clay.

sorption experiments were conducted. For comparison purposes, the initial concentrations of the binary polymer mixtures were the same as in the previous competitive adsorption studies with the exception that the second polymeric component is added to the suspension only after the first polymeric component has attained adsorption equilibrium. The results of these displacement adsorption experiments are shown in Figures 4–7.

For the case in which PVOH attains adsorption equilibrium followed by the addition of HEC, Figure 4 indicates that HEC is not capable of displacing the already-adsorbed PVOH molecules to any appreciable extent. Figure 5, on the other hand, clearly shows that the addition of PVOH to an equilibrated HEC/clay suspension results in a pronounced displacement of HEC from the clay surface, particularly at high surface coverage. Thus, when HEC is added
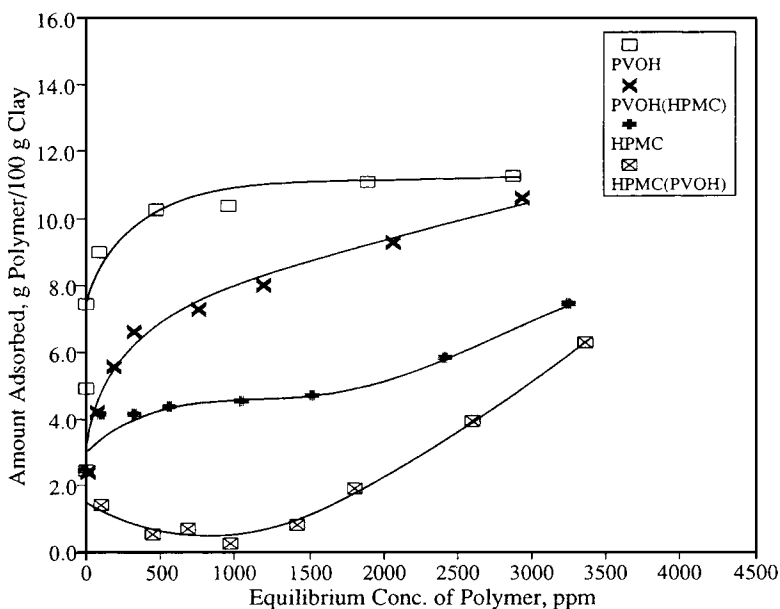

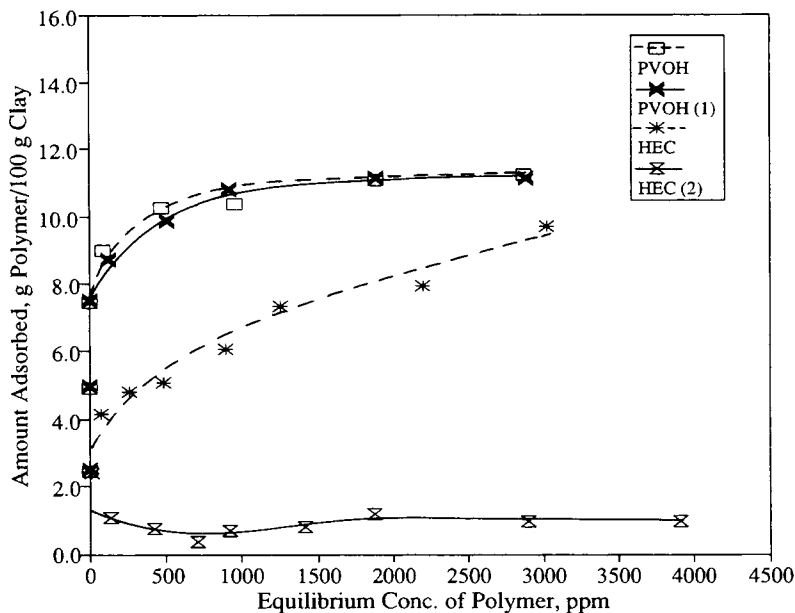**Figure 3**   Competitive adsorption of PVOH/HPMC on clay.

Figure 4   Displacement adsorption of PVOH by HEC.

before the PVOH, the adsorbed HEC molecules are readily displaced by the adsorbed PVOH molecules. In contrast, under the condition of competitive adsorption, the amount of adsorbed HEC is higher because of entrapment by entanglement and collapse of the PVOH molecules, as previously discussed. The displacement adsorption behavior of PVOH and HPMC is essentially identical to that of PVOH and HEC, as shown in Figures 6 and 7. These results

give evidence to the fact that PVOH is preferentially adsorbed onto the clay surface and the strength of the attachment to the surface is greater for PVOH than for either HEC or HPMC.

CONCLUSIONS

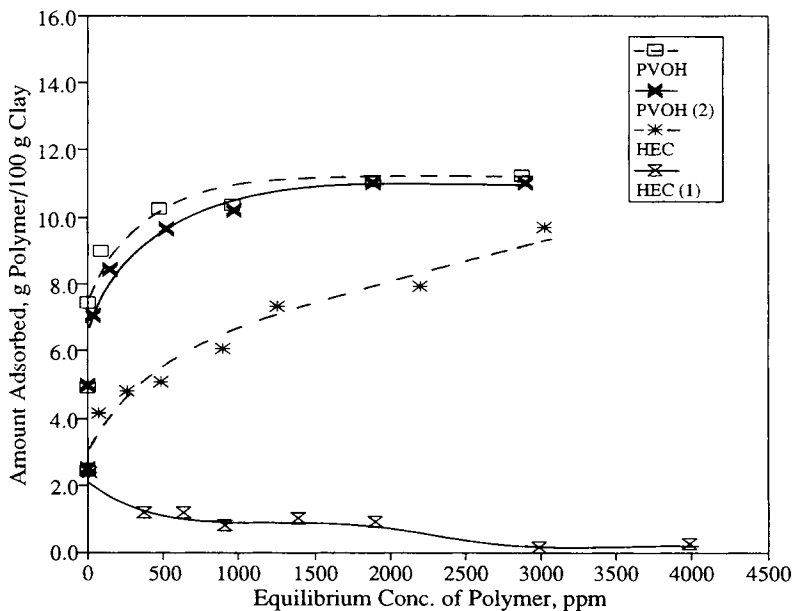Equilibrium adsorption experiments for individual polymers in an aqueous suspension of clay particles

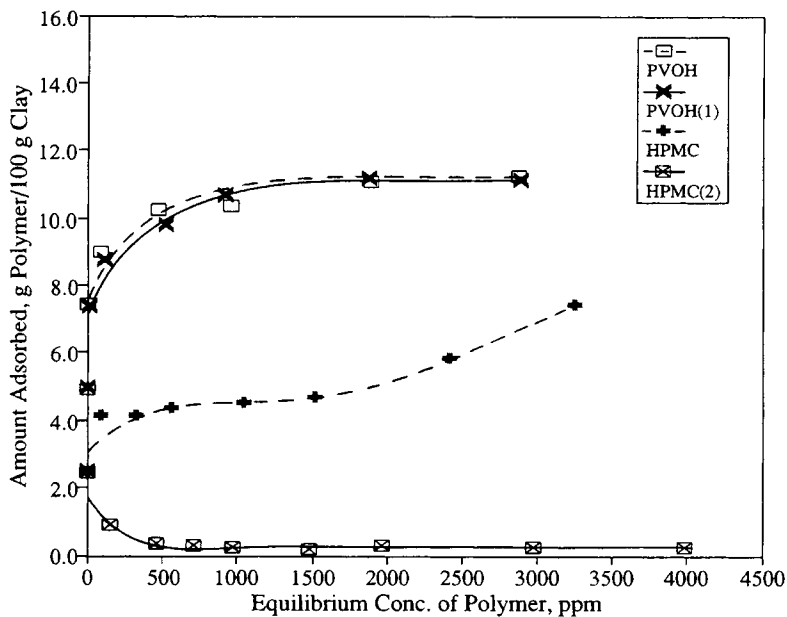**Figure 5**   Displacement adsorption of HEC by PVOH.

Figure 6   Displacement adsorption of PVOH by HPMC.

have indicated that PVOH is adsorbed to the greatest extent in comparison with HEC and HPMC. When the PVOH is present in a binary mixture with a cellulosic polymer, the amount of each polymer adsorbed is diminished in comparison to the individual adsorption levels when no competing polymeric species are present. For cases in which one polymer is permitted to equilibrate prior to the ad-

dition of a second polymer, the displacement of the first polymer by the second is dependent upon the particular nature of the components. For the species investigated in this study, PVOH is not displaced to any appreciable extent by either HEC or HPMC. However, PVOH is able to displace significantly both HEC and HPMC. These results indicate that the PVOH is preferentially adsorbed onto the at-
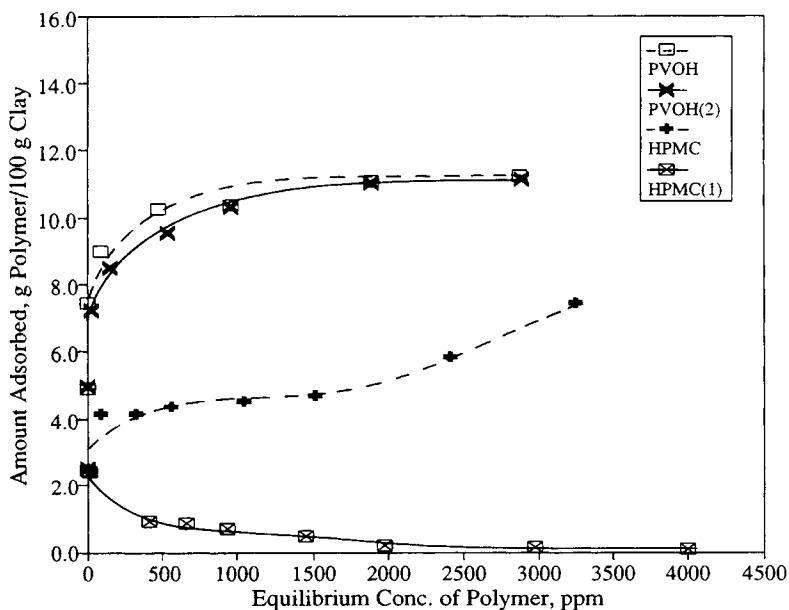

Figure 7   Displacement adsorption of HPMC by PVOH.

tapulgite clay surface and the strength of attachment is greater than for either of the cellulosic polymers studied.

The competitive adsorption experiments demonstrate that rheological and other physical property changes may occur over extended time scales in multicomponent polymeric suspensions because of the dynamic nature of the competitive adsorption process. The displacement adsorption experiments indicate that the order of addition of polymeric components to a suspension can influence the subsequent rheological behavior and performance of the system.

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