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THE ADSORPTION OF HYDROPHILIC POLYMERS AT THE POLYSTYRENE–WATER INTERFACE

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SUMMARY

The adsorption of various fractions of polyvinylpyrrollidone (PVP), sodium carboxymethylcellulose (SCMC) and acid and alkaline processed ossein gelatins at the surface of polystyrene latex has revealed that these polymers exhibit the general characteristics of polymer adsorption in that the adsorption isotherms were of the Langmuir type and the extent of adsorption increased with molecular weight. The amount of polymer adsorbed was both pH- and temperature-dependent for all the polymers investigated. The pH effects were interpreted in terms of the ionization of groups on both the polymer and the latex surface, whilst temperature effects were tentatively attributed to increases in the solvent power with temperature. The conformation of the polymer chains at the solid–liquid interface was found to be similar to that in solution; coiled in the case of PVP and linear for SCMC. The adsorbed layer thickness was not found to be a continuous function of molecular weight. A discontinuity was found for a molecular weight of 44,000 and was attributed to film thicknesses being controlled by the polymer 'tail' lengths below 44,000, whilst for fractions with molecular weights greater than 44,000, the dominant dimension is that of the polymer 'loop'.

INTRODUCTION

This paper is the first in a series of papers on the effect of hydrophilic polymers on the stability and bioavailability of suspensions.

The adsorption of hydrophilic polymers at the drug–vehicle interface results in suspensions that are either sterically stabilized or flocculated. The properties of the adsorbed film are therefore of paramount importance in determining the bulk properties and may well influence the bioavailability of the suspension. In a previous study (Najib et al., 1977) the effects of various fractions of PVP, SCMC and acid and alkaline processed gelatins on the electrophoretic mobility of polystyrene latex and sulphadimidine particles were reported. This work examines the adsorption of the same polymer fractions on the same batch of latex in order to characterize the adsorbed polymer film and hence its possible effects on the dissolution and transport of drugs, an aspect of suspension formulation not previously investigated.

In polymer adsorption studies the interpretation of the experimental data is very dependent on the selection of a theoretical equation which can satisfactorily describe the process. The Langmuir equation, although originally derived for small molecules, has been applied to several polymer systems (Koral et al., 1958; Frisch et al., 1959; Hobden and Jellinek, 1953). Simha, Frisch and Eirich (SFE) have provided a model for the adsorption of flexible macromolecules from dilute solutions (Rossoff, 1969; Kippling, 1965), from which the following equation was derived:

$$\frac{\theta}{1-\theta}\exp(2K_1\theta) = (KC)^{1/v} \qquad (1)$$

where θ is the fraction of surface covered by adsorbed segments at concentration C, v is the average number of segments adsorbed on the surface per chain, and K and K_1 are constants. This equation predicts a steep rise in the isotherm at low concentrations after which θ changes only slightly with increase in polymer concentration. v was then related to chain flexibility by the equation

$$v = f^{0.5nv^2} \qquad (2)$$

where f is a factor inversely related to chain flexibility and n is the total number of segments.

MATERIALS AND METHODS

The polystyrene latex used was prepared according to the aqueous phase initiation process of Chung-li et al. (1976), and was determined by electron microscopy to be 1.198 ± 0.005 μm (n = 100) in diameter. The latex was therefore found to be monodispersed spheres, and potentiometric titrations showed the existence of sulphate and carboxylic acid surface groups with an area of 8.40×10^{-17} m^2 per charged group. The water used was triple-distilled obtained from an all glass still apparatus. PVP 10,000, 40,000 and 360,000 were pharmaceutical grade and obtained from Sigma Chemicals, Poole, U.K. PVP 24,500 was pure, pharmaceutically and biologically tested grade obtained from Koch-Light Laboratories, Colnbrook, U.K. PVP 44,000 and 700,000 were obtained from B.D.H., Poole, U.K. SCMC P20, P40, P75 and P1000 were obtained from British Cellanese Chemicals, Derby, U.K. The acid and alkaline ossein gelatins were obtained from Croda Food Ingredients, Widnes, U.K.

Characterization of the polymers

The number average molecular weights (Mn) for PVP (solvent – water) and SCMC (solvent – 0.1 M NaCl) were obtained by membrane osmometry (Melabs CSM-2 osmometer) at 25°C. The intrinsic viscocity (η) was determined by U-tube viscometry using the same temperature and solvent.

Fraction	Mn	(η) (dl g^{-1})
PVP 10,000	9900	7.90
PVP 24,500	21,400	14.80
PVP 40,000	35,200	17.85
PVP 44,000	43,700	18.1
PVP 360,000	357,000	94.4
PVP 700,000	681,000	136.8
SCMC P20	60,000	4.3
SCMC P40	78,600	4.7
SCMC P75	94,300	5.1

For PVP the following relationship was determined:

$$\eta = 3.75 \times 10^{-4}\ \mathrm{Mn}^{0.67}$$

thus confirming that PVP exists in solution as a random coil. No such relationship was calculated for the SCMC fractions as osmotic data could not be obtained for P1000 due to the viscous nature of the solutions.

The two gelatin samples had been previously well characterized (Robinson et al., 1975).

Determination of mass adsorption isotherms

Mass adsorption isotherms were constructed by centrifuging a latex suspension in equilibrium with the required concentration of polymer at 25 ± 0.01°C and pH 5.60. The supernatant was assayed for polymer content by differential refractometry (Alan Whitehead, Colchester). The concentration was calculated by reference to an appropriate calibration curve for each polymer which was obtained by plotting the refractometer reading against the polymer concentration. The amount of polymer adsorbed was obtained by subtracting the concentration in the supernatant from the initial polymer concentration. The effect of pH on polymer adsorption was studied by preparing a series of polymer solutions (1 gl^{-1}) to span the pH range 2 to 11. To each, a known amount of latex was added and the amount of polymer adsorbed was determined as previously described. A similar procedure was adopted to study the effect of temperature (10–30°C) on polymer adsorption.

Determination of the adsorbed layer thickness

To 10 ml of polystyrene latex containing 2.16 g% (w/v), PVP 10,000 (1.14 gl^{-1}) was added. This concentration was sufficient to form a monolayer of the polymer on the particles based upon the mass adsorption isotherm of the polymer. The dispersion was then shaken at 25 ± 0.01°C for 24 h, a period sufficient to achieve equilibrium. 5 ml of this dispersion were then removed and centrifuged to provide a supernatant for diluting latex dispersions to different solid contents. This procedure was adopted by Barsted et al. (1971) to ensure that all dispersions, although at different solid content, will have the same liquid composition. For other PVP grades this procedure was repeated and in each case a weight of PVP was calculated sufficient to form a monolayer on the particles as indicated from the adsorption isotherm.

The thickness of the adsorbed film was measured by U-tube viscometry according to the method described by Saunders (1961). Flow time measurements of the supernatant and the dispersions were carried out in a M1 U-tube viscometer at 25 ± 0.01°C. The efflux time was determined in triplicate and the variation was not greater than 0.02%. The relative viscosity of the dispersion was taken as the ratio of the dispersion flow time to that of the supernatant.

RESULTS AND DISCUSSION

The mass adsorption isotherms for different fractions of PVP (Fig. 1), SCMC (Fig. 2) and acid and alkaline ossein gelatins (Fig. 3) show certain characteristic features which are common to all the polymers studied. The amount of polymer adsorbed per unit weight of latex is a rapidly increasing function of the polymer concentration in solution at low concentrations, and then reaches a 'plateau' which shows little or no change as the polymer solution concentration is further increased. This form is isotherm is characteristic of monolayer formation as predicted from the Langmuir and Simha–Frisch–Eirich (SFE) equations. The results also show that for any polymer, the higher the molecular weight of the polymer the greater the amount of polymer adsorbed. The increase in the amount of polymer adsorbed with polymer molecular weight is predicted by the SFE theory as shown in Eqn. 2. The longer the molecular chain the greater is the flexibility of the chain and hence the smaller f is and therefore the greater the amount of polymer adsorbed.

The study of adsorption as a function of molecular weight serves as a useful tool in characterizing the conformation of the polymer molecules at the solid–liquid interface. It has been shown by viscometric measurements (e.g. Najib, 1979) that PVP molecules have a coiled conformation in solution, whereas SCMC molecules have a linear conformation due to the large number of similarly charged sites regularly spaced along the polymer

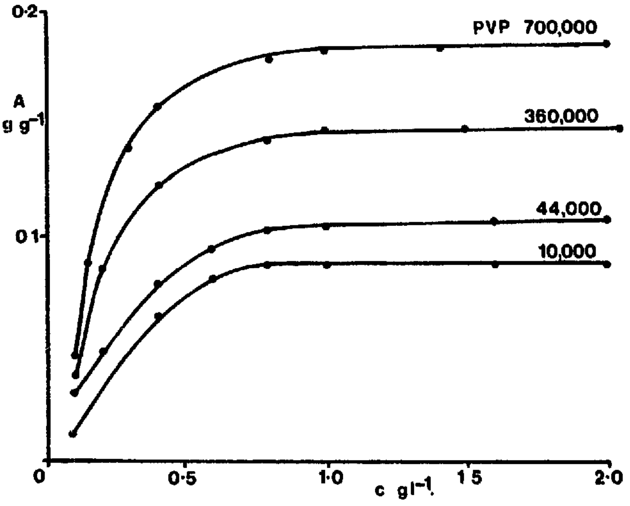
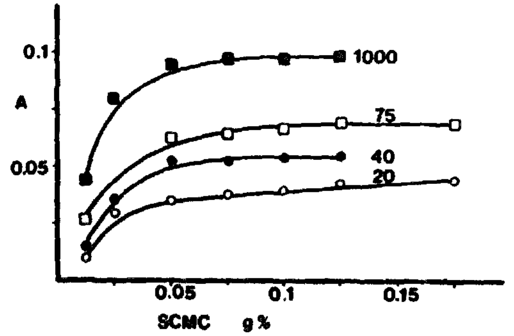


Fig. 1. The adsorption isotherms of PVP onto latex at 25°C and pH 5.6.



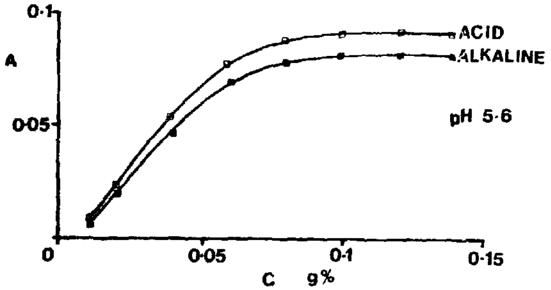


Fig. 2. The adsorption isotherms of SCMC onto latex at 25°C and pH 5.6.

Fig. 3. The adsorption isotherms of acid and alkaline gelatins onto latex at 25°C.

chain. In order to determine whether the conformation of the molecules at the solid–liquid interface is similar to or different from that in solution, the adsorption of PVP and SCMC was studied as a function of molecular weight. Perkell and Ullmann (1965) have suggested the following relationship between the monolayer saturation value (A_s) and the polymer molecular weight (M)

$$A_s = KM^{\alpha} \tag{3}$$

where K and α are constants. A plot of log A_s against log M for PVP is shown in Fig. 4 and for SCMC in Fig. 5. The value of α is the slope of these plots and is indicative of the polymer conformation at the solid–liquid interface. For PVP $\alpha = 0.16$ indicating that the polymer is adsorbed as random coils, whereas for SCMC $\alpha = 1.0$ and the molecules are therefore distributed in the adsorbed film as 'bristles', that is the polymer molecule is attached at one point to the latex surface and the remainder of the molecule protrudes into the surrounding medium. This is due to the repulsion between electrostatic charges

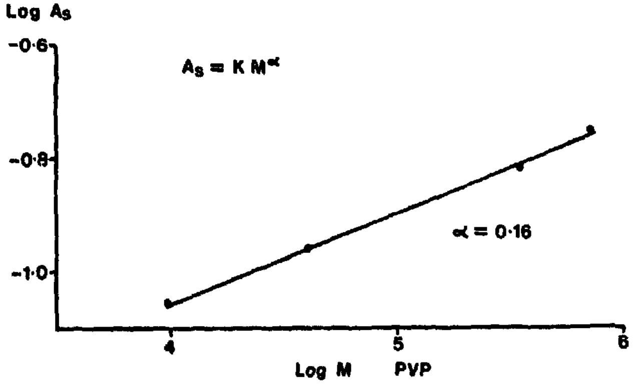


Fig. 4. Log A_s as a function of log PVP molecular weight.

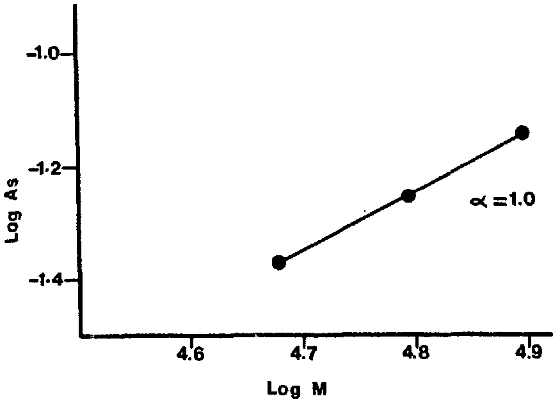


Fig. 5. Log A_S as a function of log SCMC molecular weight.

on the chains. Therefore the conformation of PVP and SCMC molecules at the solid interface is similar to that in solution.

The effect of pH on polymer adsorption is multifactorial as it can be considered due to one or more of the following: (1) a change in conformation of the molecules; (2) in ionisation of polymer groupings; (3) a change in the solvent power and solubility of the polymer; and (4) changes in the surface potential of the adsorbent.

As the polymers studied are affected differently by changes in pH they will be considered separately.

For PVP, the effect of pH on the amount of polymer adsorbed on polystyrene latex is slight as shown in Fig. 6. pH has little or no effect on the amount of polymer adsorbed up to pH 7.0. At pH >7 the amount adsorbed decreases slightly. This may be attributed to the adsorption of OH^- ions from solution on the PVP chain causing it to acquire a negative charge. Also at this pH, the latex surface groupings are negatively charged. The like charges on the polymer and the surface of the adsorbent cause a reduction in the amount of polymer adsorbed. For SCMC the situation is different in that the change in pH has a marked effect on the amount of polymer adsorbed. The pH of the dispersing media

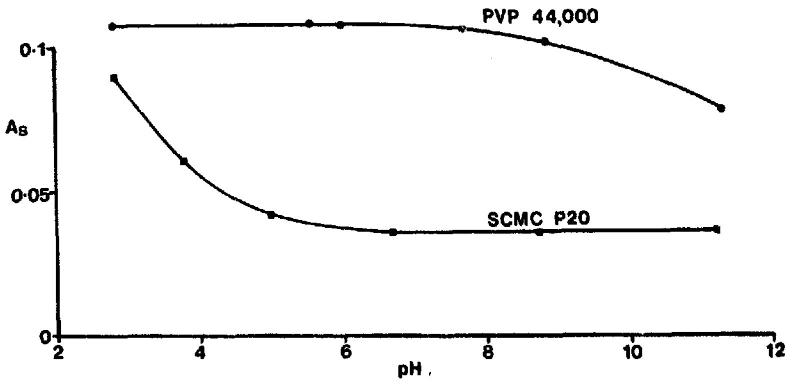


Fig. 6. The dependence of adsorption on solution pH for PVP 44,000 and SCMC P20.

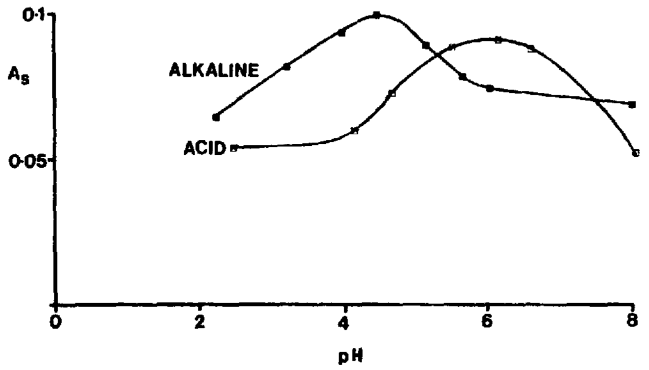


Fig. 7. The adsorption of alkaline and acid gelatins as a function of solution pH.

influences both the SCMC molecule conformation and solvent power. SCMC is more soluble in alkaline solution. The effect of pH on the adsorption of SCMC is shown in Fig. 6. It is apparent that the adsorption is greater at the lower pHs and decreases as the pH increases to pH 6. Above this pH adsorption is pH-independent. This can be attributed to the fact that at lower pH both SCMC and the polystyrene latex surface are either

TABLE 1

THE EFFECT OF TEMPERATURE ON THE A_S VALUES (g g^{-1}) OF VARIOUS PVP GRADES

Temperature (°C)	A_s for various PVP fractions				
	10,000	24,500	44,000	360,000	700,000
10	0.0986	0.109	0.121	0.169	0.179
15	0.0915	0.105	0.119	0.161	0.173
20	0.0905	0.104	0.117	0.153	0.164
25	0.0875	0.103	0.110	0.145	0.157
30	0.0870	0.100	0.106	0.140	0.151

TABLE 2

THE EFFECT OF TEMPERATURE ON THE A_S VALUES (g g^{-1}) OF VARIOUS POLYMERS

Temperature (°C)	A_s for various polymers		
	SCMC P_{20}	Acid gelatin	Alkaline gelatin
10	0.0605	0.145	0.151
15	0.0553	0.127	0.139
20	0.0490	0.104	0.105
25	0.0408	0.091	0.081
30	0.0358	0.065	0.065

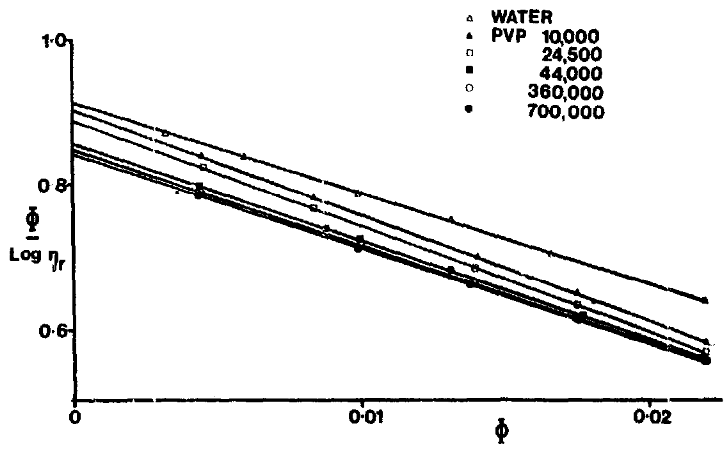


Fig. 8. $\phi/\log \eta r$ as a function of ϕ (latex volume fraction) for latex suspended in water and solutions of PVP.

uncharged or carry small negative charges. Coupled with the poor solvency of acid solvent for SCMC, the overall effect is an increase in the amount of polymer adsorbed. As the pH increases, the ionization of both SCMC molecules and polystyrene surface groupings increases until it reaches 100% ionization at pH 5.5–6.0. This corresponds to a maximum repulsion between the molecules and the surface and hence adsorption is reduced. Also the increase in the solvent power at the higher pH results in a reduced adsorption.

The effect of pH on the adsorption of acid and alkaline gelatin is shown in Fig. 7. The pH has a marked effect on the adsorption of both gelatins; adsorption being maximum at the isoelectric point. At this point the adsorption of alkaline gelatin is greater than the acid which may be due to its higher molecular weight (Robinson et al., 1975). The effect of pH here is multifactorial as it affects the conformation as well as the degree of ionization of the gelatin molecules.

The effect of temperature on the amount of polymer adsorbed, as predicted by the SFE theory, is variable. An increase or decrease in adsorption may occur upon elevating temperature. The effect of temperature on the adsorption of PVP is shown in Table 1 and for SCMC and acid and alkaline gelatins in Table 2. For all the polymers studied a

TABLE 3

THE ADSORBED LAYER THICKNESS FOR VARIOUS PVP FRACTIONS

PVP	Δ (nm)
10,000	4.45
24,500	8.25
44,000	16.34
360,000	18.72
700,000	20.09

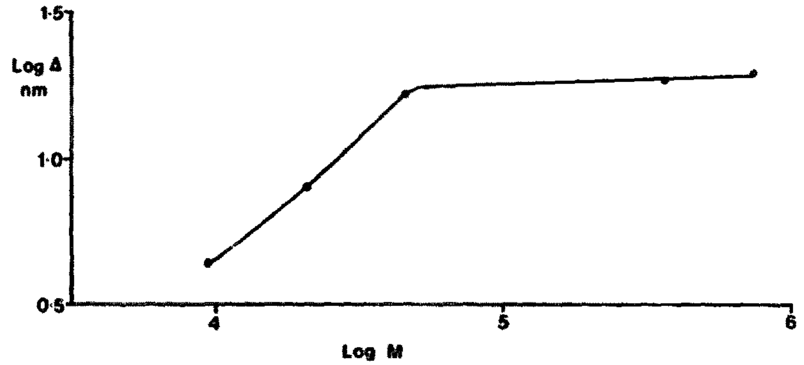


Fig. 9. The relationship between the calculated adsorbed film thickness (Δ) and molecular weight of PVP.

decrease in adsorption was obtained with increase in temperature, a result which may be attributed to an increase in the solvent power.

The adsorbed layer thickness (Δ) for various PVP fractions as calculated from Fig. 8, is shown in Table 3. When log Δ was plotted against log M, Fig. 9 was obtained. It is evident that Δ increases sharply with increase in molecular weight up to 44,000. For molecular weights >44,000 the thickness increases only slightly. This could be explained as shown in Fig. 10 by assuming that for the lower molecular weight fractions the tail length of the polymer chains is the determining factor controlling the adsorbed layer thickness, but for the higher molecular weight fractions the length of the loops become the critical dimension.

To confirm the experimental results obtained by viscometry, the adsorbed layer thick-

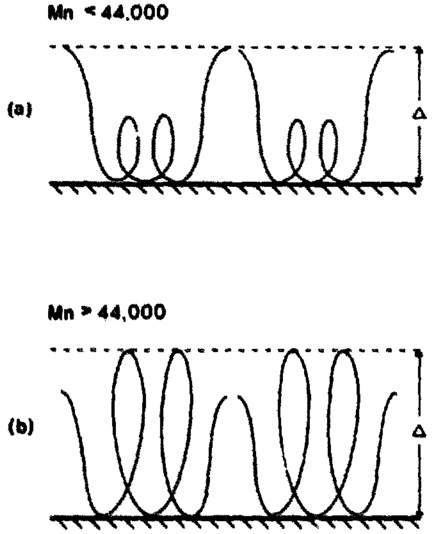


Fig. 10. Proposed model for the adsorption of PVP onto latex. a: film thickness (Δ) is controlled by the dimension of the tails when Mn <44,000. b: Δ is determined by the dimension of the loops when Mn <44,000.

ness of PVP 700,000 was determined by photon correlation spectroscopy. The result of 21 nm obtained agrees with the viscometry result of 20.09 nm suggesting that viscometry is a suitable technique for measuring the thickness of the adsorbed polymer film.

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