Bisazo Dyes Sorption to Cross-Linked Poly (N-Vinyl-2-Pyrrolidone) Gels

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Summary: Herein, poly (N-vinyl-2-pyrrolidone) hydrogels have been prepared by bulk polymerisation using N-N-methylene-bis-acrylamide as crosslinker. The variation in swelling of these gels and some other properties like diffusion and partition coefficients, number of water (N_1) and dye molecules (N_3) with concentration of azo dyes viz. Evan blue EB and Chicago blue CB in the swelling medium, were examined. In aqueous dye solution, unlike salt solutions, the swelling ratio (r) remained lower than pure water, the lowering of swelling being most marked at higher values of dye concentration. The partition coefficient expressing concentration of dye in hydrogel relative to that in swelling medium decreased sharply with dye concentration at low values, but levelled out to values of 1.025 – 0.99 and 0.98 – 0.92 at higher values of CB and EB concentration, respectively. The difference in behaviour between the two dyes was not dramatic although difference was very much present in their functional groups.

Introduction

The sorption of anionic, azo dyes and small organic molecules to Poly (N-Vinyl-2-Pyrrolidone (PVP) has been the subject of numerous studies [1-7] because it binds appropriately, displays binding behaviour similar to blood serum albumin (BSA) and provides the possibility of assessing binding forces other than electrostatic forces due to uncharged nature in the pH range 2-11. Charged dyes addition to neutral polymer results in hydrodynamic behaviour typical of poly-electrolyte [8], to limit the maximum amount of dye that can be bound and thus the same degree of binding for the dyes with similar size and charge. But different researchers obtained different results. For example, Shikama [9] studied the binding of methyl orange with PVP and BSA and found that the binding affinity of PVP is one third that of BSA. PVP, like BSA, showed a decreasing affinity for small molecules of different charge in the following order; anions > neutral molecules > cations. Scholtan [10] found that methyl orange could bind to PVP to the extent of 1mol/100 base mol, Breitenbach [11], the same dye with the capacity of 1mol / 200 base mol while Frank [12], on average, orange II of 1 dye/ 7 base mol in water, showing different dyes of similar charge have different specificity for binding.

Some results on the aqueous salt solution behaviour of new type of vinyl polymers, which include zwitterions in the side chain, suggested a new category of hydrophilic polymers [13-15]. These polymers are mainly characterized by their antipolyelectrolyte behaviour conferred by the zwitterionic group. Thus, the presence of salt ions produces the breaking of interchain and intragroup association and gives rise to chain expansion. However, other com-pounds exhibit a contrasting behaviour with organic azo dyes being one of them.

In the present paper, attention is focused on the behaviour of crosslinked PVP gels, swollen in various concentrations of aqueous Evan blue and Chicago blue solutions. The interactions of linear PVP with Evan blue in aqueous solution and the number of mole of dye bound per mole of the polymer have been noticed previously [16]. The structure of the dye and PVP are given below with some properties. It is expected that this study might yield valuable information about the swelling behaviour of PVP gels, binding specificity, PVP-dye ratio, micro-environment of bound dye and forces responsible for binding.

Results and Discussion

Polymerisation

After bulk polymerisation of the monomer, equilibrium swelling and drying, the % conversion was found to be 69.13. In this laboratory [17], the

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PVP gels were prepared from monomers with % conversion value being above 80.16 using γ-radiation source. The gels that we obtained from chemical methods were stable, soft and transparent.

Figs. 4 and 5 show the variation of swelling ratio (r) with time in water and aqueous dye solution of various concentrations for EB and CB, respectively. The swelling ratio in pure solvent and dilute dye solutions were greater than the concentrated dye solutions. There was a sharp increase from 0 to 38 in swelling for the xerogel in pure solvent and low concentration dye (dye < 0.025 mol dm^{-3}); then r became almost constant after 108 hours while for xerogel in the [dye] $< 0.025 > 0.2$ mol $dm,^{-3}$ there was a gradual increase and then became constant after 200 hours for EB. Almost the same trend was observed for CB, however the equilibrium swelling for EB was more than CB.

The calculation of the numbers of water molecules (N_1) and dye molecules (N_3) per monomer unit afforded valuable information with regards to the swelling behaviour at the molecular level. Figs. 6 and 7 show the change of N_1 and N_3 with concentration of dyes for the hydrogels. With regards to these, the main swelling features are: 1) N_1 has high value at low [dye] < 0.025mol dm^{-3} which starts to decrease till it reached [dye] = 0.1 mol dm^{-3}. After this when [dye] > 0.1 mol dm^{-3} , it becomes almost constant. The maxi-mum N_1 value attained 263 in pure solvent, 240 at [EB] = 0.0125 mol dm^{-3} and at [EB] = 0.1 mol dm^{-3} this value became 130. Similarly the maximum value for N_1 attained 222 at [CB] = 0.0262 mol dm^{-3} and came down to 143 at 0.101 mol dm^{-3}. 2): N_3 value shows opposite trend; at [EB] < 0.025 mol dm^{-3}, N_3 is constant and have lower value of 0.125 then it starts increasing up to [dye] < 0.1 mol dm^{-3} and to obtaining a constant value. N_3 value of 0.075 for [CB] = 0.0262 mol dm^{-3}, a curvature at [CB] = 0.1 mol dm^3 and again a smooth increase was observed. It becomes apparent from these findings that the swelling properties of PVP in dye solution must be divided into three regions as a function of dye concentration. In the first region ($0 <$ [dye] < 0.025 mol dm^{-3}), the dye uptake was constant. So the entrance of dye and water was equally favoured. In the second region ($0.025 <$ [dye] < 0.1 mol dm^{-3}), the presence of water promoted the dye molecules uptake (N_3 increases in this range) and reached at 0.248 at 0.1-mol dm^{-3}. In other words at this region, the entrance of dye in the hydrogel was favoured with respect to the entrance of water. In the third region ($0.1 <$ [dye] < 0.2) the dye uptake was levelled out to values 0.263 – 0.267 for EB. In this high dye concentration range, the network did not undergo any further increase in swelling. The N_1 and N_3 values for this concentration range clearly showed that the constant swelling was to be ascribed to the replacement of water molecules by the dye molecules. However the entrance of CB dye to PVP gel was still favoured because N_3 increased even beyond 0.1 mol dm^{-3}.

In our laboratory, we studied the PHEMA and PSPV with KSCN [18]. KBr and KCl and an opposite trend was observed i.e. N_1 value increased with salt concentration up to a certain limit and then became constant, while for N_3 we got a linear plot with positive slope.

The interactions / adsorption between the azo dyes and crosslinked PVP can be divided into four types:

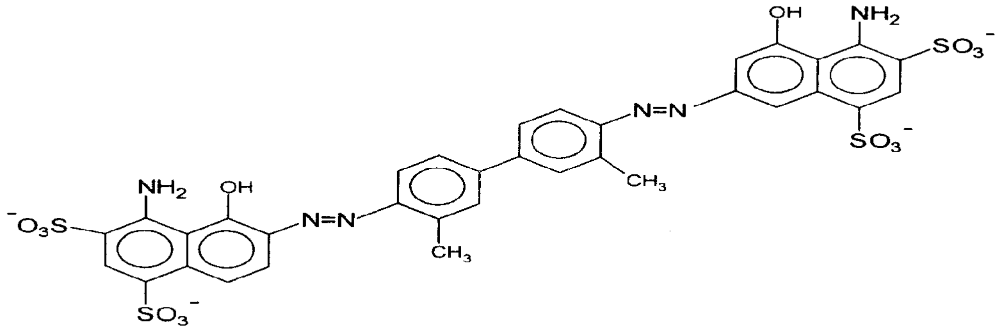

Fig. 1: Evan Blue (EB). Molar mass = 960.82, C.I.No. 23860, (λ_{max} = 606nm)

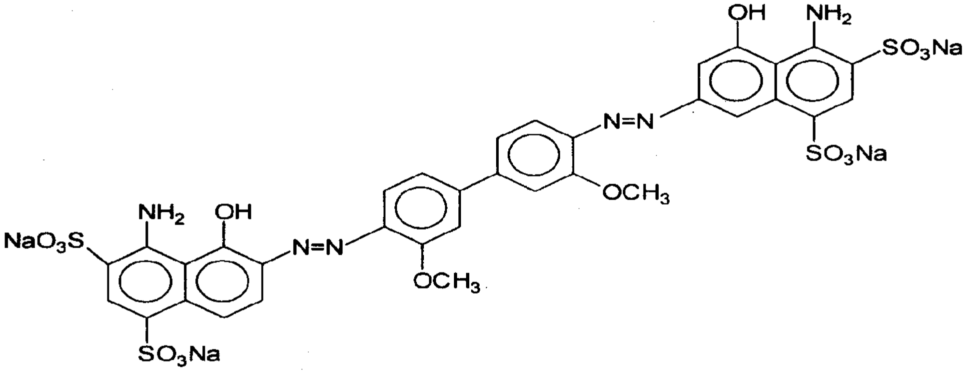

Fig. 2: Chicago Blue (CB) Molar mass = 992.82, C.I.No. = 24410, (λ_{max} = 618 nm)

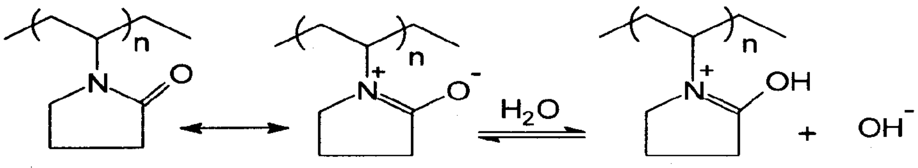

Fig. 3: Possible tautomeric forms of repeating unit in PVP Molar mass = 111.14, Amphiphilic in nature and simple model of protein.

1) Hydrophobic-specifically aqueous solution interactions, which in the present case involved the aromatic ring on the azo dyes molecule (Figs. 1 and 2) and the methane and methylene groups of PVP.

2) Dipole / induced dipole interactions occur between the highly dipolar amide group on PVP monomer unit and highly polarisable aromatic groups on the azo dyes molecules.

3) Hydrogen bonding occurs between amine groups on the azo dye molecule and the oxygen atom on the monomer unit.

4) Ion / Ion interactions occur between negative charge of sulphonyl group on the azo dyes and positive charge on the tertiary nitrogen atom on the pyrrolidone ring in polymer chain resulting in keto-enol tautomerism (Fig. 3) [19, 20].

The partition coefficient of a substance between two different phases, provides information related to the affinity of the substance for each phase and thus is a thermodynamic measure of the relative goodness of each media to the substance. Fig. 8 shows that Cp exhibits dye concentration dependence for the PVP gels. This dependence is influenced by the presence of the zwitterions group of PVP. Cp decreases for $0 < [EB] < 0.15$ mol dm^{-3} and levelled out to values of 0.92 -0.98 thereafter. For $0 < [CB] < 0.075$ mol dm^{-3}, Cp values decrease and then levelling started beyond this point and thus the concentration of dye becomes immaterial.

An alternate definition of the partition coefficient can be Cp* i.e. when water alone within the hydrogel serves as solvent for the dye equation (6). It is clear that Cp should be smaller than Cp* due to the presence of the mass g_2 within the definition of Cp. The corresponding variation of Cp* with dye concentration is also presented for comparison, although the general trend of Cp and Cp* is similar, however Cp* > Cp at each dye concentration for EB. For [CB] > 0.075-mol dm^{-3}, Cp and Cp* become similar. The definitions of Cp and Cp* show that the smaller the polymer content of the swollen gel is, the more Cp tends to Cp* which is the situation for more highly swellable PVP.

The swelling behaviour of the PVP hydrogels, Figs. 4 and 5 in conjunction with Fig. 8, can be explained by Dusek *et. al.*, [21] conclusion that

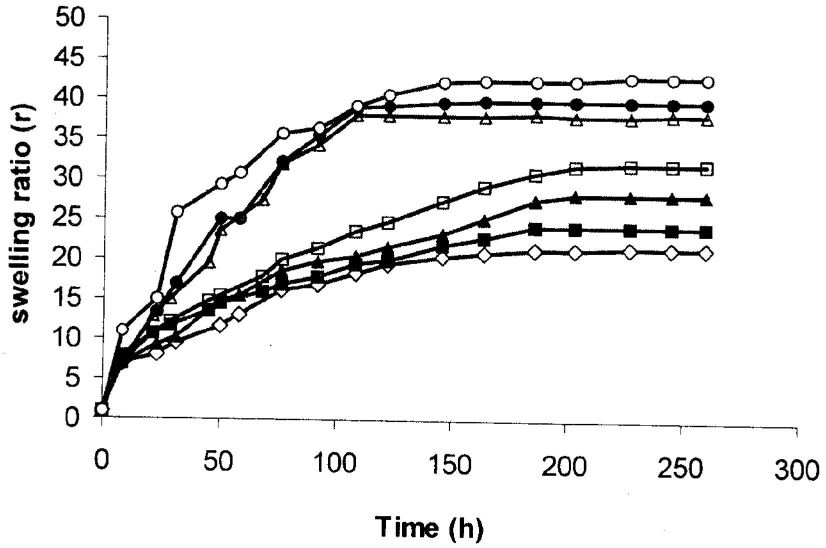

Fig. 4: Swelling ratio of PVP gel with time (h) in aqueous Evan blue solutions. [EB] = mol dm^{-3} o = water, • =0.0125M, Δ = 0.025M, □ = 0.05M, ▲ = 0.075M, ■ = 0.1M, ◊ = 0.2M

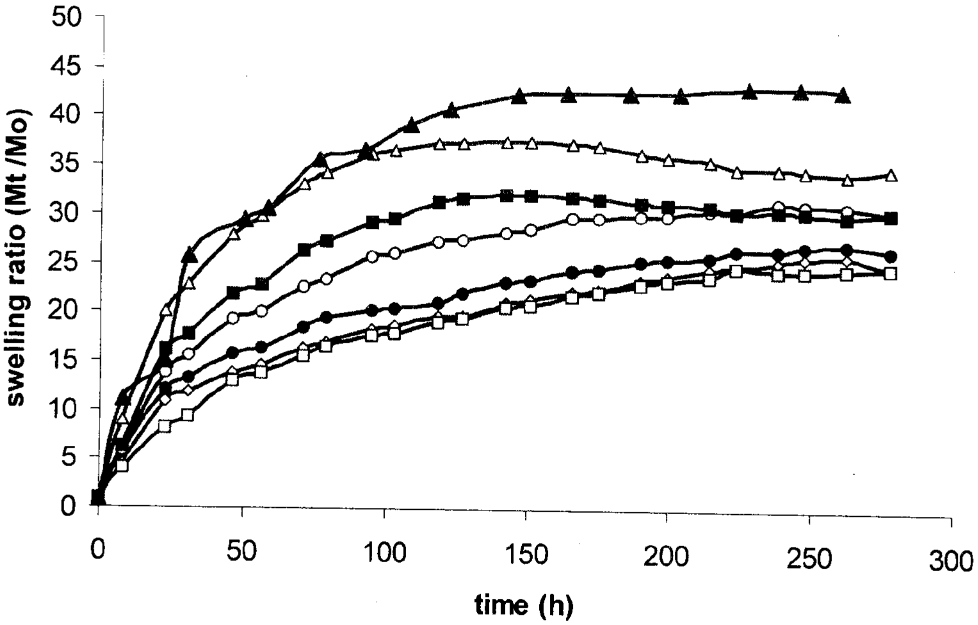

Fig. 5: Swelling ratio of PVP gel with time (h) in aqueous Chicago blue solutions. [CB] = mol dm^{-3} ▲ = water, Δ = 0.025M, ■ = 0.05M, o = 0.075M, • = 0.1M, ◊ = 0.15M, □ = 0.2M

anions play a decisive role in the swelling of hydrogels. At low dye concentration (0 < [dye] < 0.05 mol dm^{-3}), dye anions are adsorbed on to the polymer molecules, charging them negatively. Repulsion between like – like charges produces chain expansion and an increase in water uptake. Further effects of the partial negative charge of the polymer are: i) reduction of hydrophobic character of polymer chain; ii) reduction of the association of hydrophobic groups; and iii) electrostatic attraction of cations and their hydration layers. The overall effect is therefore, an increase in water content (Fig. 4) and a decrease of

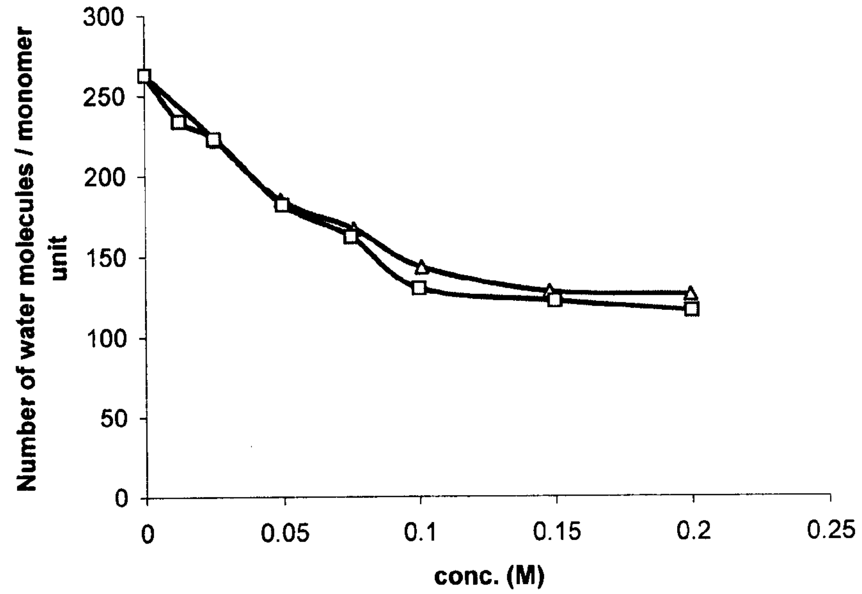

Fig. 6: Variation of number of water molecules per monomer unit of PVP with concentration of azo dye. (□) = Evan blue, (∇) = Chicago blue

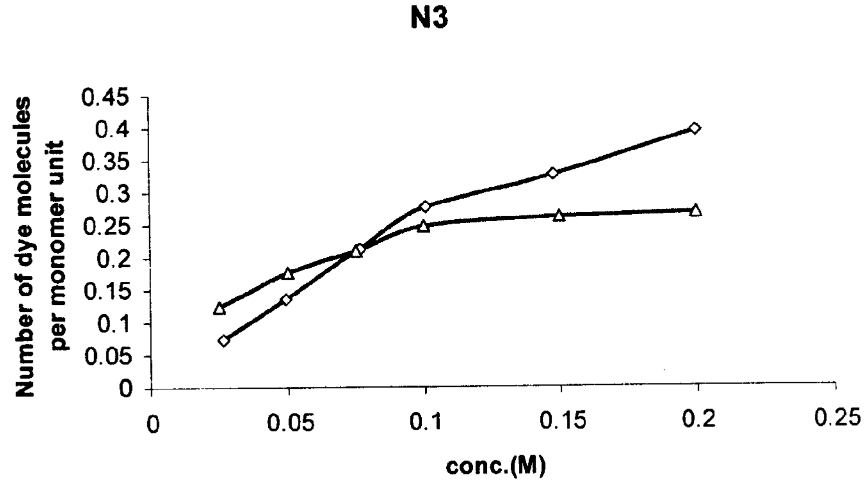

Fig. 7: Variation of number of dye molecules per monomer unit of PVP with concentration of azo dye. (◇) = Chicago blue, (∇) = Evan blue

Cp level (Fig. 8). At higher dye concentration (dye > 0.05 mol dm^{-3}), i) ionic inter-action (formation of ion pairs, ion association or complex formation), ii) dependence of the ion interaction on the composition and properties of the solvent, viz. polymer / water ratio; and iii) water structuring effect, must be considered. dN_1 / d[dye] is higher in this region than in the lower dye concentration range where it is negative. These results indicate that the number of ion / polymer decrease and there is a simultaneous decrease in the ion/ion interaction which gives rise to an increase of space between ions for water molecules, consequently decreasing Cp.

Furthermore, equation (6) was used to determine the nature of diffusion of water into

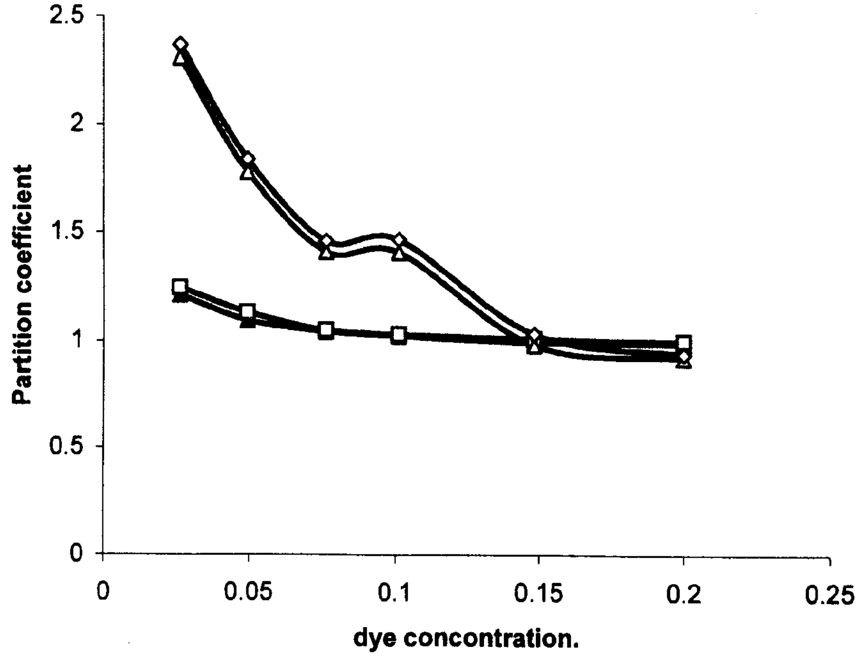

Fig. 8: Variation of partition coefficient with concentration of azo dye. (□) =Cp'= Chicago blue, (▲) = Cp = Chicago blue; (◊) =Cp' =Evan blue, (∇) = Cp = Evan blue.

hydrogel [22-24]. log M_t/M_e vs. log t gave straight line with slope equal to n. the correlation coefficient for all the concentrations gave the highest value up to second decimal affording the linearity of the plots.

M_t/M_e is the fractional water uptake, t is the diffusion time and n is the transport mode for the penetrant and k is a constant related to the structure of the network. Value $n < 0.50$ corresponds to Fickian diffusion whereas, $0.50 < n < 1.0$ shows non-Fickian diffusion [25, 26]. The values of n obtained for concentrations > 0.05-mol dm^{-3} of dye are in the range 0.30 – 0.48, showing Fickian diffusion whereas for lower concentrations of dye, these values are above 0.50 showing non-Fickian diffusion.

Table-1: Diffusion coefficient values for PVP gels in different [dye].

	[dye]	n	correlation coefficient
1	0.2 M	0.30	0.993
2	0.15M	0.32	0.996
3	0.10M	0.36	0.995
4	0.075M	0.45	0.993
5	0.05M	0.48	0.997
6	0.025M	0.51	0.985
7	0.0125M	0.51	0.979

Experimental

Material

Vinyl Pyrrolidone (VP) monomer from Aldrich was dried with anhydrous magnesium sulphate purified by vacuum distillation at boiling point 341 K and reduced 2 mm Hg pressure. Evan blue, Chicago blue and N-N methylene bis acryl amide, the crosslinker, purity 99.3 %, were used as received in a fine powdered form while the initiator, azo-isobuty-ronitrile (AIBN) from Fluka was recrystallised from ethanol. Deionised water was used as a swelling medium. The concentration range for dye solutions was 0.0125 – 0.2 Mol dm^{-3}.

Three components, vinyl pyrrolidone, cross-linking agent and the initiator were used in the preparation of PVP hydrogels. Mixture of 10 grams of VP, 0.27 gram (2 mol %) of crosslinker and 0.0035 grams (2 mol %) of AIBN were made gravimetrically, degassed with nitrogen for 15 minutes, heated on a water bath for 3 hours at 50° C, 2 hours at 60 °C, overnight at 70 °C and finally for 2 hours at 80 °C.

Conversion

After polymerisation, the reaction products were swelled in water at equilibrium to remove linear polymer / unreacted monomers, if any to know about the % conversion. Extracted gels / discs were dried at room temperature, then at 315 K in oven and 320 K in vacuum oven to constant weight. Percentage conversion of monomer-cross linking agent in to insoluble networks was based on the total weight of the cross-linking agent and monomer in the initial mixture (W_0) and xerogel (W_t).

$$r = 100\,(W_t/W_0) \qquad (1)$$

Swelling in Dye Solution

Dry xerogels were swollen to equilibrium in the aqueous solution of dyes of appropriate concentration $0 < [\text{dye}] \leq 0.2$ mol dm^{-3} for 277 hours. The swelling ratio (r), the number of water molecules (N_1) and dye molecules (N_3) per monomer unit, the partitioning coefficients (Cp and Cp$^{\cdot}$) between dye inside and outside the gel and the diffusion coefficients were determined. The swelling ratio was calculated from equation 1 in which m_t is the mass after time (t) and m_o is the mass of the xerogel.

$$r = m_t/m_o \qquad (1)$$

The residual swelling solution was also weighed and its concentration was determined by absorbance change method using UV-2000 spectrophotometre at 606 nm for Evan blue and 618 nm for Chicago blue respectively.

To obtain the mass of the dye within the swollen hydrogels, the discs were then dried at room temperature for one week and finally dried to constant weight in a vacuum oven at 30 °C. The N_1 and N_3 were calculated from equations (2) and (3) respectively:

$$N_1 = (g_1/M_1)/(g_2/M_2) \qquad (2)$$

$$N_3 = (g_3/M_3)/(g_2/M_2) \qquad (3)$$

Where g_1, g_2, and g_3 are masses of water, polymer and dye in the hydrogel at equilibrium and M_1, M_2 and M_3 are the molar masses of water (18 g / mol), monomer unit (111 g / mol) and dye (EB = 961 g / mol and CB = 993 g / mol) respectively.

Similarly, the partitioning coefficients were calculated as:

$$Cp = [g_3/(g_1 + g_2)]/(g_3^*/g_1^*) \qquad (4)$$

In equation (4), the g_1^* and g_3^* are the masses of water and dye in external solution at equilibrium. In equation (4) the dye concentration in hydrogels is the moles of dye per kilogram of dye free solvent i.e. per kilogram of (polymer + water). If water alone is considered as solvent for the dye in the hydrogel, the partitioning coefficients is somewhat different and may be denoted as Cp$^{\cdot}$:

$$Cp^{\cdot} = (g_3/g_1)/(g_3^*/g_1^*) \qquad (5)$$

Diffusion Coefficient

To study the nature of diffusion of water in to hydrogels, equation (6) was used:

$$F = M_t/M_e = k_s t^n \qquad (6)$$

Where M_t is the amount of solvent diffused into the gel at time t and M_e at equilibrium, K_s is a constant characteristic of the system and n characteristic of the mode of transport of the solvent.

Conclusion

Although reports have been made previously on the synthesis and properties of PVP hydrogels, we believe that the present communication is the first to focus on the interactions of particular azo dyes with hydrogels. At equilibrium and 0.0125 mol dm^{-3} solution of EB, the hydrogel has water content 3785 % and dye content 106 % while at higher concentration i.e. 0.2 mol dm^{-3}, the former value comes down to 1876 and the latter goes up to 179. Similarly, for CB at 0.025-mol dm^{-3} solution, % water content decreases from 3589 to 2043 at 0.2-mol dm^{-3} while dye content increases from 67 to 351. The partition coefficient of dyes, expressed as concentration within hydrogel relative to that in the external medium, decreases with [dye] in the swelling medium, the effect being more pronounced at low [dye]. In case of EB, the Cp values at low [Dye] were well above unity while for CB it is almost unity.

Acknowledgments

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