

# Adsorption of Polyacrylamide on Zirconium Dioxide

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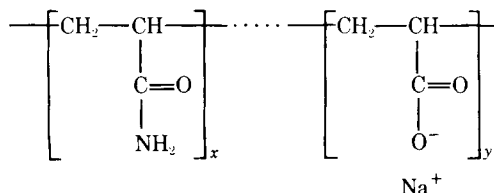
## Synopsis

The adsorption of an anionic-type polyelectrolyte (polyacrylamide) onto zirconium dioxide from aqueous dispersion has been studied as a function of pH. Polymer adsorption takes place in the acid region, obeying a Langmuir-type isotherm. Adsorption decreases with increasing pH. The zero-point of charge (zpc) at the  $ZrO_2-H_2O$  interface and the nature of the ionic charge on the polymer molecules were investigated. The behavior of polymer attachment is discussed on the grounds of a nonionic bonding mechanism including H bonding and of electrostatic interaction. It has been found that the zpc of  $ZrO_2$  is at  $pH \sim 3.5$  and that the ionic properties of the polymer molecules depend, to a noticeable extent, upon the pH of the medium.

## INTRODUCTION

In the early 1950s the development of synthetic flocculants was motivated by the requirement of enriching uraniferous phosphate liquors.<sup>1,2</sup> As a result a number of polymer flocculants have been developed, mostly for the purpose of separating colloiddally dispersed particles from the liquid phase, e.g., recovery of mineral ores, treatment of wastewater effluents, and sugar refining.<sup>3,4</sup>

The polymer flocculants commonly used are copolymers of acrylic acid and acrylamide, or homopolymers of acrylamide, which are in many cases hydrolyzed to various degrees. Polyacrylamide-based polyelectrolytes, simply denoted as PAA, may be represented by<sup>5</sup>



where  $x$  and  $y$  depend upon the degree of hydrolysis.

Most mineral particles are electrically charged in contact with water, and the dispersions are usually stable due to the potential energy barrier formed between the particles. The stable dispersion can be made unstable in the following ways<sup>6-8</sup>: (i) reduction of surface charge, (ii) compression of the protective double layer thickness, and (iii) adsorption of polymer molecules. Using an aqueous dispersion of zirconium dioxide ( $ZrO_2$ ) as substrate, the third aspect has been mainly considered in the present study.

The phenomenon of polymer adsorption is as yet at an early stage of development, not only because of the complexity of the heterogeneous polydisperse systems, but also because of the difficulty of assessing the solid-liquid interfacial interactions. Previous workers in this field often postulate the behavior of

polymer adsorption in terms of the bridging model.<sup>9,10</sup> With respect to polymer attachment on to the surface, hydrogen bonding is considered as the main process,<sup>3,9,10</sup> but the possibility of electrostatic interaction has also been proposed.<sup>11,12</sup>

There are numerous variables operative in polymer adsorption-flocculation, and extensive work has been done in recent years.<sup>9-14</sup> Fleer and Lyklema<sup>13</sup> described the importance of mixing procedures in the flocculation of AgI with poly(vinyl alcohol) (PVA). As to the effect of pH on polymer adsorption, different views have been expressed by several groups of researchers, partly due to the differences in the mineral substrates investigated. Michaels and Morelos<sup>9</sup> found that polymer adsorption decreases with increasing pH. Kuz'kin and co-workers<sup>11</sup> stated that ionization of polyacrylamide molecules depends upon the pH, and this will influence polymer flocculation through electrostatic interaction. Healy and La Mer<sup>10,15</sup> considered that in polymer flocculation chemical aspects such as pH are secondary in importance to physical aspects such as molecular weight and intensity of agitation. Špaldon and Tkacova<sup>12</sup> stated that the pH of the adsorption media can bring about a change of hydrogen-donating properties between polymer and the mineral surface. According to these workers, the dissociated carboxylate ions ( $-\text{COO}^-$ ) will act as oxygen centers, being conducive to hydrogen bonding at  $\text{pH} \geq 8.5$ . They found that polymer adsorption on a quartz surface increases with increasing pH below pH 5, that no adsorption takes place between pH 5 and 8.5, but that adsorption occurs again beyond pH 8.5.

Since the solid surface and polymer molecules are susceptible to adsorption of potential determining ions, e.g.,  $\text{OH}^-$ ,  $\text{H}^+$ , it is of interest to gain an insight into the effect of pH on the behavior of macromolecular attachment. Similar studies carried out on  $\text{TiO}_2$  surfaces will be reported in a separate communication.

## EXPERIMENTAL

### Adsorbent

Reagent-grade zirconium dioxide ( $\text{ZrO}_2$ ), from Hopkins and Williams, passed through a BS 400 sieve ( $\leq 38$  nm), was used as adsorbent. The BET specific surface of  $\text{ZrO}_2$  was determined by adsorption of nitrogen at  $77^\circ \text{K}$ .<sup>16,17</sup> The zero-point of charge (zpc) at the oxide- $\text{H}_2\text{O}$  interface was examined by acid-base potentiometric titration.<sup>18,19</sup> The surface excess of the hydrogen or hydroxyl ions was measured in the presence of sodium chloride as indifferent electrolyte. A fixed volume (1.50 ml) of 1.00M NaOH was added to 300 ml of a  $\text{ZrO}_2$  suspension (1:60) in  $10^{-1}\text{M}$  and  $10^{-3}\text{M}$  NaCl, and then titrated under a stream of  $\text{N}_2$  gas with 1.00M HCl. The equilibrium pH was measured at  $25.0^\circ\text{C}$  by means of a Beckman Research Model pH meter. The adsorption density,  $\Gamma_{\text{H}^+} - \Gamma_{\text{OH}^-}$ , was calculated in micromols/g solid, which was then plotted against pH.

### Adsorbate

An anionic-type polyelectrolyte flocculant, "Superfloc A100," from American Cyanamid, which is a partially hydrolyzed polyacrylamide homologue,\* was chosen as adsorbate. In order to obtain a homogeneous polymer solution, a stock solution containing 500 mg PAA/l. was prepared at  $\sim 40^{\circ}\text{C}$ , and PAA working solutions of varying concentrations up to 100 mg/l. were prepared by dilution of the stock solution. The stock solution was renewed weekly. Adjustment of pH was made by means of HCl or NaOH. The weight-average molecular weight ( $\bar{M}_w$ ) of PAA was determined by means of intrinsic viscosity  $[\eta]$  measurements.<sup>5,17,20</sup> PAA solutions containing 50–500 mg/l. were prepared in 1M NaCl. The viscosity was determined at  $25.00^{\circ} \pm 0.01^{\circ}\text{C}$  by a capillary viscometer of the Ubbelohde type.

The buffer capacity of PAA was measured in the usual way, using PAA solutions containing 30 and 300 mg/l. in 0.01M HCl. A 50.0-ml aliquot of each PAA solution was titrated at  $23^{\circ}\text{C}$  with 0.01M NaOH under a nitrogen atmosphere. The equilibrium pH was measured as a function of the alkali added, from which a titration curve was constructed.

The PAA solution viscosity was studied at different pH with a polymer solution containing 0.050 g PAA/dl. The viscosity measurements were conducted at  $23.0^{\circ} \pm 0.1^{\circ}\text{C}$  using an Ostwald-type viscometer. The specific viscosity ( $\eta_{sp}$ ) was plotted against pH.

### Polymer Adsorption

An adsorption experiment was carried out at  $25^{\circ}\text{C}$  as a function of pH. Throughout the experiment, a fixed speed of rotation ( $\sim 370$  rpm) and a uniform duration of agitation were provided by means of a multiple blade-type stirrer having 12 units connected in series.

Preliminary experiments showed that most of the adsorption ( $\sim 90\%$ ) took place during the first 30 min under the given conditions and that polymer adsorption was virtually complete in 1 hr; to ensure equilibrium, a stirring time of 2 hr was used. A parallel set of adsorption experiments was run at different pH. A series of PAA working solutions covering a suitable range of PAA concentrations was prepared in the usual way and conditioned at  $25^{\circ}\text{C}$  in a constant-temperature water bath. To each dilution the mineral particles were added with stirring so as to yield a solid-to-liquid ratio of 1–10 by weight. When the 2-hr stirring was complete, the mineral suspension was then allowed to settle. The resulting supernatant liquor was removed and adjusted to neutral pH for subsequent analysis. Following Crummett–Hummel's modification of the Hyamine complexation technique,<sup>9,21</sup> the residual PAA was analyzed. From the calibration curve simultaneously obtained, the amount of PAA adsorbed ( $x$ ) per gram of adsorbent ( $m$ ),  $x/m$ , was calculated.

\* Available in the form of free-flowing granules, which contain approximately 7%–8% carboxylate ions.<sup>5</sup>

## RESULTS

Figure 1 is constructed for the acid-base titration of PAA aquesol, where the dotted curve (ideal) refers to the blank titration conducted without addition of PAA. From the observed intrinsic viscosity,  $[\eta] = 16.35 \text{ dl/g}$ , the  $\bar{M}_w$  of PAA was evaluated from the Staudinger relation

$$[\eta] = K\bar{M}_w^\alpha$$

which gives  $7.6 \times 10^6$ , when the constants  $K$  and  $\alpha$  are taken to be  $8.87 \times 10^{-4} \text{ dl/g}$  and  $0.62$ , respectively.<sup>5,20</sup>

In order to examine the influence of pH on PAA solutions, Figure 2 was obtained by combining Figure 1 with the plots of PAA solution viscosity ( $\eta_{sp}$ ) versus pH.

The BET specific surface area of  $\text{ZrO}_2$  was found to be  $5 \text{ m}^2/\text{g}$ . The zpc at the  $\text{ZrO}_2\text{-H}_2\text{O}$  interface was found to be at approximately pH 3.5. Figure 3 shows the results of the potentiometric titration, which was obtained in the presence of the mineral oxide, without the addition of PAA.

Some typical isotherms resulting from PAA adsorption onto  $\text{ZrO}_2$  at  $25^\circ\text{C}$  are presented in Figures 4 and 5.

## DISCUSSION

It has been postulated<sup>6,10,14</sup> that polymer molecules are attached to solid surfaces in such a way that the chain segments lie flat at low surface coverage but are anchored vertically to the surface at high coverage. In the usual polymer adsorption-flocculation, the most likely configuration of the surface coverage would be an intermediate between these two extremes, and the polymer mole-

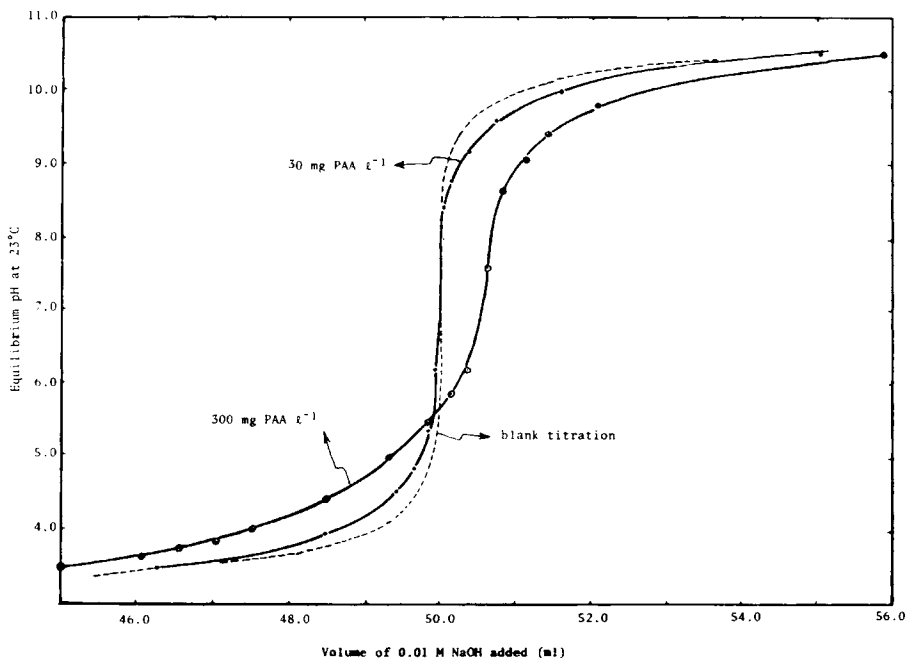


Fig. 1. Titration of PAA in  $0.01M$  HCl with  $0.01M$  NaOH.

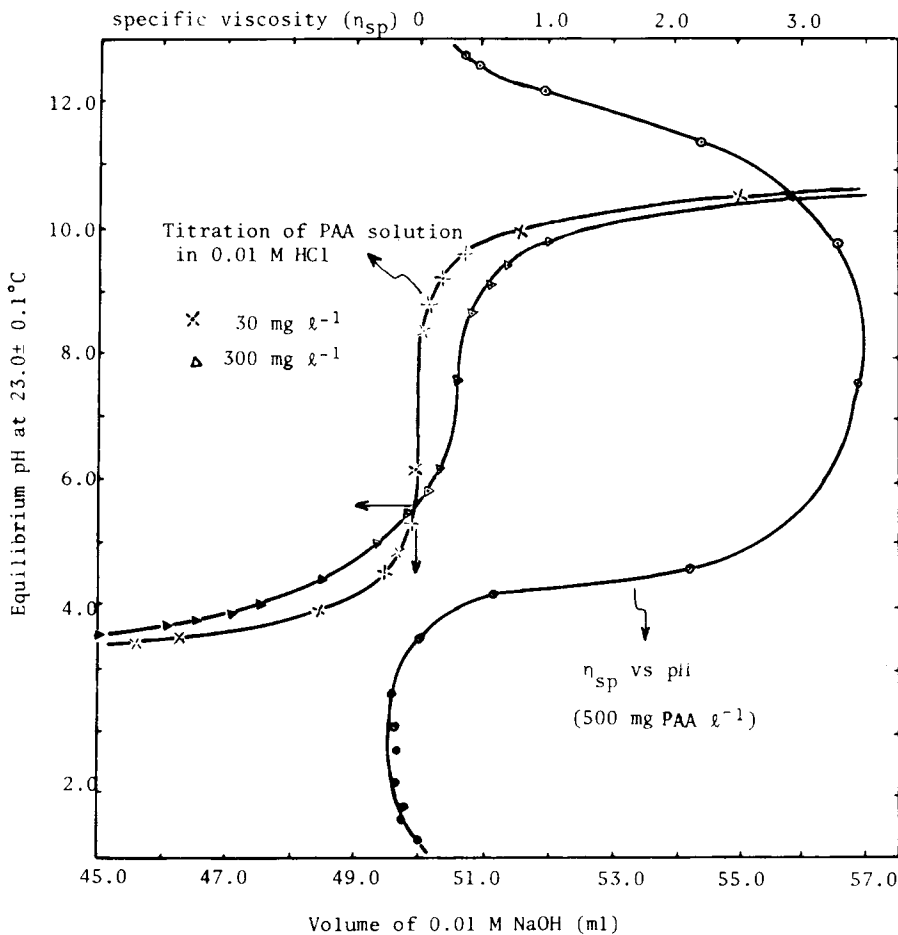


Fig. 2. Influence of pH on PAA solution viscosity.

cles would be dangling in loops from the surface. When the extended tentacles are held on to neighboring particles, or interlocked with those protruding from adjacent particles, an interparticle bridging action will then take place. Through thermal motion or mechanical agitation the bridging process will be facilitated.

In virtually all cases studied, it was found that polymer adsorption can be best represented by a Langmuir-type isotherm (Fig. 4), indicating that PAA adsorption onto ZrO<sub>2</sub> occurs as a monolayer. The relationship between the amount of PAA adsorbed and the equilibrium concentration was evaluated by means of the Langmuir equation

$$\frac{C}{x/m} = \frac{1}{K_1 K_2} + \frac{C}{K_2}$$

where  $K_1$  and  $K_2$  are constants;  $C$  is the equilibrium concentration of PAA, in mg/l;  $x$  is the amount of PAA adsorbed, in mg; and  $m$  is the mass of adsorbent, in g.

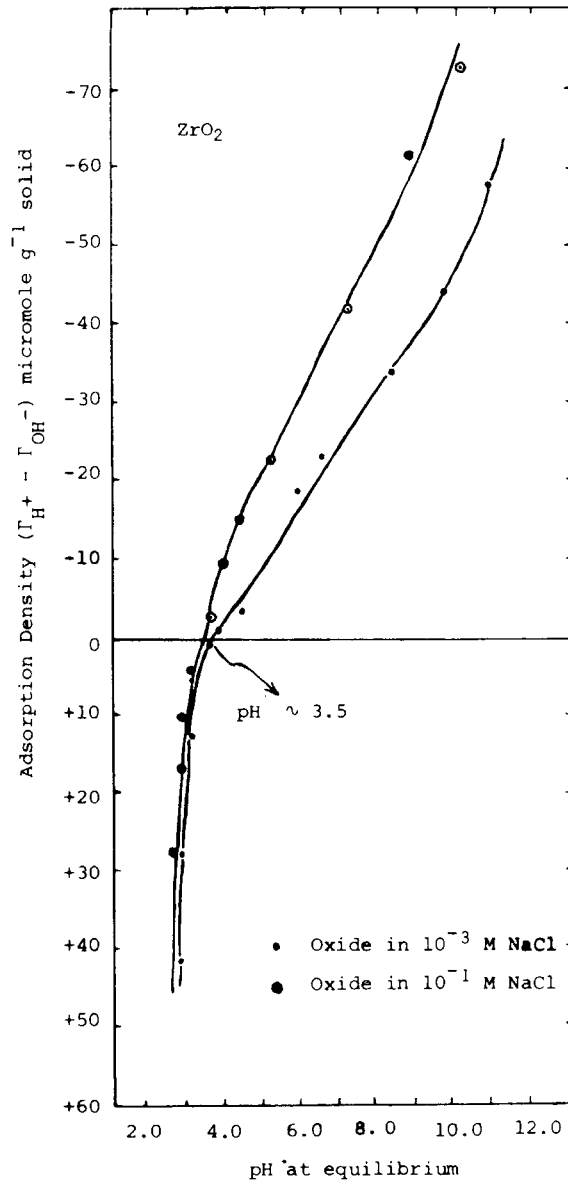


Fig. 3. Determination of zpc of ZrO<sub>2</sub> by potentiometric titration at 25°C.

When  $C/(x/m)$  was plotted against  $C$ , a straight line resulted as shown in Figure 5, confirming the goodness of fit to the Langmuir isotherm. Polymer adsorption onto a ZrO<sub>2</sub> surface showed a progressive decrease with increasing pH in the region of pH 2–6.3, beyond which adsorption was not measurable because of limitation of the analytical technique. Above a pH of 6.3 the ZrO<sub>2</sub> remains in a highly dispersed state and the Hyamine turbidimetric technique, to which reference has already been made, cannot be applied. The saturation adsorption at 25°C/pH 2 was found to be approximately 0.24 mg/g ZrO<sub>2</sub>.

A PAA molecule consists of an ethylenic linkage as a skeletal-forming carbon

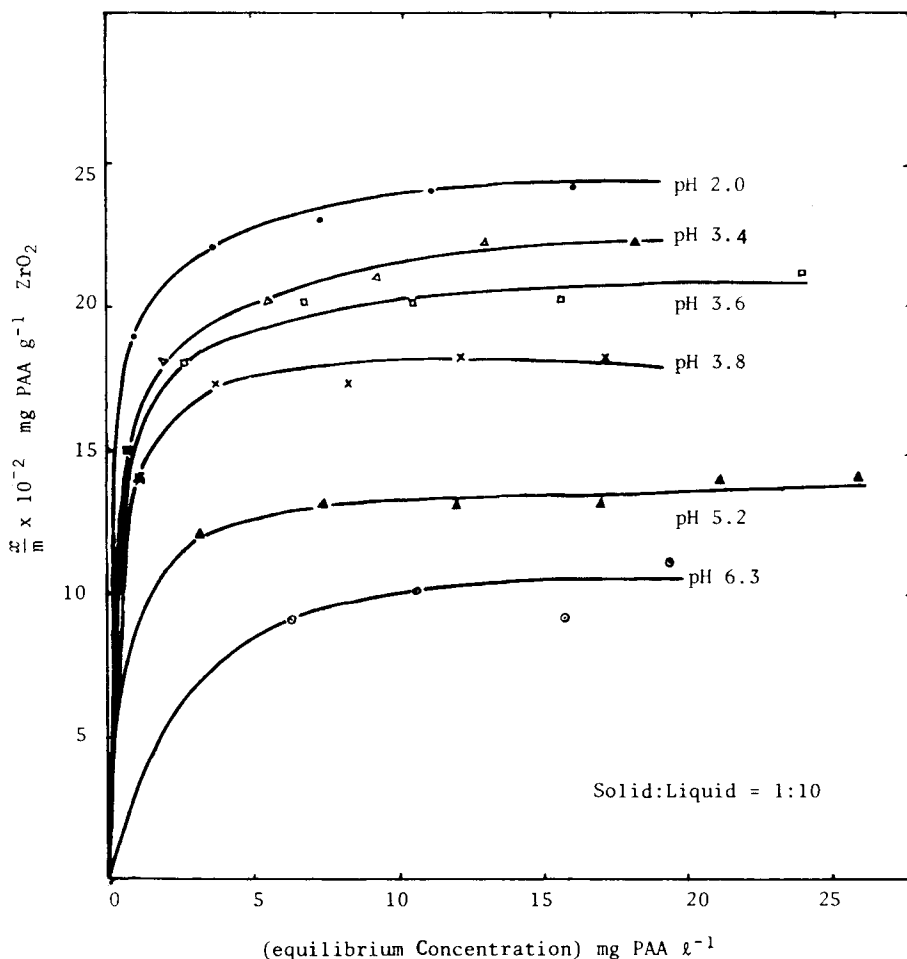
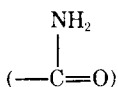
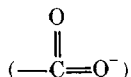


Fig. 4. Adsorption isotherm of PAA on ZrO<sub>2</sub> at 25.0°C.

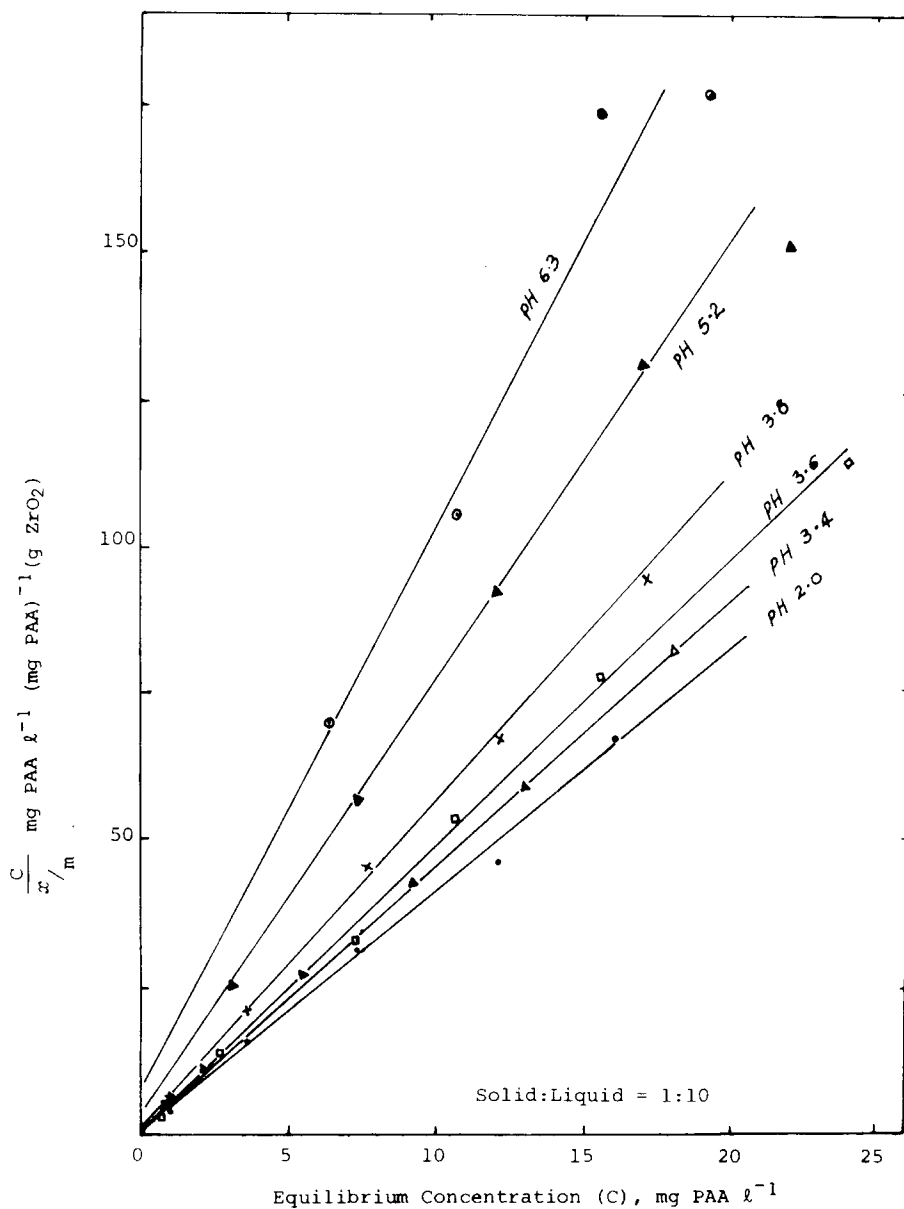
chain and amide groups



or carboxylate ions

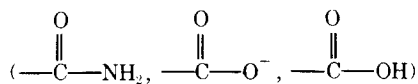


as functional groups. Michaels<sup>9</sup> attributed the powerful flocculation ability of PAA to its dual functionality by virtue of both groups. Since the backbone C—C bond is essentially apolar and the C—H bond is very weakly polar, their contributions to polymer attachment would be limited to physical forces, i.e., van der Waals-type attraction, or to low dielectric constant (see below). However, the bonding behavior of partially hydrolyzed PAA would be a compromise between

Fig. 5. Adsorption isotherm of PAA on  $ZrO_2$ .

the hydrophobic character of the unhydrolyzed polymer and the strongly ionic nature of, say, Na polyacrylate.

In regard to the mechanism by which the polymer molecules are adsorbed on to the surface sites, the concept of multiple hydrogen bonding is proposed as a principal factor, with electrostatic interaction as a complementary one.<sup>10,22,23</sup> Some IR studies<sup>24,25</sup> reveal that H bonding takes place between the functional groups of the polymer molecule





and the surface-active sites



of the dispersed phase. In the IR investigation of adsorbed carboxylic acids on  $\text{TiO}_2$ , Smith<sup>26</sup> demonstrated the presence of both ionically bonded and H-bonded acids on the oxide surfaces. In this respect, little published information on  $\text{ZrO}_2$  surfaces is available, and the results of this work are not entirely in support of earlier observations.

Information as to the zpc on  $\text{ZrO}_2$  reveals that the surface charge will be negative in an aqueous solution of  $\text{pH} > \sim 3.5$  (see below). Nevertheless, there was evidence that PAA adsorption on  $\text{ZrO}_2$  was effected at  $\text{pH} 3.5 \sim 6.3$ , where electrostatic repulsive forces would be operative between the oxide and PAA. Similar contraindications are often experienced in practical polymer flocculation, which show the successful flocculation of negative colloidal dispersions by an anionic polyelectrolyte.<sup>20</sup> In addition, combination of anionic and cationic flocculants sometimes gives better performance than individual application.<sup>12</sup>

Since the solid surface can adsorb polymer molecules in competition with water, PAA adsorption will largely depend upon the affinity of the surface to the PAA molecules in preference to the water molecules, and this may involve either physical or chemical forces only, or a combination of the two.<sup>3,6,10,27</sup> Strongly ionic polyelectrolytes will be adsorbed on colloidal dispersions of opposite charge through electrostatic attraction, whereas the adsorption of nonionic or very weakly ionic polymers is primarily controlled by physical bonding forces.

As to the mechanism by which an oxide surface acquires surface charge, a two-step process is currently postulated,<sup>18,19</sup> viz., hydration of the surface metal atoms and then ionic dissociation of the resulting surface  $-\text{OH}$  groups, depending upon the nature of potential determining ion(s) (PDI) present.

In a  $\text{ZrO}_2$  crystal, the central atom of Zr has a maximum coordination number of 8, but it is unlikely that the exposed surface atom would be bonded with 8 oxygen atoms due to steric factors. This will result in residual valence forces on  $\text{ZrO}_2$  surfaces. The surface metal atom tends to complete its coordination sphere by attracting  $\text{OH}^-$  ions or water molecules, while the vicinal oxygen atom tends to draw a proton from the surrounding aqueous phase.<sup>28</sup>

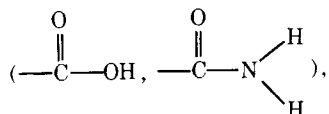
The zpc obtained (Fig. 3) indicates that acidic dissociation will take place in an aqueous solution of  $\text{pH} > \sim 3.5$ , yielding a negative charge on the  $\text{ZrO}_2$  surface, whereas basic dissociation at  $\text{pH} < \sim 3.5$  will confer a positive charge on the  $\text{ZrO}_2$  surface. Despite some difference from the published data,<sup>19,29</sup> about which there is disagreement at present, the observed zpc value is regarded as a sufficiently good approximation for a discussion of PAA adsorption behavior.

In view of the nature of the ionic charge on a PAA molecule, the specific viscosity of PAA solutions was determined as a function of pH (Fig. 2). The viscosity data reveal a parabolic dependence on pH with a maximum in the neutral pH region. For adjustment of pH, HCl or NaOH was used. The decrease in viscosity as a function of pH in the alkaline region is not as sharp as in the acid region; at extremely low pH ( $< 2$ ), there is a tendency for the viscosity to increase again slightly.

In order to account for this, two factors contributing to the viscosity of lyophilic

colloids are important<sup>7,30</sup>: (i) effective volume expansion due to hydration, and (ii) electroviscous effect due to ionic charge on the colloidal particles. It is considered that both factors would be responsible, to a different extent, for the observed variations.

The fact that PAA adsorption was favored with decreasing pH and hence decreasing ionic character appears to support a nonionic bonding mechanism (e.g., H bonding) or van der Waals-type attractive interactions rather than the concept of an electrostatic mechanism. If H bonding were to be established through surface —OH groups, according to the model proposed by Špaldon and Tkacova,<sup>14</sup> then greater adsorption should take place in alkaline pH, since the dissociation of —COO<sup>-</sup> ions will be favored in that pH region. In fact, PAA adsorption was found to decrease with increasing pH. On ZrO<sub>2</sub> there is no known evidence of surface —OH groups,<sup>28</sup> and so PAA adsorption on ZrO<sub>2</sub> in acid pH is not through surface —OH groups but most likely through surface oxygen atoms, onto which the amide (—CONH<sub>2</sub>) groups can be attached. Under acid conditions, partially hydrolyzed PAA will have two types of H-donating groups



and the H bond via —COOH is stronger than via —CONH<sub>2</sub>, because of the greater electronegativity of the oxygen atom. As the PAA molecules lose their ionic properties in acid solution, van der Waals-types of interaction will come into effect, permitting the uncharged polymer molecules to interact with the ZrO<sub>2</sub> surface. In acid media, therefore, PAA molecules should have excellent conditions for realization of their surface attachment. In contrast, in alkaline pH, the partially hydrolyzed PAA will have no carboxylic acid groups. With increasing pH, the polymer molecule will be further dissociated into carboxylate ions (—COO<sup>-</sup>), causing excessive chain extension. This will hinder polymer access to the surface sites, adversely affecting PAA adsorption.

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