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Pharmaceutical suspension studies I. A comparison of adsorption of polyvinylalcohol at the diloxanide furoate B.P. and polystyrene latex–water interface

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Summary

The adsorption of a series of polyvinylalcohol fractions onto two solid substrates has been investigated. Using diloxanide furoate B.P. as the adsorbent, adsorption of small molecular weight fractions within pores has been demonstrated. Such adsorption was not observed when using polystyrene latex as the substrate but larger equilibrium quantities were adsorbed onto this surface than onto the drug. The differences in the maximum amount of polymer adsorbed at both solid–solution interfaces have been ascribed to the different hydrophobicities of the surfaces as determined by contact angle measurements.

Introduction

As part of an investigation into the effect that adsorbed polymers play in the production of pharmaceutically acceptable suspensions, the adsorption characteristics of a water-soluble long-chain polymer onto a drug surface have been studied. The use of polymers in suspension formulation is widespread due to the increased viscosity imparted to the system at high concentrations which retards particle sedimentation. In addition to increasing the viscosity of the external phase, adsorption of polymer molecules at the solid–liquid interface will generally occur generating a steric repulsion between individual particles. At low concentrations particle

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flocculation is promoted which is interpreted in terms of the polymer bridging model (Healy and La Mer, 1964).

The present work describes the adsorption of several fractions of polyvinylalcohol onto two solid substrates and differences between the adsorption patterns are discussed.

Materials and methods

Polyvinylalcohol (PVA)

Two commercially available samples were used throughout this study, both stated by the manufacturers to be 88% hydrolysed: Moviol 8-88, Harco Chemicals, molecular weight ~ 30,000; Polyviol W25/140, Wacker Chemicals, molecular weight ~ 80,000.

The polymers were fractionated by a sequential precipitation technique involving the addition of increasing quantities of acetone and/or propan-2-ol to a concentrated aqueous solution of the polymer. The precipitated fractions were collected by centrifugation and decantation prior to redissolving in water and drying in a vacuum oven for 48 h at 70°C. The lower molecular fractions obtained from Moviol 8-88 could be obtained only in small quantities using this method and several separate fractionations had to be performed to obtain manageable amounts. The transparent films so formed were shredded and stored under nitrogen until required.

The molecular weights of the individual fractions were determined by viscometric means using the values of van den Boomgaard et al. (1978) for K and a inserted in the Mark-Houwink equation

$$[\eta] = KM^{a} \qquad (1)$$

where $[\eta]$ is the intrinsic viscosity for a fraction of molecular weight M. Flow times in aqueous solutions of the PVA fractions at 25 ± 0.01°C were determined using a Grade A U-tube viscometer (BS 188) over the concentration range 0–0.5% w/v. The flow time for distilled water was 288.4 s. Intrinsic viscosities were found using a Huggins plot of reduced viscosity against concentration (Huggins, 1942) yielding $[\eta]$ as the intercept. The values of $[\eta]$ inserted into Eqn. 1 yields the molecular weight, M.

The second method of polymer fraction characterization involved determining the percentage hydrolysis of the parent compound polyvinylacetate to PVA. A known weight of each fraction was refluxed with 5 ml M/10 sodium hydroxide for 30 min and the excess alkali back titrated with M/10 hydrochloric acid using phenol red as the indicator. The reproducibility of the technique was ± 1%.

Polystyrene latex

The latex used for adsorption studies was of mean diameter 312 nm and possessed surface carboxylic acid groups only. This material and its method of preparation have previously been described (Kayes and Rawlins, 1979). The specific surface area of the latex obtained from the mean diameter and assuming spherical geometry was 18.2 $m^2 \cdot g^{-1}$.

Diloxanide furoate B.P.

Received from the Boots, m.p. 112–114°C (114–116°C). A Coulter Counter analysis of this material in drug saturated 0.9% w/v sodium chloride solution gave a mean particle size of 16.0 μm diameter.

Preparation of samples

All adsorption isotherms were obtained at 25 ± 0.1°C. A known weight of drug was placed into 25 ml glass vials which could be sealed with polyethylene lids. The required volume of a solution of known PVA concentration was then added to the vials which were vigorously agitated by hand for 10 sec. The vials were then subjected to ultrasonification for periods of up to 1 min to further assist with dispersion and to allow the release of entrapped air. A Coulter Counter analysis of a suspension produced in this way revealed no change in the particle size distribution indicating that attrition of the particles during this process was minimal. To achieve equilibrium of the adsorbing species the tubes were clamped horizontally under water in a shaking water bath maintained at the correct temperature. The equilibration period was 24 h. Preliminary experiments revealed that equilibrium adsorption occurred at approximately 3–6 h for PVA fractions of 95,900 and 22,400 molecular weight. Suspensions produced in this way were well dispersed with lumps of undispersed powder constituting less than 3% of the total powder weight. Adsorption onto the polystyrene latex was determined using the previously described procedure (Kayes and Rawlins, 1979).

Determination of PVA adsorption

A colourimetric assay for polyvinylalcohol with a precision of ±2% (Garvey et al., 1974) was used. The presence of dissolved drug did not interfere with the assay.

Measurement of surface area

Mercury porosimetry was used to estimate the specific surface area of the drug in addition to determining the pore size distribution of the sample. The instrument used was a Micromeritics model 190 mercury intrusion porosimeter employed in the pressure range 0–50,000 p.s.i. The specific surface area of the powder (neglecting contributions from pores of diameter less than 10 nm) was 1.055 $m^2 \cdot g^{-1}$.

A value of 0.29 $m^2 \cdot g^{-1}$ was obtained through manipulation of the Coulter Counter analysis for the drug using the appropriate Hatche-Choate equation (Herden, 1960). Such equations are applicable only to spherical particles and the result demonstrates the limitations of this method in determining specific surface areas of coarse drug powders.

Confirmation of the pore size distribution measurements found by mercury porosimetry was necessary as the pore diameters of the drug found with this technique were very small and corresponded to pressures at the upper range of the instrument where accuracy is limited. Gas adsorption is a suitable alternative as more accurate determinations are possible for small diameter pores. A Quantasorb surface area analyzer (Quantochrome) was used in this respect. The BET estimate of the specific surface area of the diloxanide furoate was 1.13 $m^2 \cdot g^{-1}$.

Contact angle measurement

The method used was that described by Kossen and Heertjes (1965) involving the measurement of the maximum height of a liquid drop that can be supported on a powder compact by interfacial forces. The applicability of this technique to pharmaceutical materials has been demonstrated by Lerk et al. (1976).

Compacts of diloxanide furoate were prepared in 0.5 in. diameter dies on a Wilkinson STD1 reciprocating tablet machine. Measurements could only be performed within a narrow range of compact porosities due to lamination of the discs at high compaction forces. In addition to forming compacts by compressing between steel punches, a few discs were prepared by compression between punches faced with paper and also polyethylene films. The values of the surface tension and the density of a drug-saturated aqueous solution necessary for evaluation of the contact angle were determined by duNouy tensiometer and Lipkin pyknometer, respectively.

When dried, polystyrene latex cannot be compacted into discs and to determine the contact angle a film of polystyrene was prepared by dissolving dried latex in dioxan and evaporating the solvent after spreading the solution on a microscope slide. Distilled water was used as the contact liquid.

Results and discussion

Fifteen polymer fractions were obtained from the precipitation procedure employed with the two commercial polyvinylalcohol samples and details of their characteristics are listed in Table 1. Several sets of values for the constants K and a in Eqn. 1 have been reported by various authors (Bradrupp and Immergut, 1975; Fleer, 1971). Justification for using the values given above is demonstrated by results obtained with the unfractionated polymer samples where molecular weights of 34,600 and 80,300 are obtained. This is in reasonable agreement with the manufacturers quoted values obtained by gel permeation chromatography. The degrees of hydrolysis of the fractions of PVA show slight molecular weight dependence although this is not as marked as the values determined by van den Boomgaard et al. (1978).

Adsorption isotherms of 6 of the fractions D, F, J, M, N and O covering a molecular weight range of 5000–100,000 are shown in Figs. 1 and 2 for adsorption onto polystyrene latex and diloxanide furoate B.P., respectively. In both cases adsorption rises rapidly at low polymer concentrations with a levelling off in the amount adsorbed at approximately 300–400 ppm. In the case of adsorption onto polystyrene latex a true plateau is not attained and adsorption continues to increase over the concentration studied.

The maximum amount of polymer at the interface gives an indication of the type of adsorption that has occurred. For example, the work of Garvey et al. (1974) on

TABLE I

PHYSICAL CHARACTERISTICS OF POLYVINYLALCOHOL FRACTIONS

Fraction	$[\eta]$ ($dl \cdot g^{-1}$)	M	% hydrolysis	Sample source
A	1.10	120,000	90	Polyviol W24/140
B	1.07	113,200	91	
C	1.03	109,300	88	
D	0.94	95,900	88	
E	0.83	80,300	87	
F	0.80	76,200	88	
G	0.65	56,600	86	
H	0.62	52,900	86	
I	0.56	45,800	89	Moviol 8-88
J	0.48	36,700	87	
K	0.45	33,500	88	
L	0.38	26,300	88	
M	0.34	22,400	89	
N	0.24	13,700	87 *	
O	0.12	5100	86 *	
Unfractionated Moviol 8-88	0.46	34,600		
Unfractionated Polyviol W25/140	0.83	80,300		

* Denotes use of propan-2-ol in fractionation.

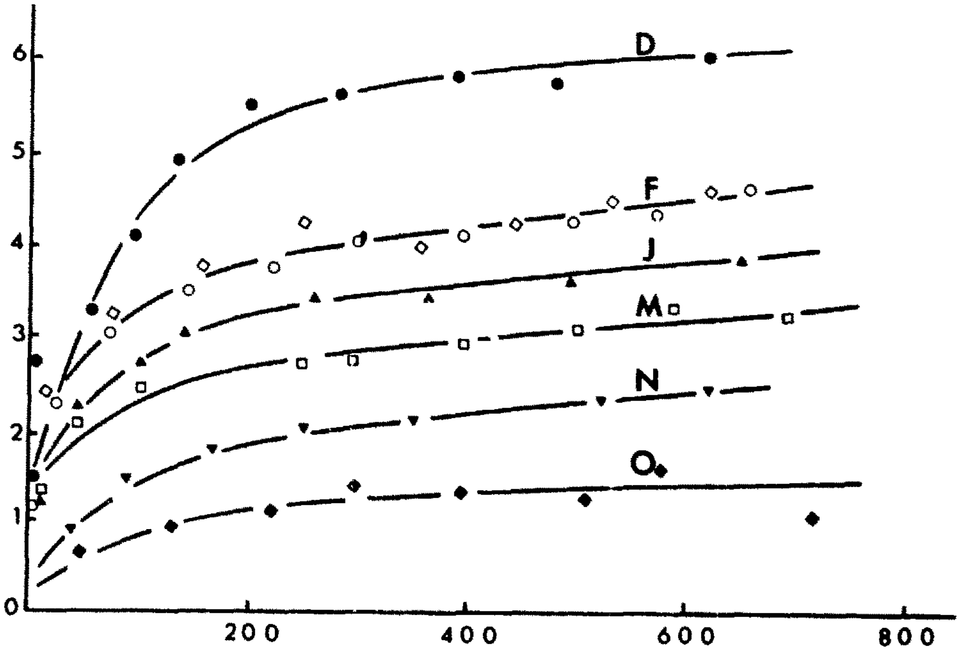

Fig. 1. Adsorption isotherms of PVA on polystyrene latex at 25°C in distilled water at pH 5.6 (◇, measurement at pH 2.5 for fraction F). Ordinate: adsorption ($mg \cdot m^{-2}$). Abscissa: equilibrium concentration (ppm).

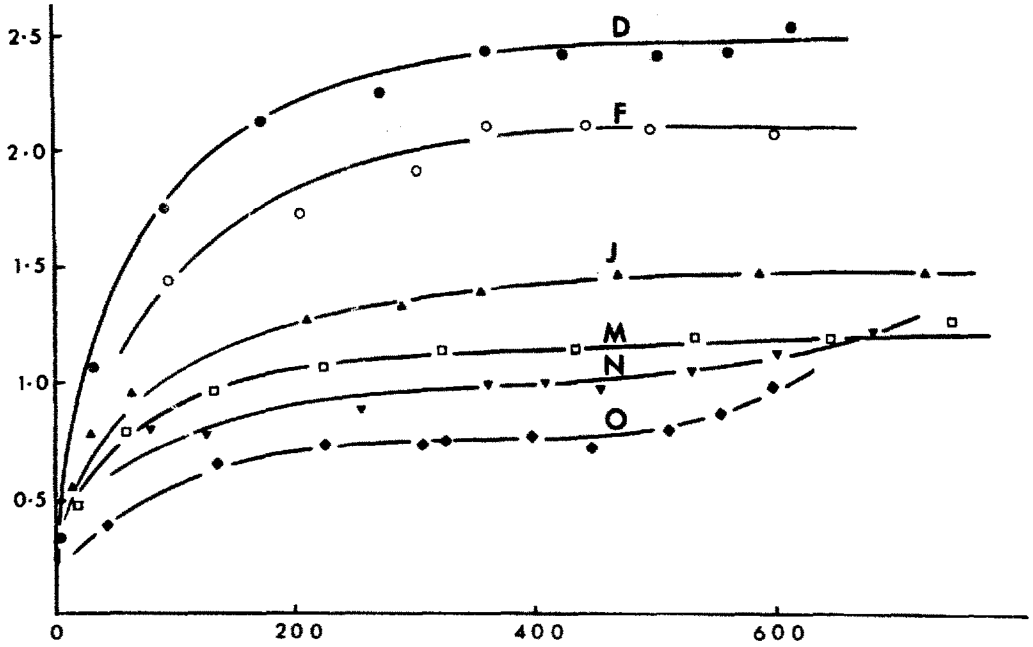

Fig. 2. Adsorption isotherms of PVA on diloxanide furoate at 25°C in distilled water. Ordinate: adsorption (mg·g^{-1}). Abscissa: equilibrium concentration (ppm).

the adsorption of PVA fractionated by gel permeation chromatography onto a latex showed maximum levels of 0.9–2.9 mg·m^{-2} for M = 8000–67,000. Monolayer polymer coverage was considered to have taken place and the volume of the adsorbed polymer coils determined experimentally was similar to that of the molecules in free solution. For monolayer adsorption of PVA (M = 53,00) onto a silver iodide sol approximately 1.5 mg polymer adsorbs per square metre at maximum coverage (Fleer et al., 1972). Adsorption onto carbon black particles gives saturation adsorption of 0.25 mg·m^{-2} (Johnson and Lewis, 1969). In this latter reference higher concentrations produced further adsorption with the low molecular weight fractions. A similar effect is found with fractions N and O adsorbed on diloxanide furoate (Fig. 2) and is thought to be due to multilayer formation. The average segment density at the interface for the low molecular weight fractions is greater than fractions higher in the series and conditions for incipient phase separation may exist (Silberberg, 1972).

The results presented here for polystyrene latex show saturation values in excess of values previously reported for monolayer coverage (Garvey et al., 1974). The molecules of PVA adsorb with either a small area of surface contact and with the majority of segments projecting outwards into the surrounding medium or through a type of multilayer formation. The latter premise is thought to be correct as comparison of results reported here with references where multilayer PVA adsorption is known to have occurred shows similar values for the maximum quantity adsorbed.

Multilayer adsorption of PVA at the paraffin–solution interface was observed by

Lankveld and Lyklema (1972) although steps in the isotherms normally indicative of multilayer formation were difficult to detect for the high molecular weight fractions used. The maximum quantity adsorbed was more in accord with the results on polystyrene latex reported here. Studies by van den Boomgaard et al. (1978) on the adsorption of PVA fractions prepared by a precipitation technique show plateau adsorption values which are greater than those observed by Garvey et al. (1974) who obtained fractions by gel permeation chromatography. Multilayer adsorption was proposed. These authors considered the observed differences were due to the type of latex surfaces used in both sets of experiments. In the former case a surfactant-free technique was used to prepare the latex while Garvey et al. employed a latex prepared by emulsion polymerization. The surfactant-free latex was considered to have a more hydrophobic surface due to the absence of charged surfactant molecules.

The nature of the surface has been shown to have a pronounced effect on PVA adsorption as the work by Tadros on the adsorption onto silica demonstrates (Tadros, 1978). Increasing the negative charge caused a reduction in the amount of polymer adsorbed. Fig. 1 demonstrates values found with this latex. Thus at pH 5.6 greater than 95% of the surface carboxylic acid groups are ionized while at pH 2.5 only 2% are ionized. Adsorption of PVA onto polystyrene latex and silica therefore occur via different mechanisms. Fleer and Smith (1976) have investigated the mechanism of adsorption on silica and suggest that for hydrophilic surfaces hydrogen bonding occurs between silanol groups and the carboxy group of the acetate residues on the polymer. For hydrophobic surfaces attachment occurs through the acetate residue and the methylene groups of the polymer. The latex used in this work has relatively large areas of styrene residues between the charged surface groupings and the surface may be considered essentially hydrophobic. Thus the mechanism suggested above for hydrophobic surfaces may apply and as a consequence adsorption will be independent of pH.

Basing the specific surface area of diloxanide furoate B.P. on 1.055 $m^2 \cdot g^{-1}$ low saturation quantities are observed in comparison with the latex. The actual values compare favourably with those of monolayer formation reported by Garvey et al. (1974) and it is a reasonable conclusion that such adsorption occurs with this system.

Application of the expression given by Perkel and Ullman (1961) relating the maximum amount adsorbed A_s, to the molecular weight, M, i.e.

$$A_s = K'M^b \tag{2}$$

does not give a good linear fit when the data is plotted logarithmically. Deviations are observed with the three lower fractions from the line which gives a value of 0.5 to the exponent, b. The dependence of A_s on $M^{1/2}$ is predicted from basic polymer theories (Frisch et al., 1953) and has been demonstrated experimentally by several authors (see for example, Garvey et al., 1974). Fig. 3 gives a clearer indication of this deviation where A_s is plotted as a function of $M^{1/2}$.

Mercury porosimetry measurements on the drug sample indicate significant quantities of pores lying in the region of 5 nm diameter (Fig. 4) and nitrogen

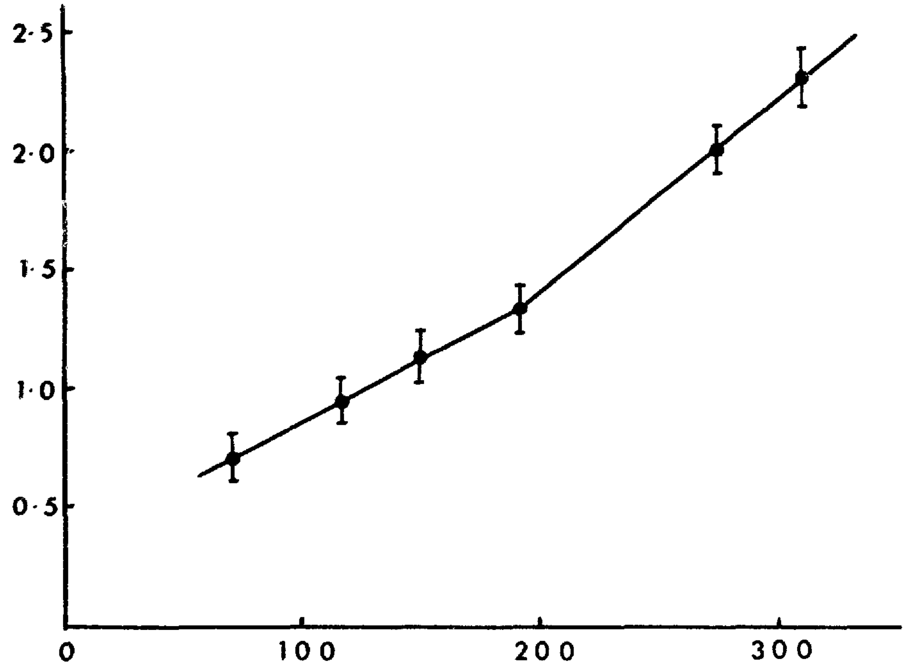

Fig. 3. The dependence of saturation PVA adsorption on diloxanide furoate B.P. on the square-root of molecular weight. Ordinate: saturation adsorption (mg·g^{-1}). Abscissa: (molecular weight)$^{1/2}$.

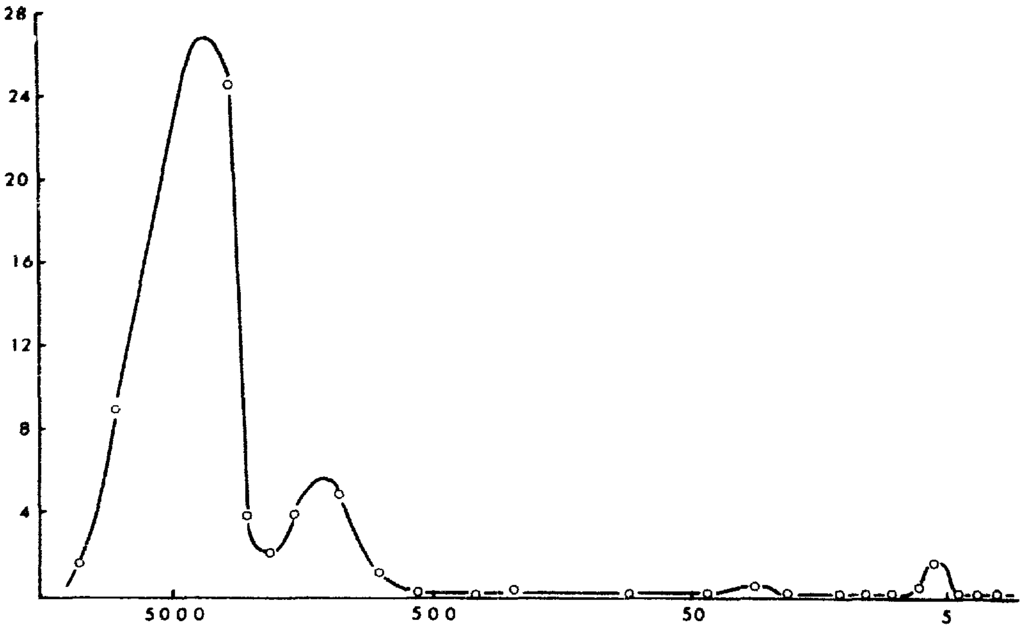

Fig. 4. Pore size distribution for diloxanide furoate B.P. Ordinate: percentage total pore volume. Abscissa: pore diameter (nm).

adsorption measurements giving an average pore size of 4.5 nm, confirm this result. The observed deviation at low molecular weights may therefore be due to the existence of surface pores which permit entry of small PVA molecules.

The dimensions of flexible polymer coils in dilute solution are obtained from the intrinsic viscosity and the molecular weight of the fractions. The Stockmayer-Fixman equation (1963) relates both these parameters in terms of the second virial coefficient, B, a constant K_θ and a universal viscosity constant for chain polymers in theta solvents, Φ (Flory, 1953). The value of Φ is not constant although a theoretical value of 2.8×10^{21} is often used. For PVA, Garvey et al. (1974) found Φ equal to 2.1×10^{21} and this value is used in this work. Thus,

$$[\eta] = K_\theta M^{1/2} + 0.51\Phi BM \tag{3}$$

where

$$K_\theta = [\eta_\theta]/M^{1/2} \tag{4}$$

and $[\eta_\theta]$ represents the intrinsic viscosity of the polymer under theta conditions (Morawetz, 1966).

A plot of $[\eta]/M^{1/2}$ against $M^{1/2}$ should give a straight line from which the intercept K_θ is obtained. In practice this applied for the higher fractions only (Fig. 5). A similar effect was found by Berry (1967) for polystyrene coils in two different solvents and he concluded that the deviation was due to an increase in chain stiffness at low molecular weights. The extrapolated value of $K_\theta(1.58 \times 10^{-3}$ $\mathrm{dl \cdot g^{3/2} \cdot mol^{1/2}})$ is in good agreement with values reported by Garvey et al. (1974). The two lowest fractions (N and O) do not lie on the Stockmayer-Fixman plot

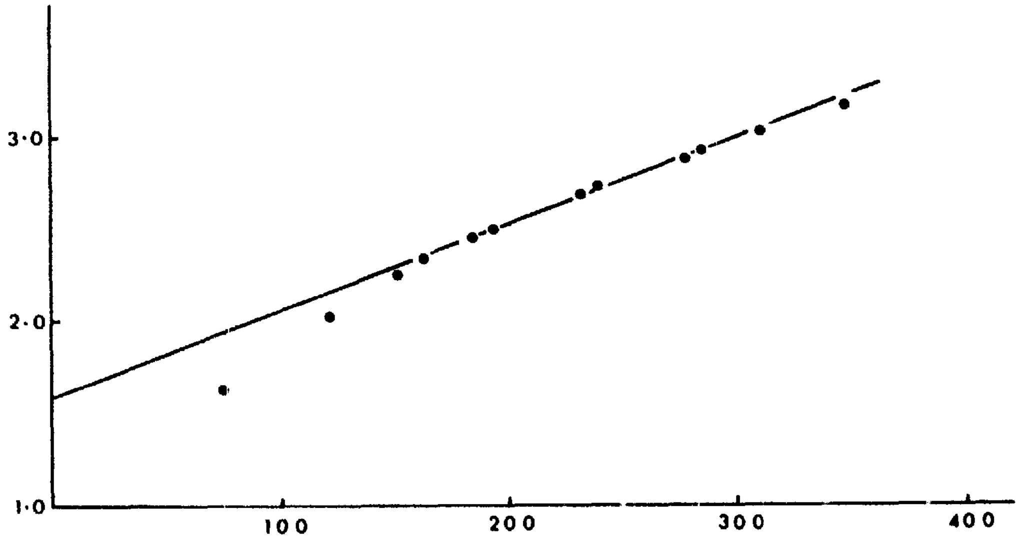

Fig. 5. Stockmayer-Fixman plot for the polyvinylalcohol fractions at 25°C in distilled water. Ordinate: $[\eta]/M^{1/2} \times 10^3$. Abscissa: $M^{1/2}$.

(Fig. 5) and this is in agreement with the results of Stacey and Arnet (1973) who found polymer fractions of molecular weight < 14,000 to be outside the range of validity of Eqn. 3.

The root mean square end–end distance of the molecules in theta solvents $\langle h_0^2 \rangle^{1/2}$ is expressed in the Flory-Fox equation (1951)

$$K_\theta = \frac{\Phi \langle h_o \rangle^{3/2}}{M^{3/2}} \tag{5}$$

The root mean square end-to-end distance in non-theta solvents $\langle h^2 \rangle^{1/2}$ is given by

$$\langle h^2 \rangle = \alpha \langle h_0^2 \rangle \tag{6}$$

where α represents the linear expansion coefficient and gives an estimate of the solvency conditions experienced by the polymer (Elias, 1977). The value of α can be approximated by the term

$$\alpha = ([\eta]/[\eta_0])^{1/3} \tag{7}$$

The radius of gyration of the molecule $\langle S^2 \rangle^{1/2}$ is given by

$$\langle S^2 \rangle = \langle h^2 \rangle / 6 \tag{8}$$

from which the hydrodynamic radius R_h is obtained

$$R_h = \xi \langle S^2 \rangle^{1/2} \tag{9}$$

where ξ has a theoretical value of 0.665.

Values of the polymer coil dimensions of the fractions used derived from Eqns. 3–9 are given in Table 2.

It is observed that the hydrodynamic radius of the coils where deviation from a straight line occurs (Fig. 3), corresponds approximately to the pore radius where

TABLE 2

MOLECULAR DIMENSIONS OF POLYVINYLALCOHOLS IN DILUTE AQUEOUS SOLUTION

Fraction	Molecular weight, M	α	$\langle h^2 \rangle^{1/2}$ (nm)	$\langle S^2 \rangle^{1/2}$ (nm)	R_h (nm)
D	95,900	1.243	35.0	14.3	9.51
F	76,200	1.224	30.7	12.5	8.31
J	36,700	1.166	20.3	8.3	5.52
M	22,400	1.129	15.4	6.3	4.19
N	13,700	1.091	11.6	4.7	3.13
O	5100	1.021	6.6	2.7	1.80

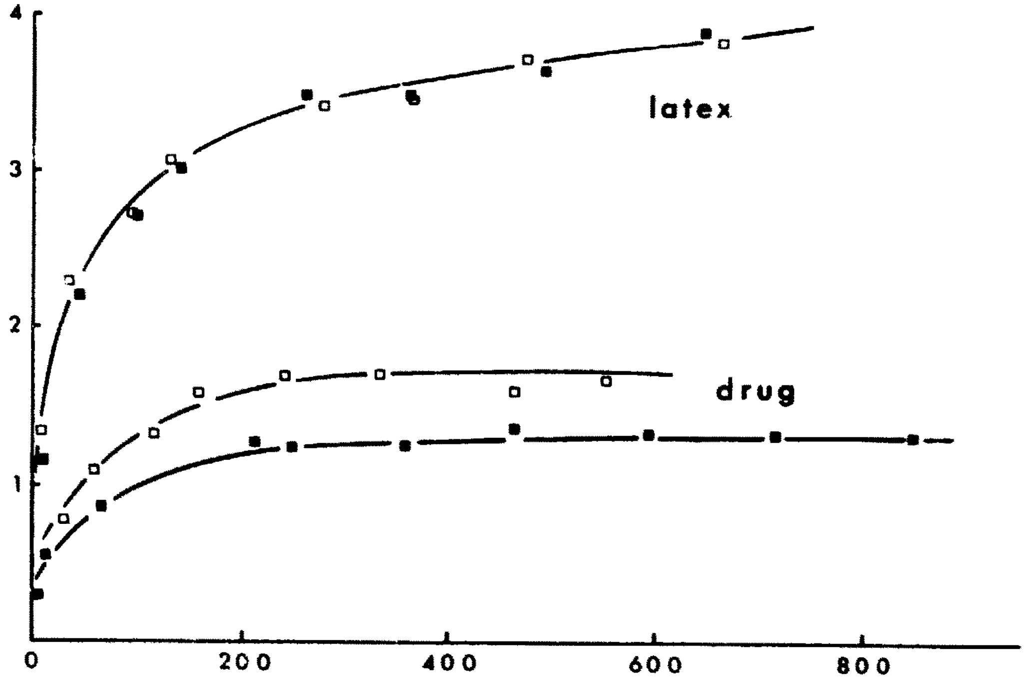

Fig. 6. Adsorption of fractionated and unfractionated PVA on polystyrene latex and diloxanide furoate B.P. in distilled water. ■, fractionated PVA, molecular weight 36,700; □, unfractionated PVA, molecular weight ~ 34,600. Ordinate: adsorption (mg·m^{-2}). Abscissa: equilibrium concentration (ppm).

significant numbers of pores are present. Confirmation that the increase in A_s at low molecular weights is due to the greater surface area afforded by the pore walls was obtained by comparing the adsorption of an unfractionated sample with the adsorption of a fraction of similar molecular weight. Fig. 6 shows the results obtained on adsorbing Moviol 8-88 and Fraction J onto latex and diloxanide furoate B.P. Little difference between the adsorption of fractionated and unfractionated samples is found on the latex whereas the unfractionated samples adsorb to a greater extent on the drug surface. Polystyrene latices do not possess pores (Ottewill and Shaw, 1967) and adsorption of the unfractionated PVA will be largely determined by the higher molecular weight species present in solution. In the case of diloxanide furoate adsorption onto the external surface of the powder proceeds as for non-porous material but smaller molecular species enter the pores giving the increase in total quantity adsorbed which is seen in Fig. 3.

It has been demonstrated that the maximum quantity of PVA adsorbed onto polystyrene latex and diloxanide furoate differ substantially. Similar findings were found for the adsorption of non-ionic surface active agents onto the same two substrates (Rawlins and Kayes, 1980). In all cases the amount adsorbed onto the latex exceeded that adsorbed at the drug–solution interface.

Possible explanations for the multilayer adsorption of polyvinylalcohol observed with the latex may be due to incipient phase separation of the polymer at the interface (Silberberg, 1972) or due to adsorption of polymer coil aggregates which

TABLE 3

CONTACT ANGLE MEASUREMENTS OF DRUG AND LATEX WITH EQUILIBRIUM SOLUTIONS

Material	Preparation	Contact angle
Polystyrene latex	–	102 ± 3°
Diloxanide furoate	steel punches	92 ± 3°
Diloxanide furoate	paper	91 ± 2°
Diloxanide furoate	polyethylene film	93 ± 2°

are known to exist in aqueous solution (Eagland et al., 1978). The approximate concentrations of the polymer fractions at the latex interface lie in the region of 5–20% w/v. No visual phase separation of a 14% w/v solution of Moviol 8-88 was apparent on heating to the boiling point and it is unlikely that incipient phase separation at the interface is responsible for multilayer adsorption. The work of Eagland et al. (1978) demonstrates the existence of two aggregating PVA species in aqueous solution occurring at 1 and 3% w/v of polymer. Such concentrations are far higher than the initial concentrations used to prepare the latex dispersions in this work and the high adsorption values cannot be explained in terms of aggregate adsorption.

It has long been recognized that the nature of the interface has a great effect on adsorption (Lipatov and Sergeeva, 1974) and some authors have indicated that the degree of surface hydrophobicity determines the extent of polymer adsorption at an interface.

As a measure of surface hydrophobicity the contact angle between solid substrate and the fluid in equilibrium with the surface was studied. The contact angles determined for the latex water system and the drug-saturated drug solution are given in Table 3. Little difference is observed between contact angles of powder compacts prepared by the various methods of compression and it can be concluded that the compression between steel punches is not a source of surface contamination.

The latex film exhibits a significantly higher contact angle indicating this to have a more hydrophobic surface than the drug. Results reported here for polystyrene are greater than those given by Ottewill and Vincent (1972) who measured contact angles by a captive bubble method. These differences may be due to the different techniques used to prepare the latices. The above authors used an emulsion polymerization technique and found the area occupied by the surface carboxylic acid groups to be 2.5 nm^2. This compares with 16.3 nm^2 for the latex used in this work. As such functional groups provide the only mechanism for surface charging this latex would be expected to be more hydrophobic. The conversion of the latex to a thin film does not affect the interfacial position of the surface carboxylic acid groups (Ottewill and Vincent, 1972), thus the greater hydrophobicity observed is not due to an artifact produced by film formation. The results of Tadros (1978) indicate that decreasing the surface hydrophobicity of silica reduces the maximum amount of

PVA adsorbed. This is in accord with the results reported here where the more hydrophilic drug surface adsorbs less polymer than the hydrophobic latex. The same applies for the adsorption of the non-ionic surface active agents previously studied (Rawlins and Kayes, 1980).

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