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AMOUNT OF POLYVINYL ALCOHOL (PVA) POLYMER ADSORBED ON THE OIL GLOBULES IN LIQUID PARAFFIN EMULSIONS PREPARED BY PVA

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ABSTRACT

A modified method for estimating polyvinyl alcohol (PVA) in solution has been developed based on the principle of formation of PVA-iodine complex which has a characteristic absorption maxima. The amount of PVA adsorbed on the oil globules in liquid paraffin oil-water emulsions prepared by the polymer was determined. This was found to be dependent on the concentration of the polymer in the continuous phase of the emulsion until it reached a saturation point. Beyond that concentration, the amount of adsorption remained steady.

Introduction

Polyvinyl alcohol polymer is used in various pharmaceutical preparations (Swinyard and Lowenthal, 1990). Emulsions can be prepared with PVA polymers having greater stability towards coalescence than do emulsions stabilized by surfactants (Lankveld and Lyklema, 1972). This may be due to the physical properties of the interfacial film between the oil and water phases, although little *work* has been done in this field. Buscall (1978) has shown that some polymers form complex with some surfactants resulting in a synergistic effect on emulsion stability, although the exact nature of the complex is not known. Mahrous and Lamberger (1968) studied the stability of hexadecane-water emulsions containing dioctyl sodium sulfosuccinate in presence of PVA and other higher molecular weight polymers. The theological, surface tension and stability of polyvinyl alcohol polymer solutions have been reported (Onogi et al., 1958; Onogi et al., 1963; Watase and Nishinari, 1983; Shiomi et al., 1984. Prokopova 4 and Stern, 1985; Ahmad et al., 1985; Ferdous, 1991a). In this study a modified method has been developed for the quantitative analysis of PVA in solution. The amount of PVA polymer adsorbed on the oil globules in liquid paraffin-water emulsions prepared by PVA have been determined. The adsorption data can be used to predict the stability of emulsions.

Materials and Methods

Polyvinyl alcohol (Fluka) polymer of three different molemdar weights, 22000 (P22), 49000 (P49) and 72000 (P72) were used. The first and third polymers were 975-995 mole percent hydrolyzed and the second polymer was 86-89 mole percent hydrolyzed. Light liquid paraffin (BDH) was used for emulsion preparation. All other reagents *were* of analytical grade.

PVA polymer solution was prepared in hot distilled water (79°C) with continuous stirring for 5-15 minutes. The solution was cooled and light liquid paraffin (50% w/w) was added to the polymer solution. The emulsion was prepared by homogenizing with a Silverson mixer emulsifier for five minutes.

The quantitative analysis of PVA was done by reacting the polymer with iodine which forms a complex and gives a characteristic absorption maxima (λ_{max}) (Zwick, 1965, 1966). This λ_{max} depends on the degree of polymerization, concentration of iodine, iodide ions and boric acid. For P22 and P72, the polymer solutions were prepared in 50 ml flask and Kl, $K10_3$, H_3BO_3 and sulfuric acid was added sequentially. The concentration of the three reactant were kept constant and the forth one was varied in a series of experiments in order to determine the optimum concentration of each reactant. Similarly for P49, the polymer solution was prepared in 50 ml flask and iodine and potassium iodide was added in varying concentration in order to determine the optimum concentration of the two reactants. The solutions were then transferred to screw cap tubes and stored at 5°C for three days. This was necessary for development of maximum color intensity after which the absorbance was measured at a specific wave length. At a certain concentration range, PVA shows linear relationship between absorbance and concentration which forms a straight line (Beer plot). The concentration of the unknown can be easily determined from the curve.

The amount of unadsorbed PVA in the emulsion was determined by centrifuging the emulsion at 4000 rpm (900 g) for two hours. The separated aqueous layer was collected and recentrifuged for 30minutes to remove any trace of oil globules. The clear aqueous layer was analyzed to determine the amount of unadsorbed PVA by the above method. Each experiment was done in triplicate and the average of the results was recorded.

Results and Discussion

The optimum concentrations of the various reactants required to produce the PVA-iodine complex and the corresponding absorption maxima are summarized in Table 1. Within the concentration range of the polymer, the absorbance of the PVA-iodine

complex follows the Beer's law. The unknown concentration of the polymer can be easily determined from the standard curve.

Table 1
Concentration of different reactants for the formation of PVA- iodine complex with the corresponding absorption maxima

Polymer mmol/l	I_2 mmol/l	KI mmol/l	KIO_3 mmol/l	H_3BO_3 mmol/l	H_2SO_4 nm	λ_{max}
PVA 22000 (0.2-1.0)	-	5	0.5	15	5	605
PVA 72000 (0.05-0.25)	-	3	0.5	50	5	610
PVA 49000 (0.1-0.5)	0.4	6.4	-	-	-	495

Fig. 1 shows the amount of PVA adsorbed on the oil globules as a function of the polymer concentration in the emulsion. In P22 emulsion, the amount of adsorbed polymer increased linearly with the concentration up to 4.5% of the polymer. Above that concentration it formed a plateau and PVA adsorption did not increase with the increase in the amount of polymer in the aqueous phase. P49 emulsion also showed initially a linear increase in adsorption of polymer similar to P22 emulsion. Above 35% of polymer concentration, the curve formed a plateau. In case of P72 emulsion, the amount of adsorption increased linearly with concentration and no plateau was observed.

In a polymer based emulsion, certain amount of polymer is adsorbed on oil globules and the remaining amount is in the continuous phase. The amount of polymer adsorbed is dependent on the concentration of the polymer and the volume of the oil phase. The amount of adsorbed polymer increases steadily until it reaches a saturation point, when further increase in polymer does not significantly alter the amount adsorbed (Fig. 1). This saturation phenomena can be explained on the basis of globule size. For P22 and P49 emulsions at 4.5% and 3.5% of polymer respectively, the globule size change was insignificant (Ferdous, 1991b). As the globule size does not change above that

concentration, there is no further increase in polymer adsorption. When the saturation point is reached, globule size is minimum and emulsion is most stable. So the stability of emulsions can be predicted on the basis of adsorption data.

Lankveld and Lyklema (1972) measured the amount of PVA adsorbed on oil globules in liquid paraffin emulsion. They prepared liquid paraffin emulsions having phase volume ratio of 0.02 and maximum concentration of PVA being 0.14%. They reported that in a typical PVA (MW 53000, 12% acetate group) emulsion at equilibrium, maximum amount adsorbed at interface was 0.07%, when the concentration of the polymer in continuous phase about 0.08% or more. In my PVA emulsions, the percentage of liquid paraffin was 50% (w/w) (q = 0.58 approx.). In my experiments with PVA 49000 polymer (12% acetate group) emulsion, it was found that at equilibrium, maximum amount adsorbed at interface was 1.95% (w/w) when the concentration of PVA in the emulsion was about 3.5%. In this experiment, emulsions were prepared where the saturation level for adsorption was achieved. For this reason greater amount of adsorption of polymer was observed which is significantly higher than those reported previously (Lankveld and Lyklema, 1972).

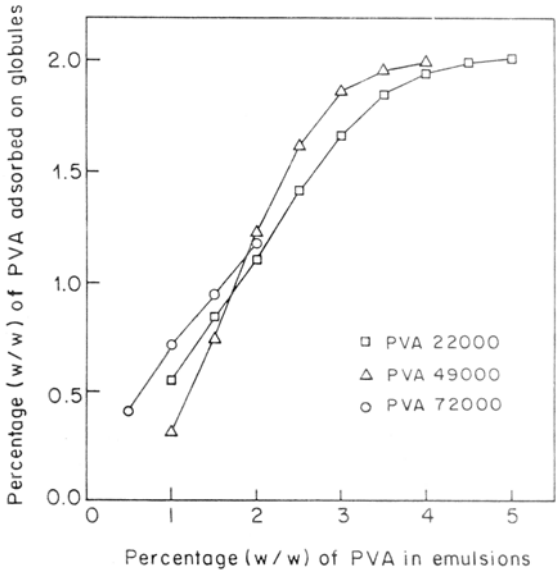

Fig. 1: Amount of polyvinyl alcohol (PVA) polymer adsorbed on the oil globules in PVA based emulsion.

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