Viscosity, vapour pressure and electronmicroscope studies of aqueous solutions of polyvinylpyrrolidone

Intrinsic viscosity-molecular weight relationships for PVP solutions have been established by Frank, Eirich & Mark (1951) and by Frank & Levy (1953) on known molecular weight fractions. Jirgensons (1951) showed that with higher molecular weight fractions the intrinsic viscosity increased with rising concentration, but was independent of concentration in the lower fractions. All these studies used relatively dilute solutions; more concentrated solutions appear not to have been investigated. In the drying of heavy magnesium carbonate granules, Rubinstein (1972) found that similar drying rate curves were obtained for granules wetted with water and PVP solution. It thus appeared that the vapour pressure of the PVP solution used to granulate the magnesium carbonate remained constant as drying proceeded and was therefore independent of concentration. It also seemed that there was little change in the viscosity of the PVP solution, since the rate of movement of liquid to the evaporative interface was not significantly impaired even at low liquid concentrations. The present investigation confirmed these assumptions and the changes in viscosity and vapour pressure have been related to the probable mechanism by which orientation of PVP molecules occurs as concentration increases.

A modified isoteniscope was used to measure the vapour pressure of a series of PVP solutions (Plasdone K 29–32 G.A.F. Corp.) ranging from 1–50% w/v at temperatures from 19 to 60°. Temperatures were controlled by a thermostated bath to $\pm$ 0·1°. Kinematic viscosities of solutions of PVP were measured at 25° $\pm$ 0·1° with a suspended level viscometer. In addition graphs of shear rate against shear stress of 6 drops of the same solutions of PVP were plotted automatically using the large cone of a Ferranti—Shirley viscometer.

The vapour pressure curves of 0, 1, 5, 10 and 50% w/v were found to be identical; one curve fitting all the five series of points. To test whether the curves were identical and to show if there was any significant differences between them, a curve fitting process was employed (Peacock, 1967). It was found that there was a straight line relation between the fitted logarithm of the vapour pressure and the reciprocal of the absolute temperature. Application of the variance ratio test indicated that there was no significant change in vapour pressure of solutions of PVP up to 10% w/v. At 50% w/v the vapour pressure was slightly reduced. It was thus concluded that PVP solutions obey Raoult's Law over the whole solubility concentration range at least within the limits of experimental error when measuring vapour pressure.

A linear relation between log (kinematic viscosity) and PVP concentration was found when these values were plotted from the experimental data. At high concentration it was expected that the solutions would be very viscous but in fact a 45% w/v solution was still pourable having a viscosity of 300·2 cs. From the Ferranti-Shirley viscometer measurements it was found that a linear relation existed between shear rate and shear stress at all PVP concentrations and there was no hysteresis. Thus even at very high concentrations, PVP solutions appeared to behave as perfect Newtonian fluids.

The viscosity and vapour pressure data indicate that with increasing concentration PVP molecules aggregate to form spheres so that a minimum interparticulate contact area exists. This was confirmed by electronmicroscopy. A 10% w/v solution of PVP was injected into an electronmicroscope wet-cell and a micrograph produced at a magnification of 20 000. Spherical particles were observed and these were found to be of a consistant diameter between 0·15 and 0·2 μm.

It would further seem that as the concentration of PVP increases, the size of the

aggregates increase, whilst the number remains about the same. If the number of particles had increased much larger values for viscosity would have been found since there would now be a much larger contact area and the solutions would not have remained Newtonian. In addition a greater lowering of vapour pressure would be expected at high concentrations. It thus seems that as concentration increases the PVP aggregates grow in size, so as to still maintain a relatively small interparticulate contact area.

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Aqueous solubility of steroid hormones: an explanation for the discrepancy in the published data

Available data on the aqueous solubility of a number of steroids are scattered, to say the least (see Madan & Cadwallder, 1973 for references). Reliable data on aqueous solubility of steroid hormones is important in many aspects of biochemical and physiological studies besides their obvious value to the chemical and pharmaceutical industry.

With the availability of radiolabelled steroids, the measurement of the steroid concentration in a given sample (of known specific activity) has been rendered simpler and highly reliable. In more recent reports, therefore, radiolabelled steroids have been used for measuring the aqueous solubility. However, in many cases, membrane filters have been employed to separate the steroid in solution from the undissolved solute (see Madan & Cadwallder, 1973 for references). But these filters adsorb large quantities of the steroids from their aqueous solutions during filtration (Batra, 1974). The amounts adsorbed varied with different steroids. For example, over 95% of progesterone and only 10% of hydrocortisone from the respective aqueous solutions was taken up by the filter (Batra, 1974). These observations led to the re-examination of the aqueous solubilities of some steroid hormones.

Aqueous solubility was determined by the use of tritium labelled steroids. $[1,2-^3H]$-progesterone (48 Ci $mmol^{-1}$) and $[6,7-^3H]$oestradiol-17β (46 Ci $mmol^{-1}$) were purchased from New England Nuclear Corporation. $[1,2,6,7-^3H]$ Testosterone (102 Ci $mmol^{-1}$), was given by the Radiochemical Centre, Amersham. Radiochemical purity was checked by thin-layer chromatography. After equilibration for a predetermined time (see Fig. 1) under continuous shaking at room temperature (23–24°), the undissolved solute was separated from the solution by filtration through glassfibre (Whatman) filters which did not adsorb any significant amount of the steroid from its aqueous solution. To compare data, samples were also filtered through membrane filters simultaneously. Since only a fraction of the labelled steroid is in solution when relatively high concentration of steroids are used in the assay (Fig. 1), it is necessary to run blanks, containing all of the radioactivity in solution, simultaneously. Blanks containing 1 μg ml^{-1} of the respective steroid and the same amount of radioactivity