BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(12), 2990—2993 (1974)

The Adsorption of the Aminoethyl Derivatives of Poly(vinyl alcohol) onto Bemberg Rayon Fibers[1]

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(Received July 24, 1974)

A series of aminoethyl derivatives of poly(vinyl alcohol) was synthesized, and their adsorption behavior onto a cellulosic fiber was investigated. The results indicate that the primary factor causing adsorption is the charge interaction at the solid-liquid interface; the adsorption was suppressed as the concentration of a foreign salt (NaCl) exceeded 0.02 M, and polymers bearing no cationic group poly(vinyl alcohol) and its aminoethyl derivatives in the un-ionized state) exhibited no appreciable adsorption. The results also demonstrate that the primary variable controlling the amount of adsorption is the charge density on the polymer; the amount of adsorption increases steeply with an increase in the charge density up to a maximum, and then decreases with the increase in the charge density.

Although numerous papers have been published and a considerable amount of information has been accumulated on the adsorption of macromolecules from solution onto solid surfaces, those concerned with polyelectrolytes are comparatively few and insufficient;[2] therefore, it seems desirable to accumulate additional experimental data. This paper will present our findings on the adsorption of a polyamine of a hydrophilic nature from aqueous solutions onto a solid of a hydrophilic nature. Incidentally, though more than 50 kinds of cationic polymers have appeared up to the present time in the literature, there are few polymers which have only primary amino groups as ionizable groups and which are, besides, soluble in water over a wide pH range. The present authors synthesized a series of aminoethyl derivatives of poly(vinyl alcohol). These polymers are unique in bearing primary amino groups together with hydroxyl groups and in their hydrophilic nature.

Experimental

Materials. A Bemberg rayon fiber, considered to have the smoothest surface among cellulosic fibers, was used as the adsorbent. The fibers were 1.31 den and 2 mm in length, with round sections 12 μ in diameter. The adsorbent was subjected to five 24 hr soaks in ethanol and four 24 hr soaks in distilled water to remove the scouring agents and any other impurities. The geometrically-calculated surface area of the fibers was 3500 cm^2/g in the wet state.

Aminoethyl derivatives of poly(vinyl alcohol) and cellulose, (henceforth referred to as AEPVA and AEC respectively) were prepared through the Hofmann degradation of the corresponding carbamoylethyl derivatives. The carbamoylethyl derivatives were prepared by means of a Michael reaction of acrylamide, with care taken to avoid the formation of carboxyl groups by using a large excess of acrylamide at low temperatures (10～15 °C). A water-soluble derivative of cellulose was prepared by dissolving cotton linters in a 40% benzyltrimethylammonium hydroxide solution and by then adding a large amount of a 35% acrylamide aqueous solution. Polymers of above 99% conversion of the carbamoylethyl group into the aminoethyl group were used as the adsorbates. The variation in the amino-group content of the polymers was accomplished by the control of the degree of carbamoyl-

Table 1. Polymers studied

Polymer	Code	DS[a]	E.W.[b]	[η][c]
Poly(vinyl alcohol)	PVA	0		0.645[d]
Hydroxyethylated poly(vinyl alcohol)	HEPVA	0.05		0.623
Aminoethylated poly(vinyl alcohol) (AEPVA)	1	0.043	1066.3	0.641
	2	0.095	506.2	0.502
	3	0.150	336.3	0.630
	4	0.204	258.7	0.714
	5	0.260	212.2	0.345
	6	0.260	212.2	0.725
	7	0.260	212.2	0.903
	8	0.278	201.3	0.802
Aminoethylated cellulose	AEC	1.01	203.4	3.23

a) Degree of substitution: per monomer unit for HEPVA and AEPVA, per AGU for AEC. b) Equivalent molecular weight per amino group. c) Intrinsic viscosity in a 1M-NaNO$_3$ solution at 30 °C. d) Number-averaged molecular weight: *ca.* 6×10^4

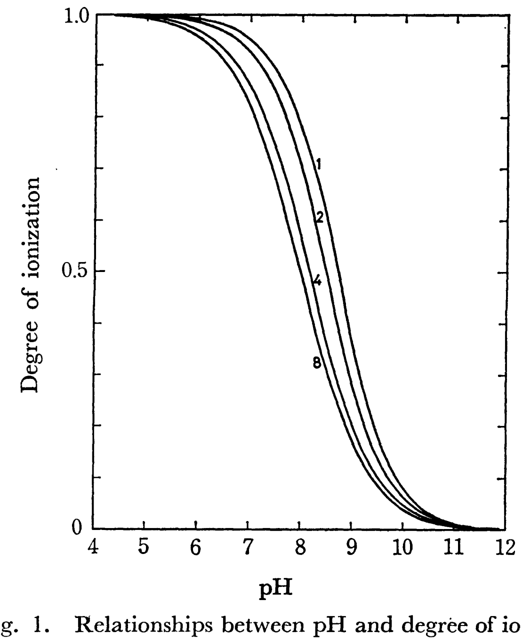

Fig. 1. Relationships between pH and degree of ionization for AEPVA.
The numbers 1, 2, 4, and 8 denote the code numbers for the polymers in Table 1.

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ethylation. The aminoethyl derivatives were subjected to fractional precipitation in a 0.5 M sodium acetate aqueous solution, with acetone as the precipitant. All the adsorbates were purified from about 0.1 M NaOH solutions by dialysis in deionized water. The properties of the polymers used are shown in Table 1, while the relationships between the pH and the degree of ionization of the aminoethyl derivatives are shown in Fig. 1.

Adsorption Procedure. A weighed quantity of wet fibers (net 2 g) and 100 ml of a polymer solution of a known concentration were enclosed in a 150-ml polystyrene vessel and shaken for 24 hr at 20 °C. After this process, the pH of the mixture was measured using a Hitachi-Horiba F5 pH meter; then the fibers were filtered off, and the solution was analyzed. The amount of adsorption was calculated from the difference in the polymer concentration measured before and after the adsorption process. The pH of the adsorption system was set by the use of acetic acid, ammonia, HCl, or NaOH.

Analytical Methods. Colloid titration[3] was used to determine the concentration of the aminoethyl derivatives before and after each adsorption run. An aliquot portion of the polymer solution was taken, buffered to pH 4 with acetic acid, and then titrated with a N/500 potassium poly(vinyl sulfate) solution, using toluidine blue as the indicator.

A spectrophotometric method[4] was used for the determination of the concentrations of poly(vinyl alcohol) (PVA) and its hydroxyethyl derivative (HEPVA). The absorbance of the colored PVA-iodine complex formed in the presence of boric acid was measured at 660 mμ.

The degree of ionization of the aminoethyl derivatives was calculated from the results of pH titration. A 200-ml portion of a N/200 AEPVA solution was titrated with M/10 HCl at 20 °C under a N_2 atmosphere by the use of a Hitachi-Horiba F5 pH meter.

Results

Adsorption of PVA and HEPVA. No appreciable adsorption took place in the 3~12 pH range, in contrast with the cases of the adsorption of PVA from aqueous solutions by titanium dioxide[5] or by sodium montmorillonite.[6] This result demonstrates that neither hydrogen bonding nor hydrophobic interactions come into play to cause adsorption in this cellulose–PVA–water system.

Effect of the pH on the Adsorption of AEPVA. As the example (Fig. 2) shows, the saturation adsorption capacity is greatly dependent on the pH of the system. The amount of adsorption increased as the pH increased, but to only a small extent in the 3~7 pH range, steeply above pH 8, and attained to a maximum at a pH of about 10.3. Above this point, the adsorption capacity decreased steeply with the increase in pH; no appreciable adsorption took place above pH 12.

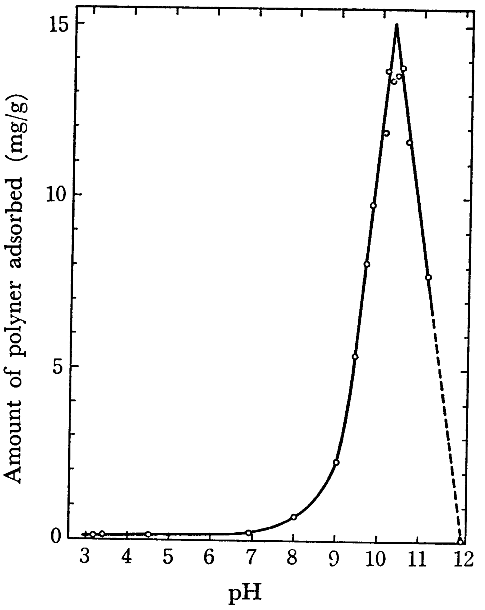

Fig. 2. Variation of the adsorption capacity with pH. Adsorbate: AEPVA-8. Concentration of foreign electrolytes added: 0.001 N.

Table 2. Amounts of maximum adsorption of AEPVA of various amino-group contents at pH 4.5 and 10.9

AEPVA	Amino-group content[a]	Amount adsorbed			
		Polymer weight (mg/g)		Ionized amino group[b] (eq/g)$\times 10^6$	
		pH 4.5	pH 10.9	pH 4.5	pH 10.9
1	0.043	5.6		5.2	
2	0.095	2.0	3.7	4.0	0.06
3	0.150	0.6	4.5	1.8	0.10
4	0.204	0.3	5.3	1.2	0.14
6	0.260	0.2	6.7	0.8	0.20
8	0.278	0.1	8.9	0.5	0.26

a) Number of the amino group per vinyl monomer unit. b) Calculated from the amount adsorbed, the amino-group content, and the degree of ionization of the corresponding polymer.

Effect of the Amino-group Content. Table 2 shows the amounts of the maximum adsorptions of AEPVA of various amino-group contents at pH 4.5 and 10.9. At pH 4.5, the amount of adsorption decreased with the increase in the amino-group content; this is consistent with the earlier finding that the increase in the charge density on the macromolecule causes a decrease in the adsorption.[2] At pH 10.9, however, the amount of adsorption increased with the increase in the amino-group content. The amount of the ionized amino group in the polymer adsorbed also varied with the amino-group content; this fact indicates that the stoichiometric interaction between the surface charge and the polymer charge does not alays determine the amount of adsorption.

Effect of Molecular Size. Figure 3 shows that the dependence of the amount of adsorption on the molecular size of the polymer is very small in comparison with that on the amino-group content at both pH 4.5 and pH 10.9. This result may confirm that the fiber surface is nonporous with regard to the adsorption of the polymers used.

Effect of Electrolyte Added. Figure 4 shows the effects of the NaCl concentration on the adsorption of AEPVA at pH 4.5 and 10.9. At pH 4.5, the addition of NaCl increased the amount of adsorption until its concentration reached about 5×10^{-3} mol/l; above this point, however, it had an inverse effect, and no ap-

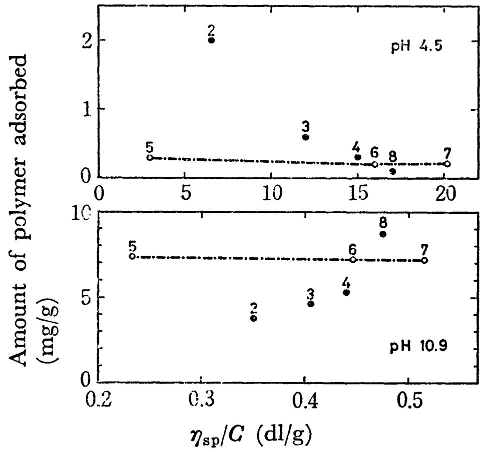

Fig. 3. Plots of the adsorption capacity against a parameter for polymer coil dimension. The numbers, 2∼8, denote the code numbers for AEPVA. AEPVA-5, -6, and -7 have the same amino-group content. The variation of the adsorption capacity can be ascribed to the effect of the amino-group content; the dotted lines show very little effect of the size of polymer molecules.

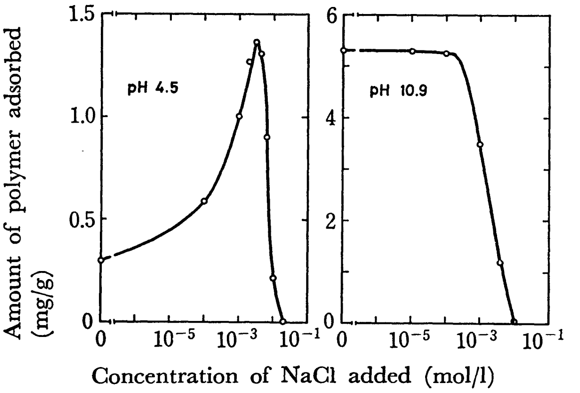

Fig. 4. Variation of the adsorption capacity with the concentration of NaCl added. Adsorbate: AEPVA-4.

preciable adsorption took place when the concentration of NaCl exceeded 2×10^{-2} mol/l. At pH 10.9, the amount of adsorption always decreased as the concentration of NaCl increased. These phenomena suggest that the primary driving force of adsorption is the electrostatic force of attraction between the solid surface and the solute polymer.

Comparison of the Adsorption Behavior of AEPVA with That of AEC. Figure 5 shows the adsorption isotherms for the AEPVA of a flexible chain and for the AEC of a rigid chain. The two polymers used are alike in amino-group content and in molecular weight. At pH 4.5, the adsorption behavior of AEPVA is almost identical with that of AEC; this result suggests that the AEPVA molecules as well as AEC molecules are adsorbed in a stretched (and flat) conformation at the surface. On the other hand, at pH 10.9, there is a remarkable difference between the adsorption isotherm for AEPVA and that for AEC. This may be due to the difference in molecular shape at the surface.

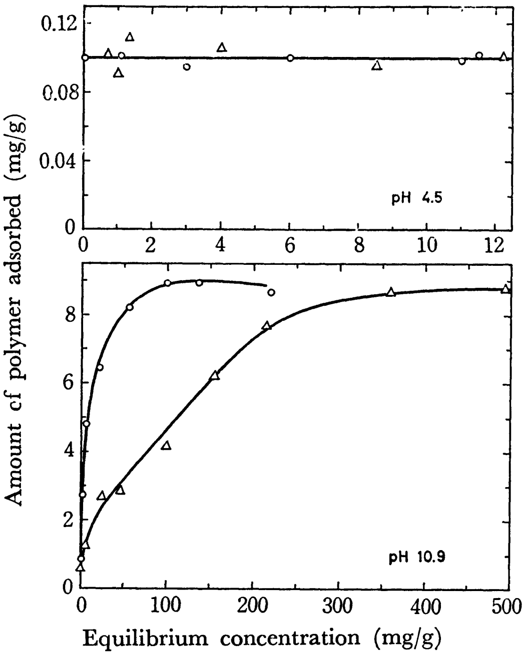

Fig. 5. Comparison of the adsorption behavior of AEPVA with that of AEC.
(○): AEPVA-8, (△): AEC.

Discussion

The results of the adsorption of PVA and the effect of the pH on the adsorption of AEPVA indicate that the aminoethyl group is essential for the adsorption of AEPVA and that the un-ionized amino group plays no important role in the adsorption. Considering these

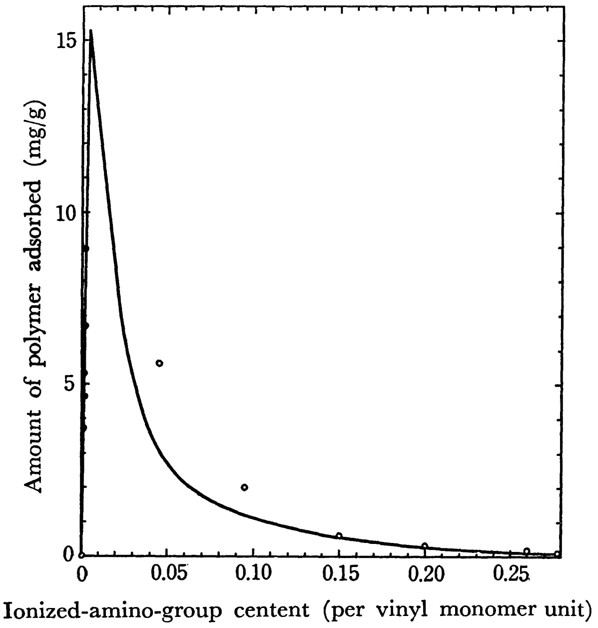

Fig. 6. Dependence of the adsorption capacity on the polymer charge-density.
Solid curve: calculated from the data on the pH-dependence of the adsorption of AEPVA-8 (Fig. 2). Points: calculated from the data on the absorption of AEPVA of various amino-group contents at fixed pH (○: pH 4.5, ●: pH 10.9).

facts in connection with the fact that the adsorption is suppressed when the NaCl concentration is increased above 0.02 mol/l, we can conclude that the primary factor causing adsorption in this cellulose-AEPVA-water system is the charge interaction at the solid-liquid interface.

It can also readily be noticed that the positive charge on AEPVA is the primary variable controlling the amount of adsorption. The dependence of the maximum amount of adsorption on the charge density of AEPVA is illustrated in Fig. 6. It is clear that the amount of adsorption is a function of the charge density on the polymer, though the variation in the charge density on the fiber surface with the pH is not taken into account in this figure. The adsorption increases steeply in approximate proportion to the charge density up to a maximum, at which the solute polymers bear the ionized amino groups in a ratio of 1 to 200~300 of vinyl monomer units, and then decreases with the increase in the charge density. Incidentally, at the point of maximum adsorption about 500 vinyl monomer units, in a rough estimation, are found per 100 Å^2 of fiber surface; if it were assumed that the polymer molecules are adsorbed in a spherical conformation at the surface, this signifies multilayer surface coverage, while if monolayer adsorption were assumed, it indicates that polymers are attached to the surface by a few segments in long loops extending out into the liquid phase. On the other hand, at the point of the ionized-amino-group content (0.278), only 3 vinyl monomer units are found per 100 Å^2 of fiber surface; this corresponds to only a one-third surface coverage even if a completely flat accommodation at the surface were assumed.

The steep rise in the adsorption capacity in the region of low-charge densities may be ascribed to the increase in the electrostatic force of attraction between the polymer and the fiber surface.

With regard to the decrease in the adsorption capacity with the increase in the charge density in the region of the ionized-amino-group content above 0.004, either of the following two explanations appears to be possible. First, it may be considered that the number of polymer molecules required to fill up the binding sites (anionic sites) of the fiber surface decreases as the positive charge on the polymer increases, thus leading to a reduction in the amount of polymer adsorbed. Another explanation is that the spatial requirement per molecule at the surface increases as the charge density of the polymer increases because of the expansion of the polymer coil by the intramolecular repulsion of the ionic groups, thus causing the reduction of the adsorption. However, in the region of higher charge densities these two explanations may be inadequate, because it is considered that, at some point (with regard to the charge density), polymers start to adsorb in a flat conformation at the surface and that, from some point, the saturation of adsorption takes place, leaving a considerable amount of surface area uncovered. In this region, the reduction of adsorption may be ascribed to the increase in the electrostatic force of repulsion between the adsorbed polymer and the solute polymer.

The authors wish to express their appreciation to Professor Isao Sakata, Faculty of Agriculture, Kyushu University, for his valuable suggestions.

References and Footnotes

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