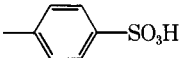
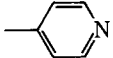


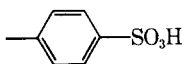
Effects of Complexation on the Water Vapor Sorption of Polymer Alloys

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Synopsis

Water sorption measurements of the polyion complex between poly(*p*-styrenesulfonic acid) (PS_{*t*}S) and poly(4-vinylpyridine) (PVP) were carried out to study the effect of the Coulombic interactions between a polyanion and a polycation. The properties of the polyion complex were examined using infrared spectroscopy (IR), X-ray diffraction, X-ray photoelectron spectroscopy (XPS), and elemental analysis.

It was found that the ionic bonds between  and  groups led to the formation of a 1:1 polyion complex between PS_{*t*}S and PVP. The nitrogen 1s level in the PS_{*t*}S/PVP polyion complex increased 2.1 eV above its level for PVP, indicating protonation of the pyridine group. In addition, at 293 K and 303 K the water sorption of the complex was larger than that of the sum of the component polymers. In the preceding paper, the water sorption properties of the polyion complex between poly(acrylic acid) (PAA) and PVP were studied. Compared to this complex, the PS_{*t*}S/PVP complex absorbed more water relative to its components. This may be due to the stronger acid strength of the



over the —COOH groups.

INTRODUCTION

Polyion complexes are a unique class of polymer alloys because their constituent polyelectrolytes interact strongly with each other through Coulombic forces. (strength; ~several 100 kcal/bond). Since the discovery in 1961 of screening solvents for polyion complexes, many papers were published about their gels. It was found, consequently, that because of the diversity of constituent components, polyion complex membranes are highly permeable to water and to small solute molecules. They have high electrical conductivity, high biological compatibility, and controllable ion-exchange capacity. In practice, commercial materials are used in ultrafiltration, medicine, and electrical engineering.

Although considerable work has been done on their water permeabilities, very little has been published about their water vapor sorption properties. This is the extension of the work reported in the preceding paper, where we investigated

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the sorption ability of the polyion complex between poly(acrylic acid) (PAA) and poly(4-vinylpyridine) (PVP).¹ It was found that the complexation enhanced the sorption ability in a synergistic manner. This tendency was eminent especially at low vapor pressures where the chemical characteristics of the polymer composition are apt to affect the sorption properties strongly. In this paper, the polyion complex composed of poly(*p*-styrenesulfonic acid) and poly(4-vinylpyridine) was studied. Compared to the previous work, the polycation was left the same but the polyanion was replaced with a polyelectrolyte with much stronger acidity. It can be expected that the difference between the two complexes will give us more information about the effects of Coulombic interactions on the water vapor sorption.

EXPERIMENTAL

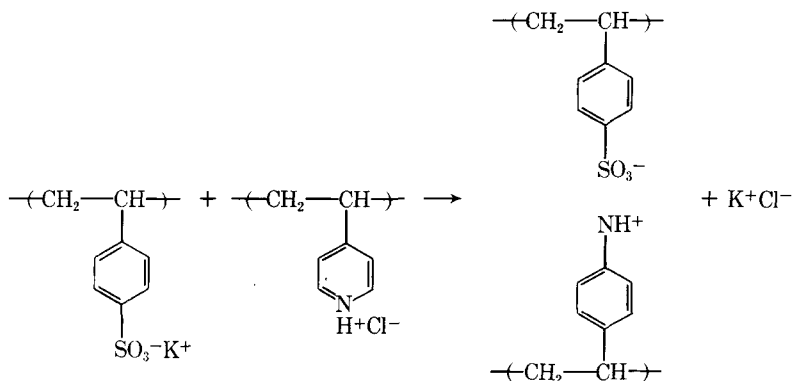
Preparation of Materials

Preparation of PS_tSK (1). PS_tSK was obtained by polymerizing potassium *p*-styrenesulfonate.² The monomer was purified by several recrystallizations from a 1:1 methanol–water solution. Then 13.5 g of this monomer was dissolved in 30 mL of water. This solution was placed in a flask fitted with a stirrer, a thermometer, and a reflux condenser and flushed with oxygen-free nitrogen which was purified by passage through a liquid nitrogen trap. A solution of 0.018 g of potassium persulfate and 0.09 g of sodium bisulfite in 10 mL of water was added as an initiator. This solution (pH 7–8) was stirred under nitrogen for 5 h at 318K. The pH, now 4–5, was adjusted to 7–8 by adding a few drops of dilute potassium hydroxide solution. The polymer was obtained as a white powder by dropping this solution into *N,N*-dimethylformamide. The PS_tSK was purified by multiple precipitation using water as the solvent and *N,N*-dimethylformamide as the nonsolvent. The product was washed with ether (bp 307.5 K) to remove the *N,N*-dimethylformamide (bp 426.0 K) and then was dried at 323 K under vacuum.

Preparation of PVP (2). The vinylpyridine monomer was purified by distillation under low pressure; the fraction with a boiling point of 350 K/3.7 KPa was taken. PVP was obtained by the usual radical polymerization in methanol solution under a nitrogen atmosphere. The PVP product was purified by the multiple precipitation method, using methanol as the solvent and ethylacetate as the nonsolvent. The sample studied here were produced in the same manner as those studied in our preceding report.¹ A more detailed description of the preparation is presented there.

Preparation of PS_tS/PVP (3). In a polyion complex there are strong interactions due to electrostatic bonds. The degree of dissociation is an important factor which affects the movement of polymer segments and determines the morphology and structure of a polyion complex.³ To obtain a 1:1 polyion complex, conditions in which each polyelectrolyte would be highly ionized were chosen. PS_tS/PVP was prepared by mixing at room temperature equimolar PS_tSK and PVP quaternized by HCl in aqueous solutions. The polyion complex rapidly precipitated out of solution in the form of a white powder. This is because the polymer molecules become hydrophobic as the ionizable groups re-

responsible for solubility of the polymers in aqueous solutions became blocked. The reaction mechanism is proposed to be as follows:



The concentration of each polymer solution was adjusted to $7.0 \times 10^{-2}M$. It was observed that above this concentration the product had a stringy appearance; however, below it the resulting precipitation was too fine to be filtered out. The small ions (K^+ and Cl^-) originally associated with the individual polyelectrolytes were removed by careful washing until a silver nitrate agent could not show traces of Cl^- presence. All solvents for this experiment were distilled prior to use.

Analyses of Compositions and Structures

For this work the structures were determined by the yield of polyion complex, elemental analyses of five elements, infrared spectroscopy (IR), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction. Detail procedures about each method can be found in the preceding paper.¹

Sorption Measurements

The water vapor sorption was measured by the weighing bottle method. Equilibrium was assumed when a sample weight changed by only $\pm 0.05\%$. Detailed procedures are found in the preceding paper.¹

RESULTS AND DISCUSSION

The Structures of Polymers

Viscosity and Molecular Weights. Dilution of nonionic polymers results in a linear decrease in reduced viscosity, η_{sp}/C , with decrease in concentration, in accord with the well-known Kuhn-Mark-Houwink-Sakurada equation. In the case of PS_tSK , the effects of dilution on reduced viscosity in water were remarkably different, as is shown in Figure 1. The reduced viscosity increased sharply with dilution and, at high dilutions, approached the ordinate almost asymptotically. This curious behavior is commonly observed in solutions of polyelectrolytes. It is believed to be due to the increase in electronic repulsion

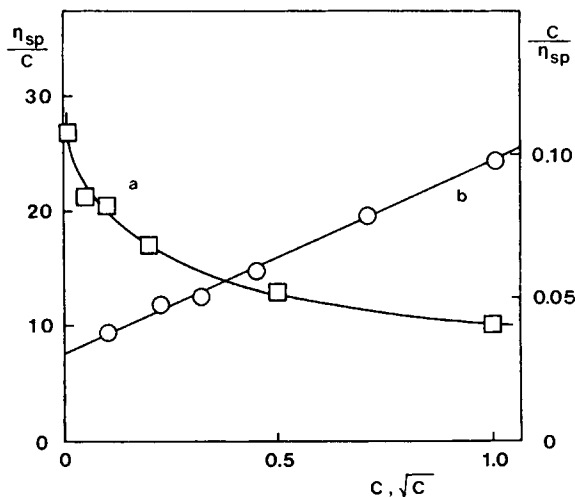


Fig. 1. The viscosity property of PS_tSK at 298 K: (a) $\eta_{sp}/C - C$ (g/dL); (b) $C/\eta_{sp} - \sqrt{C}$.

between polymer chains with dilution. Fuoss and Strauss suggested the following equation to describe viscosity in a polyelectrolyte solution⁴:

$$\eta_{sp}/C = \frac{A}{1 + B\sqrt{C}}$$

where the A term usually represents a constant similar to the intrinsic viscosity $[\eta]$ and the constant B is related to the strength of interaction between a polyion and its counterion. Our data were fit to this equation. Figure 1 shows this relation holds for the viscosity of PS_tSK in aqueous solution; with constants $A = 32.3$ and $B = 2.10$. At the concentration $C = 1.0$ (g/dL), the specific viscosity was $\eta_{sp} = 10.38$. This indicates that the resultant PS_tSK has a rather high degree of polymerization.

The molecular weight M of PVP can be directly calculated from the following Kuhn-Mark-Houwink-Sakurada equation in ethanol solution at 298 K,

$$[\eta] = 2.50 \times 10^{-4} M^{0.68}$$

where $[\eta]$ is the intrinsic viscosity (dL/g).⁵ It was found that the molecular weight of PVP was 9.40×10^4 and that of PVP prepared for PS_tS/PVP was 1.86×10^4 . Both PVP's were not very high molecular weight polymers in contrast to PS_tSK .

Elemental Analysis. If the PS_tS/PVP were to be formed with an equal number of sulfonic acid groups and pyridine rings, that is a stoichiometric ratio of interacting groups, the empirical formula of the complex would be $C_{15}H_{15}N_1S_1O_3$. An elemental analysis of the complex gave the results reported in Table I. From this data the following composition was calculated: $C_{15.4}H_{18.4}N_{1.1}S_{1.0}O_{4.2}$. This indicates that the product compound consists of a 1:1 complex of PS_tS and PVP. The slight deviation from the expected stoichiometry, a slight excess of hydrogen and oxygen, is probably due to absorption of water by the complex during its handling. This is extremely likely because of the hygroscopic nature of the complex. (In fact, its measured composition can be written as $C_{15.4}H_{16.4}N_{1.1}S_{1.0}O_{3.2} \cdot H_2O$). It was found that the yield of

TABLE I
Elemental Analysis of PS_tS/PVP (wt %)

C	H	N	S	Cl	O
58.08	5.81	5.02	10.04	0.00	21.05 ^a

^a By difference.

product in this reaction was approximately 100% with equal moles of PS_tSK and PVP-HCl being used.

IR. We investigated the structure of polymers by various spectroscopic methods. IR, for example, provided significant information about the interactions between the two polyelectrolytes. The spectra of the individual polyelectrolytes as well as that of the complex between them is shown in Figure 2. Notice that the absorption band at 1550 cm⁻¹ in PVP shifted 50 cm⁻¹ to a lower frequency in PS_tS/PVP. This band at 1500 cm⁻¹ is ascribed to ionized pyridine rings in the polyion complex. Further evidence which shows the ionization of pyridine rings by complex formation is the appearance of a shoulder at around 2600 cm⁻¹, which is presumably due to the N—H stretching vibration. On the other hand, there was no difference between the band of sulfonic groups in PS_tSK and that in PS_tS/PVP. This would be expected since sulfonic acid groups in PS_tS/PVP would be ionized in the same manner as in PS_tSK. This evidence indicates the existence of interactions between the pyridine rings in PVP and the sulfonic groups in PS_tS and the formation of a complex between them.

XPS. XPS is an effective technique to investigate the states of electrons in molecules or elements. It provides extensive information about the charge distribution of inner shell electrons without destroying the sample, which makes it an ideal tool to study polymers. The XPS results are shown in Table II. The spectrum shows that there are two nitrogen 1s peaks in PS_tS/PVP; one at 401.4 eV and the other at 398.8 eV. The latter occurs at the same energy as that of the

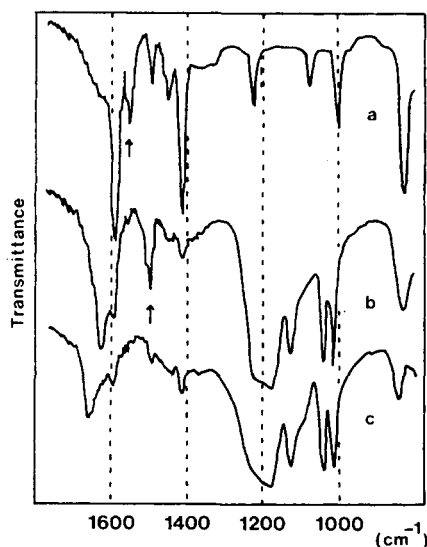
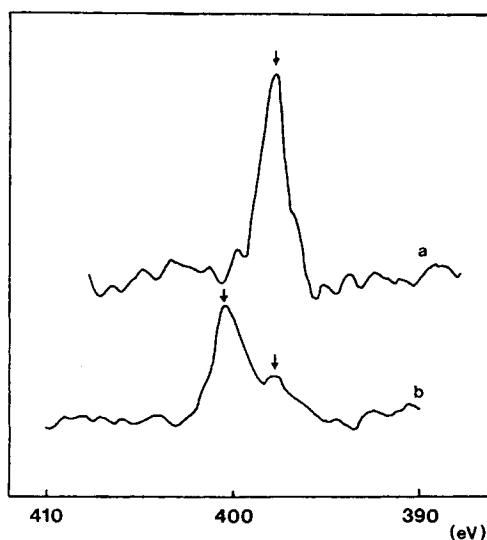
Fig. 2. Infrared spectra of: (a) PVP; (b) PS_tS/PVP; (c) PS_tSK.

TABLE II
 Energy (eV) of Ionization Measured by XPS

	PVP	PS _t S _k	PS _t S/PVP
C 1s	285.4	284.2	284.5
N 1s	399.3		398.8
			401.4
O 1s		531.6	531.4
S 2p 3/2		167.6	167.1
K 2p 1/2		295.6	
3/2		292.5	

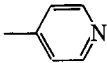
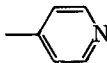
non-ionized nitrogen peak in PVP. The spectrum of PS_tS/PVP in Figure 3 shows the two peaks. The larger peak to the left can be ascribed to the nitrogen of the pyridinium ion, whereas the smaller peak to the right can be ascribed to the nitrogen in free pyridine rings. From their peak heights, it can be estimated that 70% of the pyridine rings were ionized and the rest remained nonionized. We could not detect any trace of K in PS_tS/PVP, and can thus conclude that the ionization is not due to the retention of K in the complex. As also confirmed by the elemental analysis, this complex did not have K⁺ or Cl⁻ ions, which were originally associated with the individual polyelectrolytes. In work related to this, Tsuchida et al. (1972)⁶ showed that the analogous reaction between sodium poly(*p*-styrenesulfonate) and quaternized poly(4-vinylpyridine) produces equimolar PS_tS/PVP at any mixing ratio of reactant polyions. The present system probably exhibits the same behavior. The main conclusion that can be drawn is that the interaction between functional groups are dominant in the formation of complexes. One acidic group is bound with one basic group and successive reaction to form ionic bonds occurs along the length of the polymers. Steric hindrances and other obstructions might result in the breaking of ionic bonds, and, hence, it would be observed that not all groups are bonded as shown


 Fig. 3. Nitrogen 1s peak in (a) PVP and (b) PS_tS/PVP.

by the free pyridine rings in the XPS spectrum. On the average, though, there will be an equal number of free cationic and anionic groups. As shown before by the IR data, the XPS results indicate that the sulfonic groups in PS_tSK and PS_tS/PVP are the same. It can be concluded that the sulfonic groups are ionized in both cases. This seems likely because of the high acid strength of the groups.

X-Ray Diffraction. It is important to investigate morphology as well as chemical composition in a study of sorption properties. It is generally accepted that water molecules are accessible to only the amorphous region in a polymer and can only be absorbed in this limited part. X-ray diffraction spectra showed that there were no peaks indicative of the existence of crystalline phases in PVP, PS_tSK , and PS_tS/PVP .

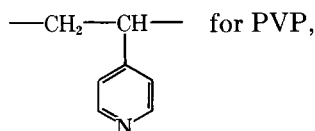
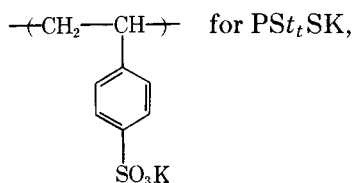
In summary, the findings concerning the structures of these samples revealed the following: When PS_tSK and PVP-HCl aqueous solutions were mixed in equal moles, the reaction proceeded stoichiometrically and a 1:1 polyion complex was produced between PS_tS (polyanion) and PVP (polycation). The charge

change of nitrogen in  and  was shown by XPS and IR.

Furthermore, X-ray diffraction spectra showed that all three samples, i.e., PS_tSK , PS_tS/PVP , and PVP, could be taken as amorphous. The presence of physical crystal structure on the sorption behavior can be considered negligible. Therefore, every functional group can be regarded as an efficient sorption site for water vapor.

The Sorption Property

It is generally accepted that water sorbed in polar polymers is bonded in two forms; (1) strongly bonded water probably forming hydrogen bonds with polar groups (sorption sites) of the polymer and (2) weakly bonded molecules of water-forming weaker interactions. The latter are frequently regarded as being more mobile. It is desirable to compare sorption isotherms expressed in moles of water per pair of repeating units. In this case, we defined repeating units as



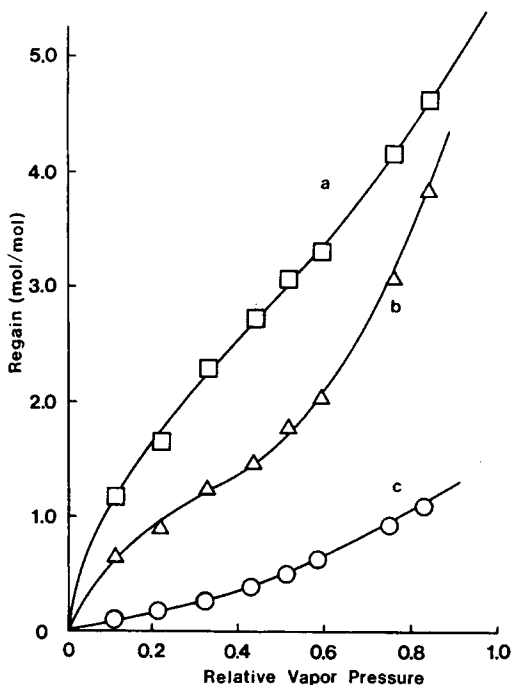
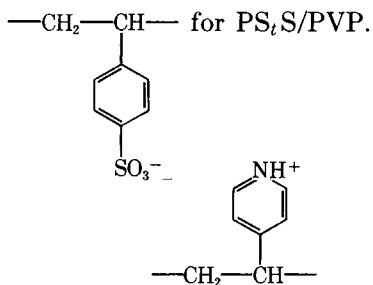


Fig. 4. The sorption isotherms of water vapor at 303 K by: (a) PS_tS/PVP, (b) PS_tSK, and (c) PVP.



Experimental sorption isotherms at 303 K are shown in Figure 4. The isotherms at 293 K were almost the same as these. Over the whole pressure range PS_tSK and PS_tS/PVP had S-shaped isotherms, while PVP had a concave-shaped isotherm. It is expected that PS_tSK will have high sorptivity because it is a strongly ionized polysalt. Its sorption measurement results confirmed this tendency. In contrast PVP did not sorb much water. This is to be expected because of the lower polarity of the unionized pyridine rings. It was found that the PS_tS/PVP sorbed more water than either of the constituent polyions. To discuss this result in detail, we refer to Figure 5 which gives a comparison of uptakes between PS_tS/PVP and the sum of PS_tSK and PVP. Results on the sorption amount of PAA, PVP, and the sum of PAA and PVP, which were reported in the preceding paper, are also added. In this figure, it is to be emphasized that the complex was formed between PS_tS and PVP, not PS_tSK and PVP.

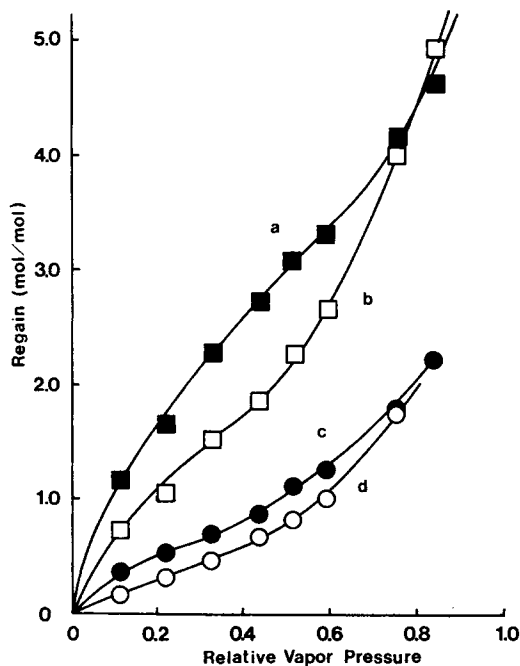


Fig. 5. The sorption isotherms of water vapor at 303 K by: (a) PS_tS/PVP ; (b) $PS_tS + PVP$; (c) PAA/PVP ; (d) $PAA + PVP$.

If the water uptake of PS_tS would have been measured, it is expected that PS_tS would have shown lesser sorption capability than PS_tSK because of the former's lower ionicity. Accordingly, the sum of uptakes of PS_tS and PVP must be less than that of PS_tSK and PVP. It is apparent that the complex, PS_tS/PVP , has higher sorption ability than the uninteracting mixture of PS_tS and PVP over the whole pressure range. What is more important is that the difference between (a) and (b) is much larger than that between (c) and (d). This can be interpreted to mean that Coulombic forces between two polyelectrolytes lead to excellent water sorptivity. The stronger the interactions between a polyanion and a polycation, the more the amount of sorption increases.

Sorption of gases on particular sites is most frequently described by the Brunauer-Emmett-Teller (BET) equation for multilayer sorption. The isotherms of PS_tSK and PS_tS/PVP at 293K and 303 K below 0.45 relative vapor pressure were in excellent agreement with this theory. This indicates that there are specific adsorption sites in these polymers which attract water vapor. The

TABLE III
BET Constants

	PS_tSK	PS_tS/PVP	PAA/PVP
293K	$N_m^a = 0.97$ $C = 12.9$	$N_m^a = 1.94$ $C = 9.72$	$N_m^a = 0.60$ $C = 9.50$
303K	$N_m^a = 0.94$ $C = 12.6$	$N_m^a = 1.74$ $C = 12.4$	$N_m^a = 0.56$ $C = 10.5$

^a mol/mol.

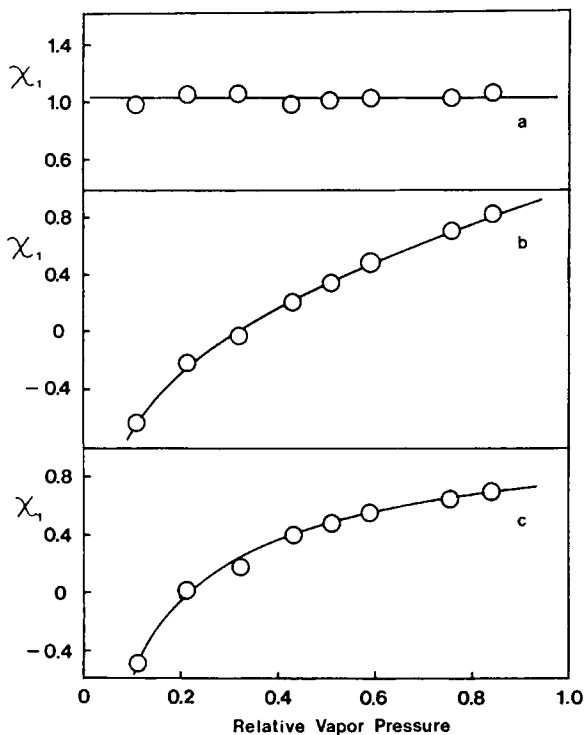


Fig. 6. Flory-Huggins parameters χ_1 at 303 K: (a) PVP; (b) PS_tS/PVP; (c) PS_tSK.

monolayer capacity N_m and the constant C related to the heat of sorption were determined and are given in Table III, which also has the previous data of PAA/PVP. It demonstrates that PS_tS/PVP absorbed a fair amount of water in forming a monolayer; 1.9 water molecules per pair of monomeric units of polyanion and polycation at 293 K and 1.7 water molecules at 303 K. Yano and Wada (1980)⁷ measured water sorption on the (1:1) complex prepared from sodium poly(*p*-styrenesulfonate) and poly(vinylphenethyltriethylammonium bromide). They found that the monolayer sorption of water vapor per pair of monomeric units of polyanion and polycation at 303 K is equivalent to two water molecules. Their result is fairly close to our data. Besides, comparing PS_tS/PVP with PAA/PVP, the constants C of PS_tS/PVP at 293 K and 303 K are larger than those of PAA/PVP. In other words, one pair of monomeric units of PS_tS/PVP can attract more water vapor than that one of PAA/PVP. Since it has already been found that PS_tS/PVP has a greater number of ionic bonds than PAA/PVP by spectroscopic methods, the former has excellent sorptivity not only quantitatively, but also qualitatively.

On the other hand the sorption behavior of PVP cannot be described by means of the BET theory. However, applying the Flory-Huggins polymer solution theory, PVP at 293 K and 303 K, gave approximately constant values of interaction parameter χ_1 over the whole range, indicating a sorption mechanism based on the assumption of random mixing of polymer segments and water molecules. The value of χ_1 parameter at 293 K and 303 K was 0.98 and 1.04, respectively. However, the same calculations for PS_tSK and PS_tS/PVP reveal that their χ_1

parameters are still changing even in the high pressure region. Particularly, in PS_tS/PVP the affinity to water decreases rapidly with increasing relative vapor pressure. Besides a calculation of the clustering function suggested by Zimm and Lundberg^{8,9} in PS_tS/PVP indicated that it had a value under -1 over the whole range. This shows that the polar sites in this complex do not lose the characteristics of attracting water vapor even at higher relative vapor pressures.

It can be concluded from this work that PS_tS/PVP , the polyion complex formed between its polyanion and polycation components has properties and a unique structure which neither polyanion nor polycation alone has. The sorption ability was increased by forming the polyion complex. Comparing the properties of PS_tS/PVP to those of PAA/PVP , it can also be concluded that stronger ionic interactions between polyelectrolytes have a beneficial effect on the water sorption properties of the complexes. As was shown for PVP , the nature of the sorption in a complex is not always the same as that of the original polyelectrolytes. However, regardless of the exact nature of the interactions the ionic sites in a polyion complex play a critical role in the sorption process.

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