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Binding of some dyes onto crosslinked poly (*N*-vinylpyrrolidone)

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Summary

Bindings of some anionic dyes containing sulfonyl group(s), namely, Acid Blue 74 (AB-74), Acid Orange 7 (AO-7), Acid Green 1 (AG-1), Direct Blue 53 (DB-53), and Calconcarboxylic acid (CCA) onto crosslinked poly(N-vinylpyrrolidone) (CPVP) have been investigated using adsorption isotherm parameter. The dyes were linked positively charged on the tertiary nitrogen atom on the pyrrolidone ring in polymer chain resulting keto-enol tautomerism from sulfonyl group on the benzene ring in the dyes molecules. In the experiments of adsorption, L (*Langmuir*) type adsorption in the Giles classification system was found. Monolayer coverages (n) of polymer/dye system were founds by "B point" methods. Adsorption studies indicated that monolayer coverages of CPVP by the anionic dyes containing sulfonyl group(s) were increased with following order; CCA > AG-1 >> DB-53 > AO-7 > AB-74.

Key words: crosslinked poly(N-vinylpyrrolidone), anionic dye, binding, adsorption.

Introduction

Poly(N-vinylpyrrolidone) (PVP) is a polymeric compound that is widely used for textiles, cosmetics and toiletries, pharmaceuticals, etc. It has the property of forming complexes with a variety of substances. The interaction of PVP have been discussed with certain inorganic and organic compounds. The interactions between PVP and anionic dyes have been studied only to a limited extend, and sufficient information is not available on the effect of polymer chain or the composition of the anionic dyes containing sulfonyl group in the interaction. Crosslinked poly(N-vinyl pyrrolidone) (CPVP) has similar behaviour as PVP. CPVP is also the adsorbent for the chromatographic separation of aromatic acids, aldehydes, and phenols (1-5).

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Synthetic dyes represent a relatively large group of organic chemicals which are met in practically all spheres of our daily life. It is therefore possible that such chemicals have undesirable effects not only on the environment, but also on man. In order to minimize the possible damages to man and environment arising from the production and applications of the dyes, several researches were made. The potential toxicity of some dyes has been known for many decades (6).

Dyeing and finishing wastes in the textile industry have high color and organic content. Dyestuff production units and dyeing units have always had a pressing for techniques that allow economical pretreatment for dye removal from wastewater has made it an ideal alternative to other expensive treatment options. Colored waters are also objectionable on aesthetic grounds for drinking and other municipal and agricultural purposes. Some groups have used various adsorbents for the removal of acidic and basic dyes from aqueous solutions (7-11).

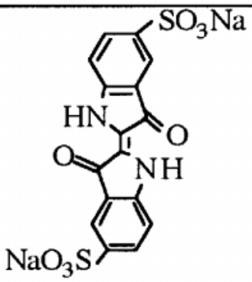
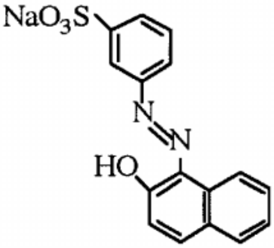
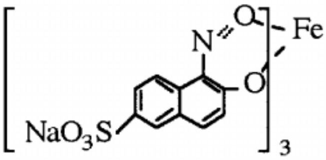
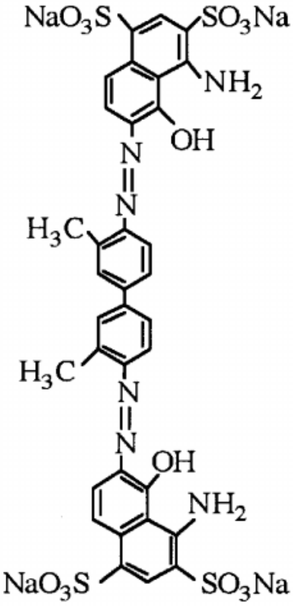
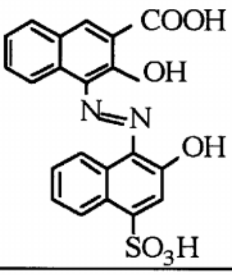
In our previous studies, adsorptions of some cationic dyes by radiation induced acrylamide - based hydrogels with diprotic moieties (11-18) or by silica gels (19) and removal of some anionic azo dyes (20, 21), textile dyes (22) and herbicides (23) by crosslinked poly(N-vinyl pyrrolidone). In this study, the adsorptions of some anionic dyes containing sulfonyl group such as Acid Blue 74 (Acid Blue W, Food Blue 1, Indigo Carmine), Acid Orange 7 (Orange II), Acid Green 1 (Naphtol Green), Direct Blue 53 (Evans Blue) and Calconcarboxylic acid onto CPVP from their aqueous solutions have been investigated. Acid Blue 74, Acid Orange 7 and Acid Green 1 are acidic dyes while Direct Blue 53 is an anionic direct dye and, Calconcarboxylic acid is an indicator. The anionic dyes containing sulfonyl group(s) such as Acid Blue 74, Acid Orange 7, Acid Green 1, Direct Blue 53 and Calconcarboxylic acid which are the resemble the textile dyes are biological stains.

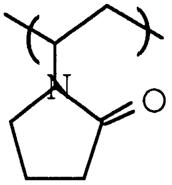
Experimental

The anionic dyes containing sulfonyl group(s) such as Acid Blue 74 (AB-74), Acid Orange 7 (AO-7), Acid Green 1 (AG-1), Direct Blue 53 (DB-53) and Calconcarboxylic acid (CCA) were purchased from Sigma (St. Louis, USA). CPVP was supplied by BASF (Ludwigshafen, Germany). The structure of anionic dyes containing sulfonyl group(s) and crosslinked poly(N-vinyl pyrrolidone) in the experiments are shown in Table 1 and Scheme 1, respectively.

The synthetic aqueous solutions of the anionic dyes containing sulfonyl group(s) were prepared in the desired concentration in mg L^{-1}. CPVP weighing 0.1 g were transferred into 50 mL of aqueous solutions 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 adsorbent. Spectrophotometric measurements of the solutions were carried out using a Shimadzu A 160 model UV-VIS double beam spectrophotometer, at ambient temperature. The absorbance of these dyes solutions was recorded at the desired wavelength (λ). Distilled water was chosen as a reference. The equilibrium concentrations of the anionic dyes containing sulfonyl group(s) were determined by means of precalibrated scales.

Table 1. Some properties of the anionic dyes

Dye	Chemical formula	Molar Mass	Color Index	λ / nm
Acid Blue 74		466.3	73 015	608
Acid Orange 7		350.3	15 510	483
Acid Green 1		878.5	10 020	714
Direct Blue 53		960.8	23 860	611
Calconcarboxylic acid		438.4	—	560



Scheme 1. The structure of CPVP.

Results and Discussion

Binding of anionic dyes onto CPVP

To observe adsorption of anionic dyes containing sulfonyl group(s), CPVP was placed in synthetic aqueous solutions of the anionic dyes such as AO-7, AB-74, AG-1, DB-53 and CCA allowed to equilibrate for two days. At the end of this time, CPVP in the solutions of the anionic dyes showed the dark colorations of the colours of the original solutions.

The interactions between the anionic dyes and CPVP can be: hydrophobic effects, dipole/induced dipole forces, hydrogen bonds, and ion/ion interactions (24, 25):

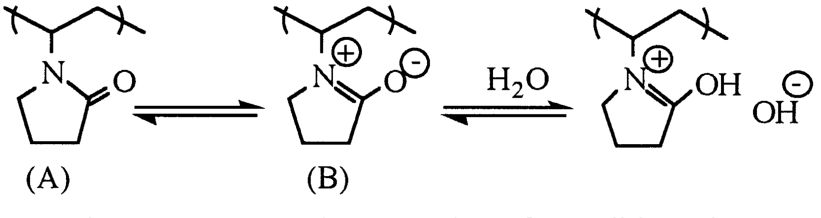
a. Hydrophobic effects. These are specifically aqueous-solution interactions, which in the present case will involve the aromatic ring on the anionic dyes molecule and the methine and methylene groups of on CPVP chain.

b. Dipole/induced-dipole-forces. These will occur between the highly dipolar amide group on CPVP monomer unit and highly polarisable aromatic groups on the dyes molecules.

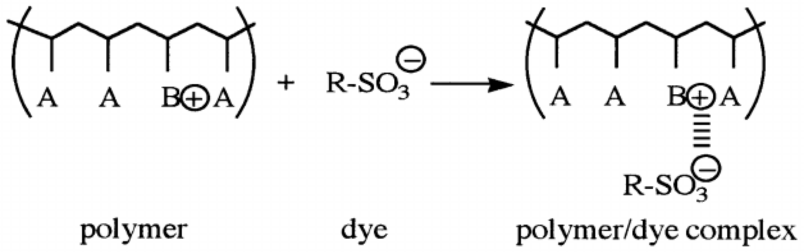
c. Hydrogen bonds. Bondings of this type will be expected to occur between amine groups on the dye molecule and the oxygen atom on the monomer units.

d. Ion/ion interactions: These may occur between negative charge of sulfonyl group on the anionic dyes and positive charge on the tertiary nitrogen atom on the pyrrolidone ring in polymer chain resulting keto-enol tautomerism (26). A schematic representation of keto-enol tautomerism of pyrrolidone ring and possible ion/ion interaction between negative charge of sulfonyl group on the anionic dye and positive charge of polymer are shown in Scheme 2 and 3, respectively.

The oxygen atom on the pyrrolidone ring is exposed to the aqueous environment and strongly hydrated with water molecules, whereas the nitrogen atom is shielded from water by the neighbouring hydrocarbon groupings. It is likely that the pyrrolidone group bears a partially charge in aqueous solution. The positive charge in pyrrolidone ring plays significant role in the binding of small organic anions.



Scheme-2. Keto-enol tautomerism of pyrrolidone ring.



Scheme-3. Ion/ion interaction between negative charge of sulfonyl group on the anionic dye and positive charge of polymer.

Binding isotherms of anionic dyes onto CPVP

To observe uptake of the anionic dyes containing sulfonyl group(s), CPVP was placed in aqueous solutions of the anionic dyes and allowed to equilibrate for two days. At the end of this time, CPVP in the aqueous solutions of the anionic dyes, showed the dark colorations of the original solutions.

In a batch adsorption system at equilibrium, total solute concentration (C_I, mol L^{-1}) is (24)

$$C_I = C_B + C \qquad (1)$$

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

$$r = CB / P. \qquad (2)$$

Thus with C_B in mol L^{-1} and P in base mol (moles of monomer units) L^{-1}, r then represents the average number of molecules of solute bound each monomer unit at that free solute concentration.

Plots of the binding ratio (r) against the free concentrations of the anionic dyes containing sulfonyl group(s) in the solutions (C, μmol dye L^{-1}) are shown in Fig. 1.

Fig. 1 shows that adsorption of the anionic dyes containing sulfonyl group(s) within CPVP correspond to type L (*Langmuir type*) adsorption isotherms in the Giles classification system for adsorption of a solute from its solution (27, 28). In this type of 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 available. This implies either that the adsorbed solute molecule is not vertically oriented or that there is no strong competition from solvent (27, 28).

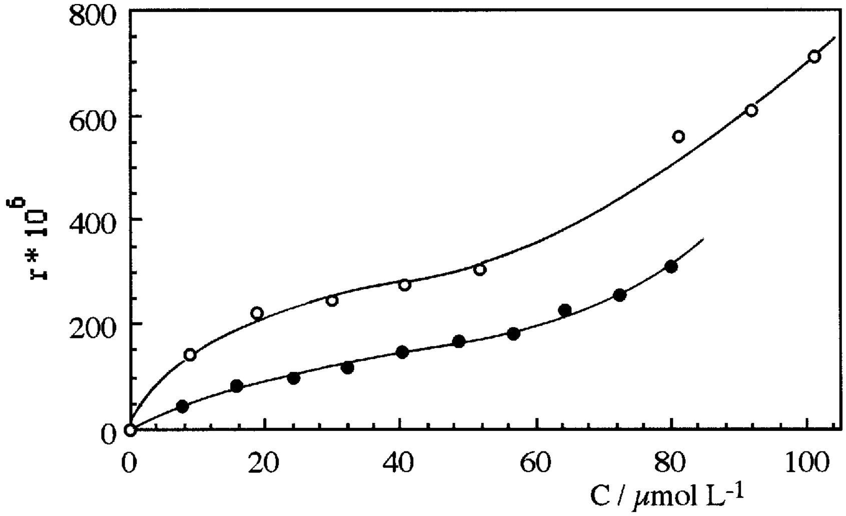


Fig. 1a. Adsorption isotherms of the dye/CPVP binding systems. ●; AB-74, ○; AO-7.

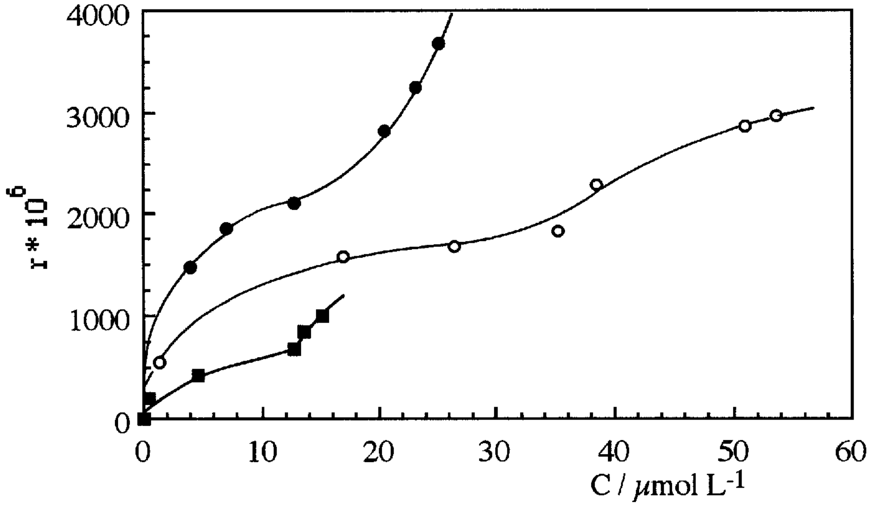


Fig. 1b. Adsorption isotherms of the dye/CPVP binding systems. ●; CCA, ○; AG-1, ■; DB-53.

The types of system which give this curve do in fact fulfil these conditions. Thus they have one of the characteristic: (i) the adsorbed molecules most likely to be 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) system in which monofunctional ionic substances with very strong intermolecular attraction, are adsorbed from water by ion-ion attraction (27).

Langmuir type isotherms obtained experimentally display a rather long straight portion yields following an inflection point. The point at which this linear portion begins was termed "Point B" and was taken to indicate the completion of the monolayer, so that the adsorption at Point B, say n,

Table 2. The values of monolayer coverage and the site size of the anionic dye/CPVP systems.

Dye	n μmol dye/mol CPVP	u	number of sulfonyl group on the dye
AB-74	35.1	28 490	2
AO-7	167.7	5 963	1
DB-53	303.1	3 299	4
AG-1	1 345.1	743	3
CCA	1 556.6	642	1

should be equal to the monolayer coverage (27). 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 saturated. The monolayer coverages of CPVP for the anionic dyes in the aqueous solutions were found by method of Point B from Fig. 1. The values of monolayer coverage and the site-size are listed Table 2.

If Table 2 is examined, it is shown that the values of monolayer coverage of the CPVP by the anionic dyes are increased following order:

CCA > AG-1 >> DB-53 > AO-7 > AB-74.

The reason of this order may be molecular structure of the dyes (Table 1). The values of the site-size of the CPVP/dye systems are increased following order;

AB-74 > AO-7 > DB-53 >> AG-1 > CCA.

As expected, this order is the reciprocal of n values and, the site size of AB-74 is 28 490 mol monomeric unit of the gel per one mol dye, while it is dropped to 642 mol monomeric unit of the gel per one mol of dye for CCA.

Table 2 shows that there are not any relation between the number of the sulfonyl group(s) on the anionic dyes and their values monolayer coverages. Thus, it is said that, one of the sulfonyl group(s) on the anionic dyes is interacted with the positively charged on the tertiary nitrogen atom on the pyrrolidone ring in polymer chain resulting keto-enol tautomerism, and the adsorbed dye molecules were most likely to be adsorbed flat.

CONCLUSION

The present work given an information on the binding mechanism of some anionic dyes containing sulfonyl group(s) with crosslinked poly(N-vinyl pyrrolidone). For understanding the binding isotherms, B point method has been used. Monolayer coverage and site-size were found. It is seen that crosslinked poly(N-vinyl pyrrolidone) may be used as an adsorbent for removal of some agent such as anionic dyes containing sulfonyl group(s).

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