A Comparison of Adsorption Isotherms of Crosslinked Poly(N-vinylpyrrolidone)/Basic Brown 1 Binding System

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In this study, the binding of a basic dye such as basic brown 1 [BB 1] onto a crosslinked poly(N-vinylpyrrolidone) [CPVP] was investigated. Adsorption of the azo dye onto the CPVP was studied by the batch adsorption technique at 25°C. In adsorption experiments a Langmuir type (L) adsorption was found with respect to the Giles classification system. Binding parameters such as initial binding constant (K_i), equilibrium constant (K), monolayer coverage (n), site-size (u), and maximum fractional occupancy $(\hat{\theta})$, and thermodynamic parameters such as heat of adsorption (ΔH), free energy of adsorption (ΔG) and entropy of adsorption (ΔS) for the CPVP/BB 1 system were calculated by using Klotz, Scatchard, and Langmuir linearization methods.

Key Words: crosslinked poly(N-vinylpyrrolidone), basic brown 1, binding, adsorption isotherm

Introduction

Poly(N-vinyl pyrrolidone) (PVP) is a polymeric compound that is widely used in the production of textiles and dyes, cosmetics and toiletries, pharmaceuticals, etc. It has the property of forming complexes with a variety of substances. Some researchers have discussed the interaction of PVP with certain inorganic and organic compounds. The interactions between PVP and disazo dyes have been studied only to a limited extent and sufficient information is not available on the effects of polymer chains or the composition of the dyes in the interactions. Crosslinked poly(N-vinylpyrrolidone) (CPVP) behaves similarly to PVP. CPVP is also used as an adsorbent for the chromatographic separation of aromatic acids and aldehydes, and phenols[1-5].

Synthetic dyes represent a relatively large group of organic chemicals which are encountered all spheres of our daily life. These chemicals have undesirable effects not only on the environment, but also on man. The potential toxicity of some azo dyes has been known for many decades. Some azo dyes have been banned because they have been found to be carcinogenic. Disazo dyes based on benzidine are also known to be carcinogenic[6].

Removal of the dye pollutants is necessary because of their toxicity and color. In water treatment, the most widely used method is adsorption of the surface of active materials. Researches have generally
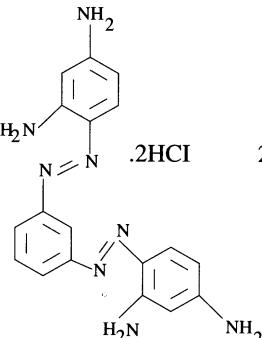
used gas or vapour adsorption isotherms in solute-solid adsorption systems. However technique has resulted in insufficient determinations about the interactions between the solute and the solid. Solvent effects are very important in solute-solid adsorption studies. Giles adsorption classification system[7,8] must be used in solute-solid adsorption. Giles adsorption isoterm has been linearized by Langmiur, Klotz and Scatchard methods[9] for calculating the binding parameters such as initial binding constant (K_i), equilibrium constant (K), monolayer coverage (n).

In our previous studies, the adsorptions of some anionic azo dyes by CPVP (10), and some cationic dyes and some heavy metal ions by acrylamide/maleic acid and acrylamide/itaconic acid hydrogels have been evaluated[11-15]. In this study, a comparison of adsorption isotherm of the CPVP/basic brown 1 system has been investigated. Basic brown 1 (BB 1) has been selected for its uses in the dyeing of wool and leather, and for its toxic and carcinogenic properties.

Experimental

CPVP was obtained from BASF (Germany). BB 1 was purchased from Sigma (USA). They were applied as received. The chemical formula and other properties of BB 1 is given in Table 1. The chemical structure of PVP is shown in Scheme 1.

Table 1. Some properties of BB 1

Name	Chemical Formula	C.I.Nr.	Molar mass	λ_{max} /nm
Basic Brown 1 (BB 1) [Bismarck Brown Y, Leather Brown, Manchester Brown, Vesuvin, Excelsior Brown, Phenylene Brown]	.2HCI	21 000	461.4	468
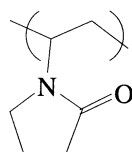
Scheme 1.

The synthetic aqueous solutions of BB 1 were prepared in the concentration range 10-100 mg L^{-1}. CPVP weighing 0.1 g was transferred into 50 mL of aqueous solution of the aqueous dye solution and allowed to equilibrate for two days at 25°C in a water bath. Supernatants of these solutions were separated by decantation and centrifugation from the CPVP. Spectrophotometric measurements of the solutions were carried out using a Shimadzu A160 model UV-VIS double beam spectrophotometer at ambient temperature. The absorbance of these solutions was recorded at a wavelength of 468 nm. Distilled water was chosen as the control. The equilibrium concentrations of BB 1 were determined by means of a precablibrated scale.

To examine the influence of temperature on adsorption, experiments were carriedout synthetic aqueous solution of BB-1 at constant concentration (100 mg L^{-1}), and at different temperatures in the range 25-50° C.

FTIR spectra of CPVP and CPVP-dye binding system were determined with a Mattson 1000 model FTIR spectrophotometer.

Results and Discussion

Binding of BB1 onto CPVP

The interactions between the dye and the CPVP can be considered as a result of hydrophobic effects, dipole/induced dipole force, dipole/dipole force and hydrogen bonds[9,16].

a. Hydrophobic effects. These are specifically aqueous-solution interactions, which in the present case will involve the aromatic ring on the dye molecule and the methine and methylene groups of the CPVP chain.

b. Dipole/induced-dipole(van der Walls-Debye) forces. These will occur between the highly dipolar amide group of the CPVP monomer unit and the highly polarisable aromatic groups of the dye molecules.

c. Dipole/dipole (van der Walls-Keesom) forces. These will involve the amid group of the monomer unit and the aromatic ring dipol of the dye molecule.

d. Hydrogen bonds. Bondings of this type are expected to occur between amine groups of the dye molecule and the oxygen atom of the pendant groups in the PVP chains.

The schematic representation of the non-covalent interactions in the binding of BB1 by CPVP are shown in Figure 1.

polymer chain units	bound dye molecule	types of interaction	interaction polymer	groups on dye
H-C-P	NH$_2$	hydrogen bonding	carbonyl group in P	amine group
H-C-H P-C-H H-C-H	H$_2$N .2HCl	dipole/induction dipole forces and/or dipole/dipole forces	amide group in P	benzene rings
P-C-H H-C-H H-C-P	N			
H-C-H	H$_2$N NH$_2$	hydrogen bonding	carbonyl group in P	amine group

Figure 1. Schematic representation of non-covalent interactions in the binding of BB 1 by CPVP were P represents the pyrrolidone ring

To understand the binding of CPVP and BB 1 the FTIR spectra of the CPVP and CPVP/BB 1 system were evaluated and are presented in Figure 2 and 3, respectively. In the FTIR spectra of the CPVP and CPVP-dye system, the much broader absorption peaks in the regions of 3100 and 3500 cm^{-1} are N-H peaks, and the peaks at 1650-1700 cm^{-1} show -NH-CO- amide groups of the CPVP. It is thought that the weak peaks at 1000 and 1200 cm^{-1} C-N bands and the weak peaks at 2850 and 1400 cm^{-1} show -CH$_2$- groups on CPVP[17]. If the differences between the spectra of CPVP and the CPVP-dye system is investigated, a new band corresponding to new binding between CPVP and CPVP-dye system can be seen at 2390 cm^{-1}.

The cause this band is the HCl groups in the dye. These results support the hypothesis there interactions between CPVP and BB 1.
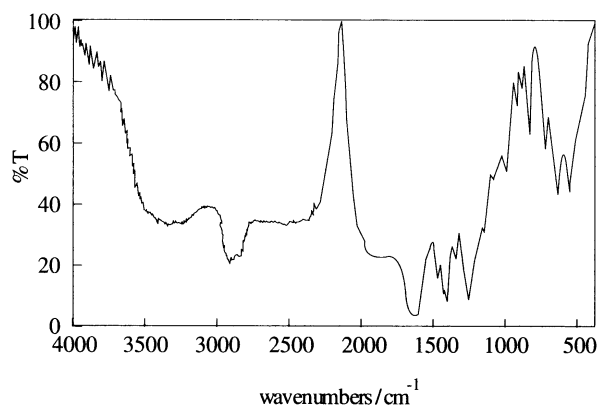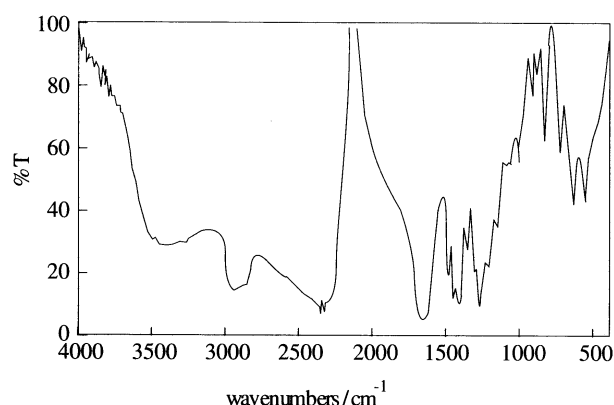

Figure 2. FTIR spectrum of CPVP

Figure 3. FTIR spectrum of CPVP/BB 1 binding system

Binding isotherms of BB 1 onto CPVP

In a batch adsorption system at equilibrium, total solute concentration C_I, (mol L^{-1}) is[16].

$$C_I = C_B + C \tag{1}$$

where, C_B is the equilibrium concentration of the solute on the adsorbent in mol per liter (bound solute concentration) and C is the equilibrium concentration of the solute in the solution in mol L^{-1} (free solute concentration). The value of the bound concentration may be obtained from equation 1. For a fixed free solute concentration, C_B, is proportional to the polymer concentration in the binding system; the amount of binding can therefore be conveniently expressed as the binding ratio, r, defined by

$$r = C_B/P. \tag{2}$$

Thus with C_B in mol per liter and P in base mol (moles of monomer units) in liters, r then represents the average numbre of molecules of solute bound to each monomer unit at that free solute concentration. (Molar mass of monomeric units of CPVP was taken as 111.14 g mol^{-1}).

Plots of the binding ratio (r) against the free concentrations of the dyes in the solutions $(C, \mu mol$ dye $L^{-1})$ are shown in Figure 4.

Figure 4 shows that adsorption of the dye within the CPVP corresponds to type L (*Langmuir type)* adsorption istotherms in the Giles classification system for adsorption of a solute from its solution[7,8]

In this type adsorption isotherm, the initial curvature shows that as more sites in the substrate are filled it becomes increasingly difficult for a bombarding solute molecule to find a vacant site avilable. This implies either that the adsorbed solute molecule is not vertically oriented or that there is no strong competition from the solvent[7,8].

The types of system which give this curve do in fact fulfill these conditions. Therefore they must have one of the following observance characteristics: (i) the adsorbed molecules most likely are adsorbed flat or (ii) if adsorbed end-on, they suffer little solvent competition; examples of (ii) are (a) systems with highly polar solute and adsorbent, and a non-polar solvent, and (b) a system in which monofunctional ionic substance with very strong intermolecular atraction, are adsorbed from water by ion-ion attraction. It is

possible that in this case (system b) the adsorbed ions may have conglomerated into very large clusters for adsorption take place[7].
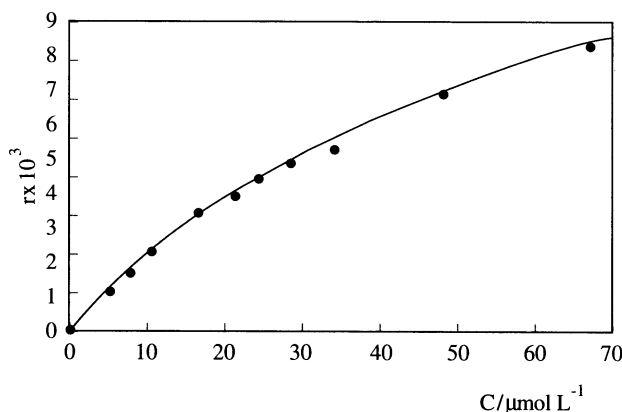

Figure 4. Binding isotherm of CPVP/BB 1 binding system

The binding data was interpreted on the basis of the uniform site-binding model (u.s.b), which in statistical-thermodynamic terms corresponds to the formation of an ideal localised one-dimensional monolayer of solute on the polymer chains[16]. This leads to the hyperbolic *(Langmuir)* from of the binding isotherm, which applies to many polymer/solute binding system:

$$r = \frac{nKC}{1 + KC} \tag{3}$$

where K is the binding constant, i.e. the equilibrium constant for the attachment of a molecule of dye D onto a site S by a specific combination of non-covalent forces:

$$D + S = D \sim S$$
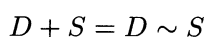
and n is the site density i.e. the limiting value of r for "monolayer" coverage, which is therefore of density of the sites S along the polymer chain. The reciprocal of n is the site-size, u, which may be taken to represent either average number of monomer units occupied by the bound solute molecule, or more generally the average spacing of solute molecules when the chain is saturated. The initial binding constant, K_i is the inital slope of the binding isotherm, and therefore the avarge binding strength of a solute molecule by a single monomer unit on an occupied chain. In the u.s.b model it is equal to the product Kn.

There is a wide variety of methods available for testing whether or not the data from a particular binding system fits the hyperbolic of Equation 3 and for obtaining the 'best' estimates of the parameters K and n.

Whatever the method for testing and fitting chosen, the values K and n obtained should always be checked by plotting the predicted binding isotherm and showing that the experimental data does fit this within the limits of uncertainty. If the fit is not satisfactory, the parameters K and n may be adjusted either until the optimum fit is obtained, or until it is evident that the data connot in fact be fitted satisfactorily to this model.

To get the best values for the binding parameters from the experimental data, the linearization methods of equation 3 have been developed by some researches such as Klotz, Scatchard and Langmuir[9].

a. Klotz Method

If the isotherm (Equation 3) is multiplied out and then divided throughout by $C K n r$, this gives[9]:

$$\frac{1}{r} = \frac{1}{n} + \frac{1}{nK}\frac{1}{C} \tag{4}$$

Thus if this isotherm holds than a plot of $1/r$ vs. $1/C$ will be straight line of slope $1/Kn$, ordinate intercept $1/n$. This is very simple method of plotting, with the scatter in the r and C values reflected in the scatter in the ordinate and abscissa values, respectively. Its limitations are that the intercepts may be small and hence difficult to read off.

The Klotz plot of CPVP/BB 1 is shown in Figure 5., and the binding parameters for the CPVP/BB 1 system were calculated from the intercepts and slopes of the Klotz plots.
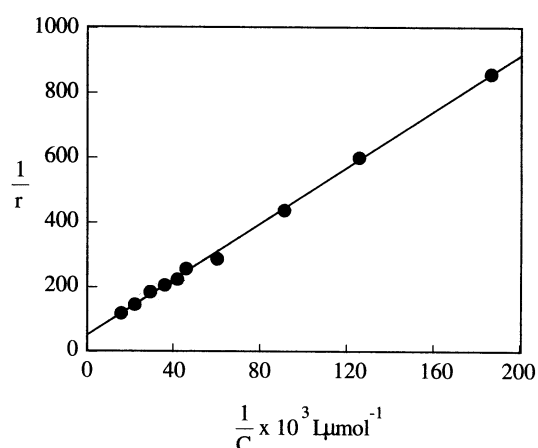

Figure 5. Klotz plot of CPVP/BB 1 system

b. Scatchard Method

Multiplying Equation 4 by Knr and rearranging gives[9]:

$$\frac{r}{C} = Kn - Kr \tag{5}$$

so that in this case a plot of r/C vs. should be a straight line of slope $-K$, ordinate intercept Kn.

The Scatchard plot of CPVP/BB 1 is shown in Figure 6 and the binding parameters for the CPVP/BB 1 system were calculated from the intercepts and slopes of the Scatchard plots.

c. Langmuir Method

Multipying the Klotz form of Equation 3 by C gives[9]:

$$\frac{C}{r} = \frac{1}{nK} + \frac{C}{n} \tag{6}$$

so that here a plot of C/r vs. C should be straight line slope $1/n$, ordinate intercept $1/nK$.

The Langmuir plot of CPVP/BB 1 is shown in Figure 7, and the binding parameters for the CPVP/BB 1 system were calculated from the intercepts and slopes of the Langmuir plots.
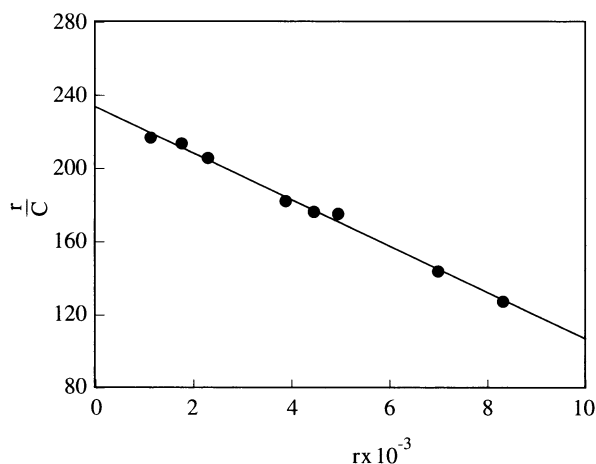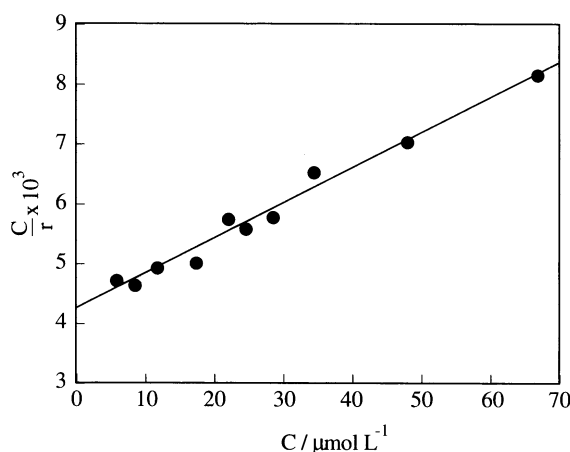
Figure 6. Scatchard plot of CPVP/BB 1 system

Figure 7. Langmiur plot of CPVP/BB 1 system

The derived values of the binding parameters K and n are listed in Table 2 for the dye with CPVP. The final column contains the derived values of the $\hat{\theta}$, the maximum fractional occupancy attained experimentally, calculated from the definition of fractional occupancy θ:

$$\theta = r/n \tag{7}$$

using the value of r at the maximum experimental free dye concentration, and with the site-density obtained for the u.s.b. model[16].

The values of the binding parameters calculated from the binding isotherm methods are also given in Table 2.

Table 2. Binding Parameters for CPVP/BB 1 System

Method	$Ki/$L mol^{-1}	$K/$L mol^{-1}	$nx10^2$	u	$\hat{\theta}$
Klotz	230.6	12.065	1.911	52.316	0.435
Scatchard	233.0	12.866	1.811	55.213	0.459
Langmiur	235.4	13.350	1.750	57.133	0.475

To determine the themodynamic parameters of the CPVP/BB 1 binding system, adsorption experiments were repeated in the synthetic aqueous solution of BB1 at a constant concentration $(100$ mg L$^{-1})$, and at different temperatures in the range 25-50°C. The adsorption heat (ΔH) of this system was determined following the equation[18].

$$lnC = -\frac{\Delta H}{R}\frac{1}{T} + constant \tag{8}$$

where, C is the free dye concentrations at the absolute temperature, T. R is universal gas constant. $1/T$ versus lnC was plotted, and is presented in Figure 8.

Adsorption free energy and adsorption entropy of the CPVP/BB1 binding system was calculated following the equations;

$$\Delta G = -RT\,ln\,K \tag{9}$$

$$\Delta G = \Delta H - T\Delta S \tag{10}$$

$\Delta H, \Delta G$ and ΔS are heat of adsorption, free energy of adsorption, and entropy of adsorption, respectively.

As already pointed out, physical adsorption is an *exothermic* process. This can be seen in the well-known thermodynamic equation, $\Delta G = \Delta H - T\Delta S$ where changes $\Delta G, \Delta H$ and $T\Delta S$ are defined as the free energy, the heat and the entropy, which occur during a physico chemical process such as adsorption. If adsorption is to take place spontaneously, then the free energy must diminish during the process so that ΔG must have a negative value. ΔH must be negative, i. e., the process is exothermic[18].

ΔH is calculated from the slope of the line in Figure 8. The other thermodynamic parameters such as ΔG and ΔS of the CPVP/BB 1 binding system were calculated at $25°\,$C and are tabulated in Table 3.

Table 3. Thermodynamic Parameters for CPVP/BB 1 System

Method	ΔG/J mol^{-1}	ΔH/ kJ mol^{-1}	ΔS/J mol^{-1}K^{-1}
Klotz	-12.064	-7.402	15.636
Scatchard	-10.180	-7.402	9.317
Langmiur	-10.227	-7.402	9.475

As shown in Table 3, the sorption process is associated with negative enthalpy and positive entropy. Hence both energetic and hydrophobic forces are involved in the sorption process. Hydrogen bonding from the aromatic- substituted amino groups is drobable for the energetic forces. The intermolecular attraction between the substrate molecules after sorption and the hydrophobic interaction, if any, between BB 1 and CPVP cause changes in the water layer around the binding sites and may be a contributive process towards the observed positive entropy [3].

If Table 2 and 3 are examined together, it can be seen that there are differences between the three linearization methods for calculating the binding and thermodynamic parameters for the CPVP/BB 1 binding system. These linearization methods (Klotz, Scatchard and Langmuir methods) can be used in the hyperbolic binding systems for solute-polymer binding processes.

Conclusion

The interactions between BB 1 and CPVP arise from hydophobic forces, dipole/induced dipole forces, dipole/dipol forces and hydrogen bonding forces. Adsorption of BB 1 onto CPVP is found to be a Langmuir type istoherm in the Giles adsorption classification system. The present work has provided quantitative information on the binding characteristic of BB 1 with CPVP.

To determine the binding isotherms, Klotz, Scatchard, and Langmuir linearization methods were used. Binding and thermodynamic parameters were evaluated. Average value of K_i was 233.0 L mol^{-1}. This value shows that the interaction is very strong between BB 1 and CPVP. Average equilibrium constant was 12.7×10^3 L mol^{-1}. This value of K indicates that BB 1 has been sorbed very efficiently by the CPVP. The monolayer capacity of CPVP is 1.824×10^{-2}. The value of $\hat{\theta}$ equals 0.456. The value shows that CPVP is completely unsaturated by BB 1 with these experimental conditions. It is said that half the monolayer coverage of CPVP is saturated by BB 1.

If the thermodynamic parameters are examined, it can be seen that the binding of BB 1 onto CPVP is spontaneously ($\Delta G < 0$) and exothermic ($\Delta H < 0$). ΔS is positive, because both energetic and hydrophobic forces are involved in the sorption process.

The calculated parameters determined by using Klotz, Scatchard and Langmuir linearization methods are nearly equal to each other. When the FTIR spectra are examined, it can be seen that the interaction between the dye and the CPVP is physical.

Finally it can be seen that crosslinked poly(N-vinylpryrrolidone) may be used as an adsorbent for the removal of some agents and dye molecules, because the disazo dyes such as BB 1, the most toxic one are found among cationic dyes.
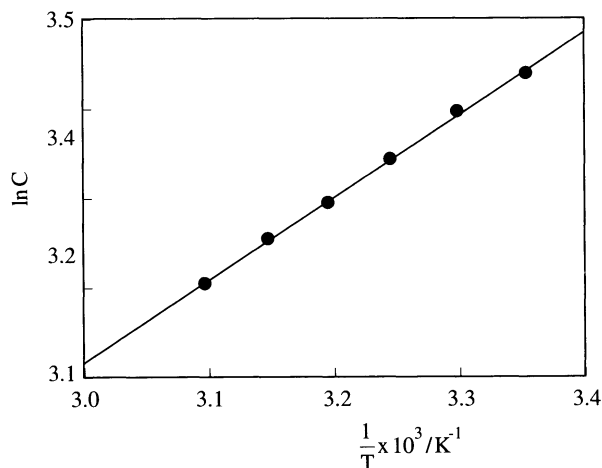

Figure 8. ln C-1/T plot of CPVP/BB 1 system

Acknowledgment

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