〈Research Paper〉

Interaction between Poly(vinylpyrrolidone) and Ionic Dyes in Aqueous Solution System（Ⅰ）

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Abstract: The binding isotherms of ionic dyes with Poly(vinylpyrrolidone) in aqueous solution were determined by the dynamic dialysis technique. The shape of the isotherms of cationic dye, C. I. Basic Red 18 with poly(vinlypyrrolidone) showed a partition type. It suggests that the binding involves a non-cooperative mode. Isotherms of an anion dye, a synthesized dye by coupling of diazotized m-trifluoromethylaniline with 2-naphthol-6-sulfonic acid, were sigmoid type and showed multimode interaction. The results were interpreted by the McGhee von Hippel theory. The thermodynamic parameters for the complex formation of the dyes-polymer were calculated from their temperature dependences of the intrinsic binding constant.

Keywords: *poly(vinylpyrrolidone), ionic dye, multimode interaction, binding isotherm, sigmoid type, thermodynamic parameter*

1. Introduction

Much attentions have been paid to the interaction of small molecules with macromolecules in aqueous solution and polymer matrix systems. It has become clear, however, that this binding is a complicated physicochemical process. The obvious significance of the binding of small molecules (e.g. metal ions, dyes, surfactants, fiber finishing agents, nucleotides and antibiotics etc.) to bio and synthetic polymers has stimulated great interest in such processes, especially in those which display the phenomenon of cooperative binding. Exploration of the nature off the interactions between polymers and small molecules such as dyes, substrates and coenzyme has been a subject of keen interest.

Generally, this important effect refers to a mechanism where occupation of one changes site binding site affects in some way the binding properties of the other site. A simple basic model for cooperative binding to a linear biopolymer with merely one type of equivalent binding site restricts cooperative interaction only to nearest neighbors. This was essentially suggested by Bradely and Wolf [1] with respect to the binding of certain cation to polyphosphate and polynucleotides.

On the basis of combinatorial methods quantitative expression [2-6] were given for the fraction of isolated ligands bound to the polymer in the case of complete binding.

Schwarz [2] has developed a general method to calculate experimentally accessible thermodynamic and kinetic quantities of any type of cooperative transition by using a procedure applied to the most general case of nearest neighbor cooperativity with the use of the linear ising model and matrix method of evaluation, and he has calculated binding parameters of cationic dye with poly(a-L-glutamic acid) by means of spectroscopic measurements.

McGhee and von Hippel [3] represented a relatively simple equation describing the binding of both noninteracting and interacting ligands to homogeneous one dimensional lattice. This equation was derived in terms of ligand site size, the number of consecutive units in the polymer for accommodating a ligand, intrinsic binding constant and ligand-ligand cooperation.

Bresloff and Crothers [4] calculated a nonlinear Scatchard plot by a Monte-Carlo method as a limiting case in his treatment of the much more complex problem of a heterogeneous lattice; in addition he set up the non interacting ligand problem for homogeneous lattice by

a matrix method and provided parameterized equations with which to calculate binding isotherms.

Furthermore Ramanathan and Schnlitz[5] have represented an exact model considering this effect by the use of matrix method.

The interactions of water-soluble bio and synthetic polymers with small molecules are of important in the fields of biochemistry, pharmacology, dyeing chemistry, and polymer science and technology.

Studies on the interaction are ever increasing, and the knowledge in molecular level has reached to allow mankind to design certain molecules that interact with others as intended.

Especially, Ando et al.[7] have found interesting results in some polymer-small molecule systems which reveal a cooperative interaction. For example, binding isotherms of butyl orange with poly(vinylpyrrolidone) (PVP) clearly show cooperative interaction.

The author et al.[8] had already reported the interaction of cationic dye, C. I. Basic Red 18 (Red 18) with carboxymethyl cellulose, an interpreted cooperative binding mechanism by means of McGhee and von Hippel theory. This was a system in which strong electrostatic interaction was expected.

As an extention of a preceeding work, interaction of ionic dyes with PVP in aqueous solution was investigated to elucidate the binding mechanism of small molecular to polymer in homogeneous system.
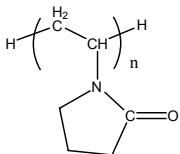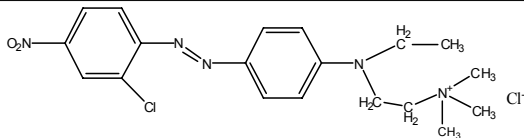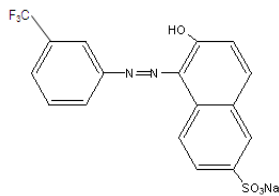
2. Experimental

2.1 Materials

PVP samples were kindly supplied by Daiichi Kogyo Seiyaku. co. The samples were purified by repeated precipitation from aqueous solution by ethanol.

Two azo dyes were obtained in two ways: (1) A cationic dye, Red 18 kindly supplied by Hodogaya Chemical Co.. It was purified by re-crystallization from dilute hydrochloric acid solution at 80℃. (2) An anion dye, FTS was synthesized by coupling of diazotized m-trifluoromethylaniline with Schaeffer's acid (2-naphthol-6-sulfonic acid) in an alkaline condition. The dye was purified by repeated recrystallization from aqueous ethanol solution and finally by passing through a silica gel column. The dye have been used a model, such as a absorbent for organic sensor material, and a penetrant for permselective membrane and was also chosen as a model dye of bio and material system for its high stability in boiling water in the pH range from 2-8.

The characteristics of PVP and ionic dyes are shown in Table 1.

The water was purified by distillation after passing an ion exchange column. The dialysis membrane was cellulose visking tube (36/32, Union Carbide Co.) and was used after soaking repeatedly in boiling water before using dynamic dialysis.

Table 1. Samples used in this work

PVP	Mw 36,000 Base$_{mol}$ 111.4	
Red 18 (Cationic dye)	Mw 430 λ_{max} 488nm ε_{mol} 2.92×10⁷(l/mol · cm)	
FTS (Anionic dye)	Mw 418.32 λ_{max} 476nm ε_{mol} 1.81×10⁴(l/mol · cm)	

2.2 Methods for determing binding isotherm

The binding isotherm was determined by the dynamic dialysis technique. Apparatus used for dynamic dialysis experiments are shown in Figure 1. The details of the procedure were given elsewhere[7,8].

The content of dialysised dye was determined from absorbance measured by a Shimadzu spectrophotometer with 1cm cell.
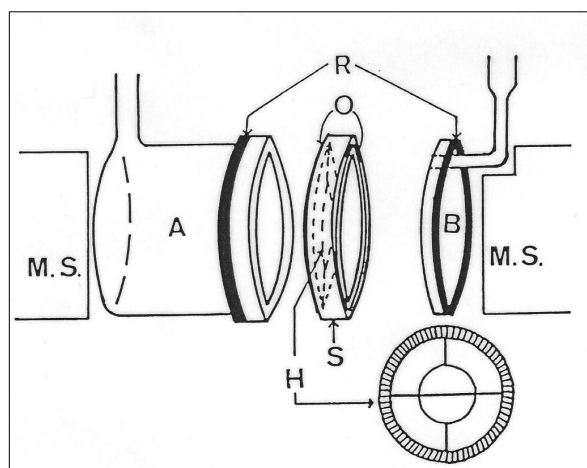

Figure 1. Apparatus for dynamic dialysis.

A: compartment
B: glass disk, cell(B)
O: o-ring
B+S: compartment
H: membrane supporter (stainless steel)
S: membrane holding spacer (stainless steel)
R: flat rubber ring for screw assembler
M.S: magnetic stirrer

3. Results and Discussion

3.1 Dynamic dialysis of ionic dyes in aqueous solution system

Dialysis constant of dye $[K_f]$, the free dye content $[D_f]$, and the bound dye content $[D_b]$, can be calculated by the equation (1), (2), and (3). If the content of permeated dye $[M_t(㏖)]$ through the dialysis membrane against time $[t(min)]$, follows the condition of $D_t \gg M_t$ against total dye content $[D_t(㏖)$ in cell (B)] and sink condition is maintained, the instantaneous rate of dialysis $[-dD_t/dt]$ from with in the cell(B) is related to the remaining free dye content, $[D_f(㏖)]$, by the equation(1)

$$-dD_t/dt = K_f D_f \quad \text{......................} (1)$$

Where $-dD_t/dt$: the dialysis rate of dye from the cell(B) in ㏖/min

K_f: the dialysis rate constant, which characterizes the diffusion process and which incorporates the area and thickness of the membrane.

D_f: the free dye content in ㏖ assuming that the intrinsic dialytic rate constant $[K_f]$ is independent of polymer content.

The intrinsic dialytic rate constant K_f, can be calculated from the experiment involving the condition $D_t = D_f$, in the absence of polymer.

Dialysis data for the variation of D_t against time, t are fitted to an equation of the from

$$D_t = D_0 + at + bt^2 + ct^3 \quad \text{....................} (2)$$

Where, D_0 is the initial preservative content in cell(B)

The bound dye content, D_b can be calculated by the equation(3)

$$D_t = D_b + D_f \quad \text{..........................} (3)$$

Where, D_b is the bound dye content(㏖).

Figure 2 and Figure 3 comprise data for the dynamic dialysis of ionic dyes plotted as the total content of penetrant in cell(B), D_t against dialysis time, t.

In the absence of PVP polymer the plots are curvature over a wide range of concentration.

The curved nature of the plots indicates that the interaction cannot be described as a simple partition phenomenon for the reasons given above.

The dialytic rate constant, K_f of ionic dye, Red 18 and FTS was determined from the plot, $-dD_t/dt$ versus D_t in Figure 2 in the absence of polymer. The values of that were $8.24 \times 10^{-3}(min^{-1})$ for Red 18 and $4.50 \times 10^{-3}(min^{-1})$ for FTS, respectively.

The content of bound small molecule (㏖), $[D_b]$ to polymer, PVP can be calculated using the polynomial regression technique of experimental plots.
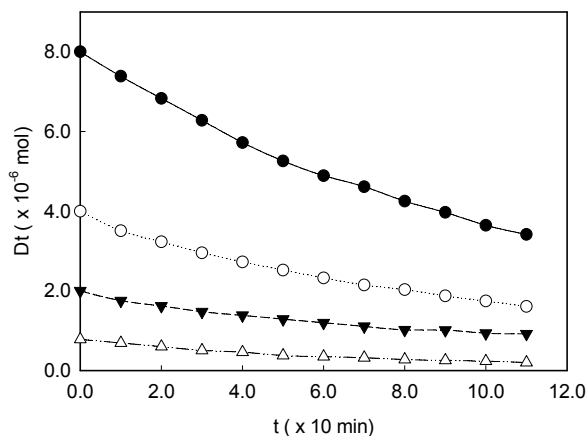
Figure 2. Dynamic dialysis of Red 18 in an acetate buffer solution (pH 4.2, I=0.02) at 30℃. Conc. of Red 18 = 5.5($\bullet$), 4.0($\circ$), 2.0($\blacktriangledown$) and 1.0($\triangle$) ($\times 10^{-4}$ ㏖/ℓ).

Figure 4. Dynamic dialysis of Red 18 in an acetate buffer solution. (pH 4.2, I=0.02) in the absense ($\circ$,$\triangledown$) and presence ($\bullet$,$\blacktriangledown$) of PVP at 30℃. Conc. of Red 18 = 4.0 ($\circ$,$\bullet$), 2.0($\triangledown$,$\blacktriangledown$) ($\times 10^{-4}$ ㏖/ℓ). Conc. of PVP = 1.04 ($\times 10^{-1}$ base ㏖/ℓ).
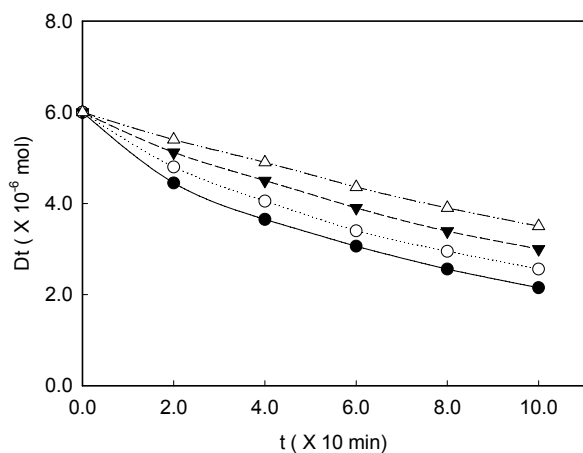

Figure 3. Dynamic dialysis of FTS in a phosphate buffer solution. (pH 6.67, I=0.0108) at 20 ~ 50℃. Conc. of FTS = 4.75 ($\times 10^{-4}$ ㏖/ℓ). 20℃($\triangle$), 30℃($\blacktriangledown$), 40℃($\circ$) and 50℃($\bullet$).
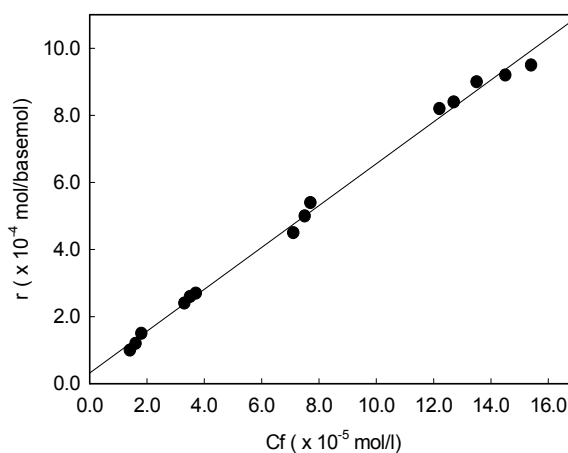
Figure 5. Isotherms for binding of Red 18 with PVP in an acetate buffer solution(pH 4.2) at 30℃.

3.2 Interaction of a cationic dye, Red 18 with PVP

Figure 4 shows the results of the dynamic dialysis experiments in which Red 18 alone and in the presence of PVP was allowed to escape though the dialysis membrane.

The amount of bound dye to polymer in cell(B) at any dye concentration can be calculated from equation (3). Isotherms of Red 18 were shown in Figure 5. Scatchard plot of the isotherms are given in Figure 6.

The shape of the isotherms was partition type and showed that the binding involves a non-cooperative mode.
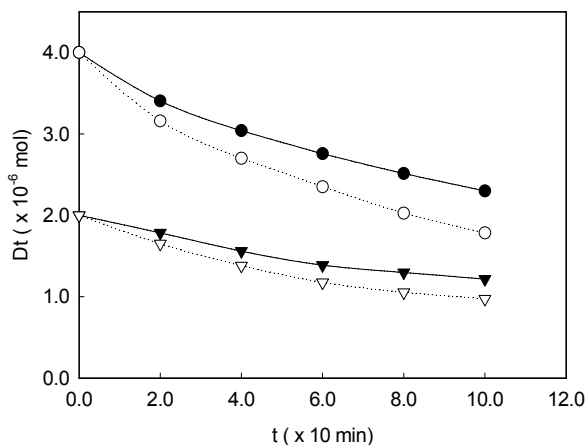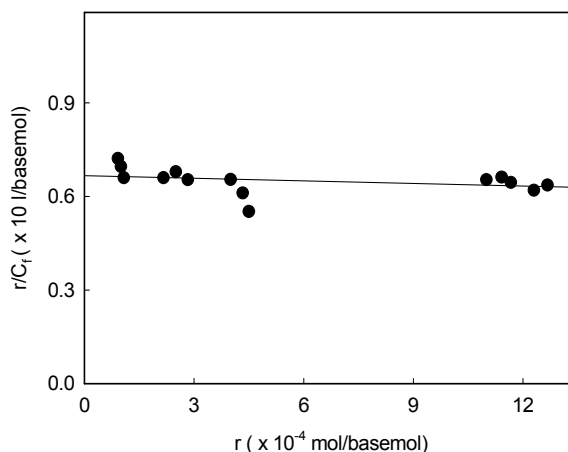

Figure 6. Scatchard plots for binding Red 18 with PVP in an acetate buffer solution. (pH 4.2, I=0.02) at 30℃.

To interpret the results, McGhee and Von Hippel's equation[3] was applied. McGhee and Von Hippel presented a relatively simple equation describing the binding of both non-interacting and interacting ligands to a homogeneous one-dimensional lattice. This equation was derived in terms of ligand site size, and the number of consecutive units in the polymer for accommodating a ligand, intrinsic binding constant and ligand-ligand cooperativity.

The binding equation for cooperative ligands was given in a form analogous to the Scatchard formulation:

$$\frac{r}{C_f} = R(1-nr)\left(\frac{(2\omega-1)(1-nr)+r-R}{2(\omega-1)(1-nr)}\right)^{n-1}\left(\frac{1-(n+1)r+R}{2(1-nr)}\right)^2 \quad \cdots (4)$$

$$R = \left[\left\{1-(n+1)\right\}^2 + 4\omega r(1-nr)\right]^{1/2} \quad \cdots\cdots\cdots (5)$$

for non-interaction ligands

$$\frac{r}{C_f} = K(1-nr)\left(\frac{1-nr}{1-(n-1)r}\right)^{n-1} \quad \cdots\cdots\cdots\cdots\cdots (6)$$

where C_f is the concentration of free ligand in mole/liter, r is the binding density in units of moles of bound ligand per mol of total lattice residue, K is an intrinsic binding constant in liter/mole, n is the number of consecutive lattice residues covered by a ligand molecule, and ω is the cooperativity parameter.

It was considerable that dye-dye interaction was not allowed between nearest neighbors, bound without intervening free lattice polymers. This restriction results in three distinguishable types of dye binding sites.

From the intercepts on the ordinate and abscissa of Scatchard plot of the isotherm, intrinsic binding constant, K=0.632($\times 10^2$l/basemol) for Red 18 was estimated. In this experiments PVP-Red 18 system had a weak interaction, comparing with other system. It was considerable that it has a hydrophobic interaction between the groups of PVP and that of Red 18. In the interaction system of PVP and Red 18, cooperative interaction was not presented as that of CMC-Red 18 system in aqueous solution.

Many studies on the interaction between water-soluble polymers such as PVP and small molecules have

been carried out. For exmples, a partition isotherm for PVP-ethyl orange system[9], a sigmoid or Langmuir isotherm for cationic polyelectrolyte- MO and its homologes[10], and a langmuir isotherm for PVP-triphopan system[11] have been reported.

Molyneux and Ahmed[12] analysed a langmuir isotherm for PVP- $NaO_4S(CH_2)_{12}SO_4Na$ system by Klotz plot and obtained K=16.

3.3 Interaction of an anion dye, FTS with PVP

The results of the dynamic dialysis were shown in Figure 7. Isotherms of FTS were shown in Figure 8. Scatchard plot of the isotherms are given in Figure 9. The shape of the isotherms showed sigmoid type which
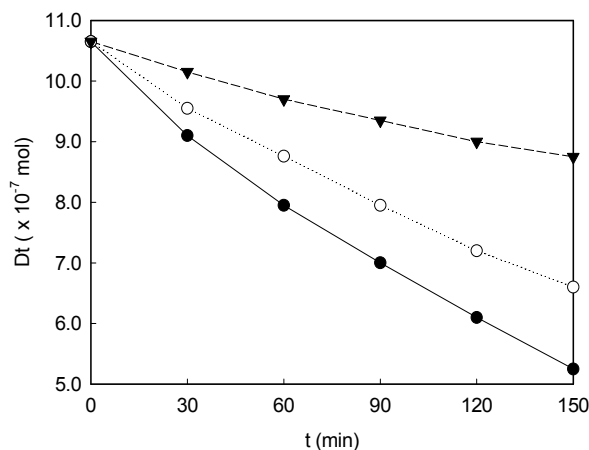

Figure 7. Dynamic dialysis of FTS in a phosphate buffer (pH 6.67, I= 0.0108) at 25℃. Conc. of FTS=5.0(●)($\times 10^{-5}$ mol/ℓ), Conc. of PVP=5.0 (○), 10.0 (▼)($\times 10^{-3}$ base mol/ℓ).
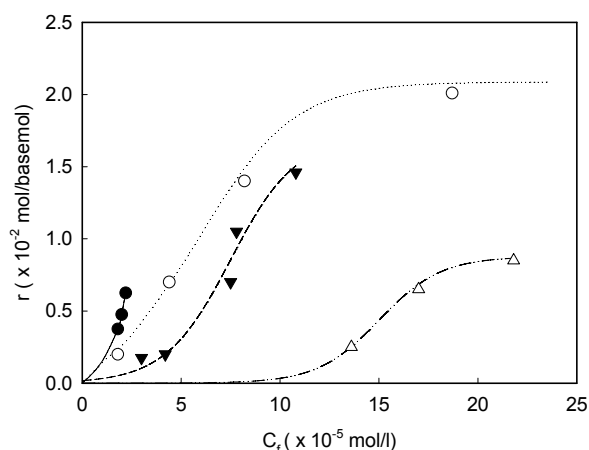

Figure 8. Isotherm for binding of FTS with PVP in a phosphate buffer solution. (pH 6.67, I=0.0108). 20℃(●), 30℃(○), 40℃(▼) and 50℃(△).
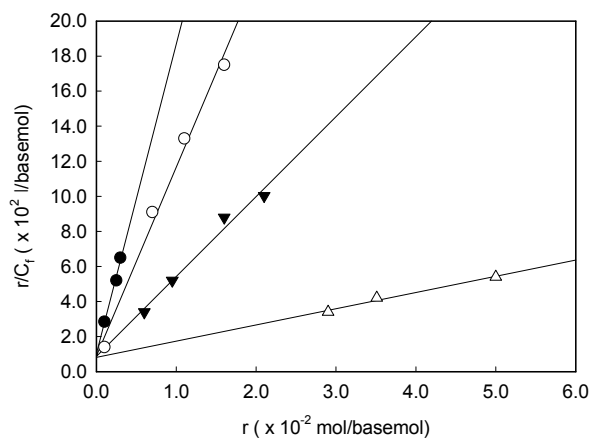
Figure 9. Scatchard plot for binding of FTS with PVP in a phosphate buffer solution. (pH 6.67, I=0.0108). 20℃(●), 30℃(○), 40℃(▼) and 50℃(△).

composed of bimodal and multi-layer. The binding isotherm and Scatchard plot comprised a multimode interaction. The intrinsic binding constants of the dye, FTS to PVP from their results were obtained and were listed in Table 2.

As shown in figures this system showed a more higher intrinsic binding constant than previous PVP-Red 18 system. These results strongly suggest that the interaction between two groups of PVP and FTS is due to mainly hydrophobic and hydrogen interaction in PVP-FTS binding system.

The thermodynamic parameters for the binding formation of the PVP-FTS were calculated from their temperature dependences of the intrinsic binding constant equation(7).

From the Van't Hoff plots of In(K) versus the reciprocal absolute temperature, thermodynamic parameters were obtained at 20 ~ 50℃ and also listed in Table 2.

$$\ln(K) = \frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad \text{(7)}$$

where, R is the gas constant, T is the absolute temperature, respectively.

As is evident from the results, the binding process was accompanied by two factors, an exothermic enthalpy change and an entropy gain.

The main component of the free energy change of the polymer-dye binding is largely the negative enthalpy of the binding, predominating over a positive entropy contribution: that is the binding is mainly enthalpy controlled. Negative value of ΔG in the dye-polymer interaction slightly increased with increasing temperature at this temperature range. This is the characteristic of the interaction, composed of hydrogen and hydrophobic interaction.

All positive ΔS is likely to the disruption of highly ordered water. It seems to be clear that the binding process is a composite one, involving as it does two species, the polymer and dyes, both of which exist in aqueous solution in some hydrated form.

Takagishi and Kuroki et al.[9,10] have investigated the interaction between PVP and polycation and MO and its homologes, and between PAA, PMA, PAAm and PMAAm and disperse dyes by an equilibrium dialysis method. They analysed the isotherms obtained in each system by use of Klotz equation, and produced the apparent binding parameters.

From their results of the system of PVP-MO homologes the enthalpy change, $\Delta H < 0$, and entropy change, $\Delta S > 0$ were obtained from the binding constant and its temperature dependence, and these changes increase with increasing alkyl length of MO homologes focusing on the hydrophobic interactions. In the binding of disperse dyes[13] with PMA, the favorable binding process involves two main contributions; an entropy gain and an exothermic interaction.

Table 2. Thermodynamic parameters for binding of FTS by PVP in a phosphate buffer solution(pH 6.67, I=0.0108)

Temp (℃)	Binding constant K(ℓ/base ㏖)	-△G (KJ/㏖)	-△H (KJ/㏖)	△S (J/deg)
20	92.0	11.07		
30	83.6	11.16	8.181	9.852
40	74.5	11.26		
50	70.0	11.29		

They estimated that the electrostatic bond[14] between dissociation groups of polymer and dyes and between polymer and polar groups of dyes except for the hydrophobic interaction take part in each of these binding systems.

4. Conclusions

The interaction of ionic dyes, Red 18 and FTS with PVP in aqueous solution were investigated to elucidate binding mechanism. The binding isotherm was determined by the dynamic dialysis technique. The thermodynamic parameters for the complex formation of FTS-PVP can be calculated from their temperature dependences of the intrinsic binding constant.

The results obtained from this work were as follows:

1. The shape of the isotherm for binding of Red 18 with PVP was partition type. The binding isotherms showed a non-cooperative mode composed of weak hydrophobic binding.

2. The isotherms of FTS with PVP showed sigmoid type. This showed multimode interaction composed of hydrophobic and hydrogen binding.

3. The main component of the free energy change of FTS-PVP binding was largely the negative enthalpy of the binding, prodominating over a positive entropy contribution.

Acknowledgement

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