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SPECTROPHOTOMETRIC STUDIES ON THE INTERACTION BETWEEN BENZOCAINE AND POLYMERS/MIXED POLYMER SYSTEM

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Abstract

The dynamical and morphological behaviour of PVP in presence of different additives was studied. Here-in we report the existence of different morphological arrangement and hydration states of PVP chain in aqueous medium. Interaction of benzocaine with PVP in presence of Sucrose, NaCl and Na_2SO_4effects the absorbance intensity (A_{max}) at λ_{max} which is due to the extent of delocalization of pi electrons in the aromatic moiety. The variations in absorbance values at different concentrations of PVP were determined using highly hydrated salt like Na_2SO_4 the PVP-water interaction lessen up and promote more of the intra-chain PVP-PVP interaction. As a result, the PVP-PVP complex become more compact with the increase in concentration of Na_2SO_4 and in return its solubilizing capability for benzocaine increases as indicated by increase in A_{max} value. Interaction between Benzocaine and PVP-gelatin mixed system and Benzocaine PVP-starch mixed system results in dilation of PVP chains with coiling, encapsulation and solubilisation of benzocaine as indicated by the increase in A_{max} values.

Keywords: Spectrophotometric, Benzocaine, Polymers, Mixed polymer,PVP

INTRODUCTION

The polymer-drug interactions have received an increasing attention in the last two decades because of its vast applications. Polymers are used in pharmaceutical techniques as thinner, suspending agent, emulsifier and solubility enhancer. They are also used to control drug release rate, enhance effective drug solubility, minimize drug degradation, and reduce drug toxicity. The studies on the polymer-drug interactions help to meet these objectives. The commonly used techniques available areviscometer, NMR spectroscopy, UV-Vis spectroscopy, *etc*. UV-vis spectra and steady state Fluorescence spectroscopy are rapid and relatively inexpensive analytical technique, which allows great application on study of the interaction in complicated systems containing chromophore composition. The general properties of polymers, drug, surfactants and additives are highlighted here before the presentation of polymer-drug interaction studies. Polymers are high molecular mass material composed of repeated monomer units. It shows unique physical properties like toughness, viscoelasticity and a tendency to form glasses. Most of the polymersconsists hydrocarbon as their backbone in which carbon-carbon atom linked to each other to form long chains [1]. All polymers are macromolecules, but all macromolecules are not polymers.There are varieties of polymers that have been reported so far, but our interest is with the water soluble polymers which can be useful as drug carries, to reduce the drug toxicity and degradation, to control drug release rate, *etc.* Some of the water soluble polymers arepolyethylene glycol (PEG),poly vinyl alcohol (PVA), Poly(vinyl-pyrrolidine) (PVP), etc. These are considered to be non-toxic, safe and biocompatible by FDA [2].Poly(vinyl-pyrrolidine) (PVP) is a synthetic polymer consisting of linear 1-vinyl-2-pyrrolidone groups [3]. Its backbone contains an amide group, having a poly-n-vinyl-amide structure.The radical polymerisation of

International Journal of Modern Agriculture, Volume 9, No.3, 2020
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N-vinyl-pyrrolidone can be done by bulk, suspension or solution polymerisation to yield polymer with degrees of polymerisation between 10 and 10^5.

PVPis water soluble, nontoxic, biocompatible, chemically inert, pH stable, non-ionic, temperature resistance and colourless polymer. It can absorb 40% of water by its weight. The glass transition temperature (Tg) of PVP can vary from 100°C (for $M_w = 2.5 \times 10^3$ g mol^{-1}) to 175°C (for Mw of $\sim 10^6$ g mol^{-1}) depending upon its average molecular weight.It interacts with various organic solvents, including alcohols, some chlorinated compounds such as chloroform, methylene chloride and ethylene dichloride, nitro-paraffin, and amines). At and above a certain concentration, the solution becomes highly viscous [4].

PVP is widely used in pharmaceutical industry and medicine due to its excellent biocompatibility and capability to form stableassociation compounds and complexes with many active substances [5]. PVP has many applications in all kinds of drugs and, since its particle sizes are between 1-100nm, it simply passes through the kidney when it is taken orally[6]. However, the polymer is not metabolized by the body, resulting that after parenteral administration; high molecular components may remain within the organism in small quantities. However, many investigations have shown that when PVP used as a coating to delay the release of the drug in order to have a prolongedactivity and to eliminate daily multiple dosage.

Benzocaine is an ester group containing local anaesthetic and has been used predominantly as an external pain reliever. It is obtainedfrom the esterification of p-amino benzoic acid (PABA) and ethanol[7]. It is white odourless powder having crystalline structure, stable, combustible and incompatible withoxidizing agents. It has low water-solubility. The melting point of benzocaine is 88–90ºC, and the boiling point is about 310°C. It is more soluble in dilute acid and very soluble in ethanol.

Hydrophilic polymers are those polymers which dissolve in, or are swollen by water[8]. More than two-thirds of hydrophilic or water-soluble polymers used in industry are derived from polymers of natural origin, coming from renewable resources (harvested crops, trees, waste animal products and so on), rather than petrochemical sources of finite availability.Hydrophilic polymers have the potential to be biocompatible and have therefore attracted extensive attention in biomedical and drug delivery applications.They can be tailor-designed at both the molecular level and the device level. At the molecular level, they can be synthesized as homo-polymers of a single hydrophilic monomer, or as random or block copolymers of a hydrophilic monomer with either hydrophilic or hydrophobic monomers. They can also be grafted onto the backbone of other polymers, or made into branched structures with varying degrees of branching [9]. At the device level, hydrophilic polymers can be fabricated into a variety of physical forms, including cross-linked hydrogel matrices of different geometries and dimensional cross-linked micro-particles and nanoparticles. In nature hydrophilic products like protein, keratin or wool are responsible for water vapour permeability. The easiest way to obtain water vapour permeability for a chemist should be the use of hydrophilic polymer. There are a lot of existing polymeric materials which are hydrophilic, e.g. proteins, cellulose, polyethylene glycols ethers, polyamides and polyacrylic amides etc.

Water soluble polymers (polymer in aqueous solution) with pendant hydrophobic substituents associate with water to form extensive varieties of structures [10]. Solutions of the polymers have important applications in technologies ranging from paints and paper coatings (as rheology modifiers) to DNA sequencing (where the network structure serves as a sieving medium). To enhanced control of rheology behaviour it is necessary to take polymer in aqueous solution which builds viscosity through transient polymer association. These systems exhibit several unusual properties, and the broad variation of behaviour with polymer composition, architecture and type; and degree of hydrophobic substituent offers broad versatility for their applications [11]. Polymer dissolve in solvent according to its solubility capability, some are more crystalline cannot dissolve at room temperature, thereby high temperature (60-70ºC) can be used or we can say crystalline polymer generally dissolve near their melting temperature.

Criteria for solubility of polymer [12]

1. The dissolution process: Dissolution of polymer has two steps:
   - Formation of swollen gel (high polymer-polymer intermolecular forces because of crosslinking, crystallinity, strong H-bond).
   - Complete dissolution of polymer molecules (When overcomes the intermolecular forces).
2. Polymer texture:
   - Size difference in polymer, solvent molecules, viscosity of the medium and polymer system, nature of solvent or temperature,large molecular weight and molecular weight distribution in polymer.
3. Cross-linked polymers do not dissolve but swell in solvent.

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4. Other thermodynamics parameters also required.

Physical mixtures of different types of polymers (blends or alloys) are utilized extensively to produce commercially useful materials having combinations of properties not normally found in a single polymer. Many of the properties and processing characteristics of a blend of two polymers depend on whether they are miscible or not, the nature of the phase diagram, or interfacial behaviour in phase separated mixtures [13]. The quantitative methods developed to evaluate the compatibility of two different polymer systems are based upon the fact that repulsive interactions cause shrinkage of the macromolecular coils so that the viscosity of the mixture decreases with respect to the viscosity of the binary mixtures formed by the polymers. There is a reason, since in such dense and entangled systems fundamental interactions maybe too complex and it is unclear how they relate to macroscopic gel behaviour. So, it is necessary to explore the knowledge of interaction parameters. Polymer-polymer mixtures are governed by the same thermodynamic principles that apply to mixtures of small molecules; however, there are some important differences in the relative magnitudes of certain terms owing to the high molecular weight of polymers and potential complications owing to polydispersity of molecular weight. The simplest theory that accounts for the issues of polymer chain size is the Flory-Huggins theory for the free energy of mixing [14]. The present study was undertaken in order to test the consistency between the polymer 1 and polymer 2 interaction parameters calculated from technique i.e. UV-Spectrophotometer.

Effect of electrolytes on the solution properties of polymer

Addition of electrolytes to the aqueous polymer/s solution can alter the solubility of polymer/s. Aqueous system of water soluble polymers and electrolytes undergo phase separation into polymer-rich phase and electrolyte-rich phase with water as solvent in both phases. The aqueous nature and difference in properties of both the phases have increased their use in partitioning and phase separation of biological materials like enzymes, proteins, metal ions, dyes, drugs, small organic molecules and nano/microsolidparticles from the complex mixtures in which they are produced [15]. The effect of addition of salts in polymer solution is very complex because large number of different type of intermolecular interactions comes into play between ions and water, polymer/s and water, ions and polymer/s. This is further complicated by the fact that the extent of interactions varies in relation to the types of ions and polymers involved. The presence of salts in the aqueous polymer/s solution alters their dynamical and morphological behaviour in the solution [16]. When the diffusion layer is compressed to a thickness close to zero, the negative charge on the surface of the polymer molecular chain is nearly completely neutralized, which leads to the reduction in its hydrodynamic size, the electrical shielding of its ionic groups, the weakening of the repulsive force within polymer molecular chain, and then resulting in curled up polymer molecules [17].

Present investigation has been undertaken with the perspectives to explore the dynamical and morphological behavior of PVP in aqueous medium in the absence and presence of other water soluble polymers and additives. The structural change in the polymer aggregates is known to influence the degree of association with certain organic molecules. Benzocaine is UV-Visible active molecule and its binding with polymers is largely depends upon the nature and structure of polymer aggregates. The binding between benzocaine and polymer influence the π-electron transitions and therefore the change in the absorbance intensity by benzocaine is observed. The benzocaine molecule is used here as sensor to monitor transition in the polymer aggregates in the absence and presence of other additives through the variation in absorbance values.

MATERIALS AND METHODS

Benzocaine (with purity ~99% was purchased from Himedia, Mumbai, India). The stock solution of benzocaine of 5.0×10^{-3} mol dm^{-3} was prepare in ethanol. Polyvinyl pyrrolidone K-30 (PVP) with an average molecular weight (MW) of 40,000 was supplied by CDH, New Delhi, India. Using double distilled water stock solution of PVP (5%), starch (2.0 %) Gelatin (2%) Sucrose (1.0×10^{-1} mol dm^{-3}), NaCl(1.0×10^{-1}mol dm^{-3}), Na_2SO_4 (1.0×10^{-1}mol dm^{-3}) were prepared.

Genesys10S UV/Visible double beam spectrophotometer (ThermoFisher scientific, Madison, USA) having multiple cell holders was employed to carry out the spectroscopic measurements. The spectralscans were recorded each time at constant interval by taking the aliquots in 3 mL quartz cuvette of 10 mm path length.

RESULT AND DISCUSSIONS

Interaction between Benzocaine and PVP

The solution sets containing benzocaine (3.0×10^{-5}mol dm^{-3}) along with different [PVP] (2.0 % to 8.0 %) were spectrophotometrically scanned in between 230-350 nm wavelengthband. The change in absorption spectra with

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the change in the concentration of PVP at fixed [Benzocaine] is shown in Fig. 1(a). The obtained result is a consequence of π-electron delocalization in the benzocaine structure in presence of PVP and also due to the solubilisation of benzocaine by the aid of PVP solution.For clear demonstration of the obtained results regarding the absorbance variation at λ_{max} (284 nm) with changing [PVP] a graph has been plotted for A_{max} *versus* [PVP] as shown in Fig. 1(b). Also the value of A_{max} corresponding to their [PVP] has been listed in Table 1.

The A_{max} *versus* [PVP] plot depicts a linear increase in the A_{max} values from 1 – 3% [PVP] (Region I), thereafter, a consistency in the A_{max} values have been shown in between 3 – 5% [PVP] (Region II) and finally an abrupt increase in the A_{max} values have been reported from 5 - 8% [PVP] (Region III). The obtained pattern in the behaviour of A_{max} *versus* [PVP] plot is the result of associated complex formation between benzocaineand PVP with different morphological arrangement of PVP chains at different concentration in the aqueous phase. Hydrophobic and electrostatic interaction might be the responsible forces for the interaction among the benzocaineand PVP which help in the transition of π-electrons in the benzocaine molecule that leads to the change in the absorption intensity of the obtained spectra for the solution [18, 19]. Also with the change in [PVP], the polymer chains acquire different conformations that influence the extent of interaction between benzocaine and PVP and in return the absorption intensity of the spectra changes.
Region I (Fig. 1(a)) outlining the linear increase in absorption intensity provides an idea about the existence of uncoiled, dilated PVP chains in the solution whose interaction with Bz increases with increase in its concentration from 1 – 3%. The plateau region with almost constant absorption intensity in region II suggests the polymer-polymer interaction region of PVP. The intra-chain interactions among the different PVP segments are dominant over benzocaine-PVP interaction in this region and hence reported uniformity in the absorption intensity. In region III the PVP chains start forming dense entanglements that encapsulates the benzocaine molecules inside them and hence increase their solubilisation as well as delocalization of π-electrons.

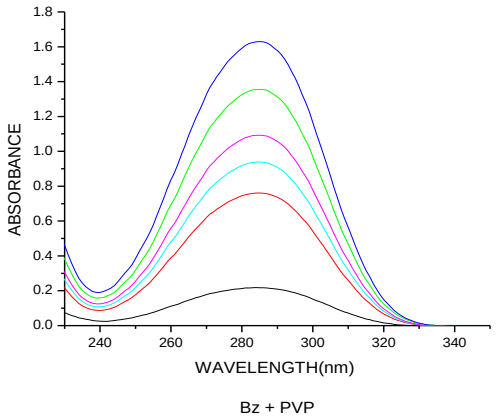

Fig. 1(a): Absorption spectra for fixed benzocaine at different [PVP].

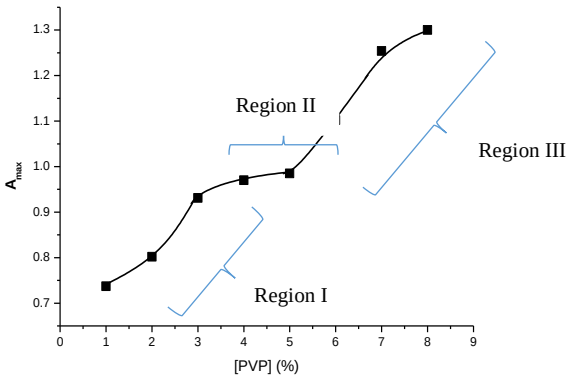

Fig. 1(b): A_{max} vs [PVP] plot for solution containing 3.0×10^{-3} mol dm^{-3} benzocaine.

Inter[illegible]ed system

The interaction behavior of benzocaine with PVP-gelatin mixed medium has been studied spectrophotometrically at fixed [benzocaine] (3.0×10^{-3} mol dm^{-3}) and [PVP] (2% / 4%). Two different concentration of PVP i.e. 2% and 4% has been chosen each from dilute polymer region (region I; Fig. 1(b)) and polymer-polymer interaction region (region II; Fig. 1(b)) respectively in order to study the role of their morphology on the mixed system. Benzocaine containing solution (3.0×10^{-3} mol dm^{-3}) andPVP (2% / 4%)were scanned at different gelatin concentration ranging from 0.1×10^{-2}%to 2.4×10^{-1}%. Fig. 2(A) shows the variation in absorption intensity of the spectra with the change in [Gelatin] at fixed [benzocaine](3.0×10^{-3} mol dm^{-3})and [PVP] (2%). The plot for A_{max} versus [Gelatin] for PVP (2%) is shown in Fig. 2(b). The plot show double peak behavior with the increase in [Gelatin]. There have been evidences of miscibility of PVP and gelatin with one another due to the interaction among the functional groups of the synthetic and biological components of these polymers. The C=O group of PVP form H-bond with –OH groups present in the gelatin backbone. Moreover the presence of positively ($-NH_3^+$) and negatively ($-COO^-$) charged monomeric groups in the gelatin backbone impart it amphoteric nature which in turn provide different conformational arrangements and segmental

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ISSN: 2305-7246

interactions (H-bonding, hydrophobic effect and electrostatic interactions) of the polymer chain in the aqueous medium [20].

In case of Bz + PVP (2%) + Gelatin mixed system, the peaks might be the result of increased solubilization of benzocaine molecules by the H-bonded complex formed between the dilated PVP (2% corresponds to dilution region; Fig. 1(b)) chains and the gelatin segments. With further increase in gelatin concentration the conformation of the gelatin chains might get changed that disfavors the complexation with PVP segments and hence drop in benzocaine solubilization.

The change in absorption intensity with the change in [Gelatin] for solution containing benzocaine, PVP (4%) and different [Gelatin] is shown in Fig. 3(a). Fig. 3(b) shows the change in A_{max} with varying [Gelatin].The traced plot initially show peak behavior and thereafter an abrupt increase in the A_{max} value with the increase in [Gelatin].In this case the PVP chains were in polymer-polymer interaction region (PVP 4%; Fig. 1(b)), on the addition of gelatin, the PVP-gelatininteraction get dominant over intra-chain PVP-PVP interaction. As a consequence the resulting PVP-Gelatin complex will start solubilizing the benzocaine molecules, aiding π-electron transition in its structure and hence the increase in A_{max}. Beyond certain [Gelatin], the change in gelatin conformation weakens the PVP-Gelatin interaction and brings downfall in A_{max}values. Finally the sudden rise in the A_{max}values suggests the conformation of gelatin again suitable for favorable interaction with PVP segments.

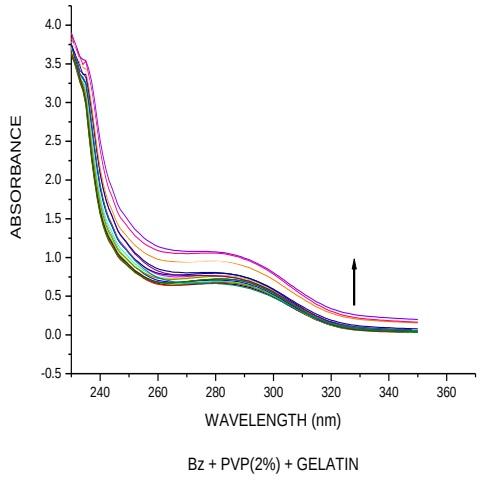

Fig. 2(a): Absorption spectra for solution with fixed benzocaine, PVP (2%) different [Gelatin].

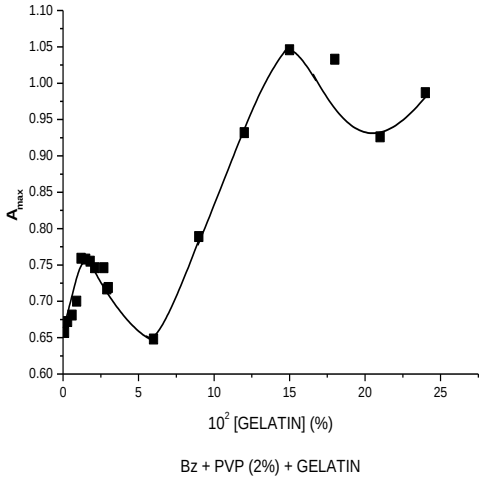

Fig. 2(b): A_{max} vs [PVP] plot for solution containing 3.0×10^{-3} mol dm^{-3} benzocaine and 2% PVP with different [Gelatin].

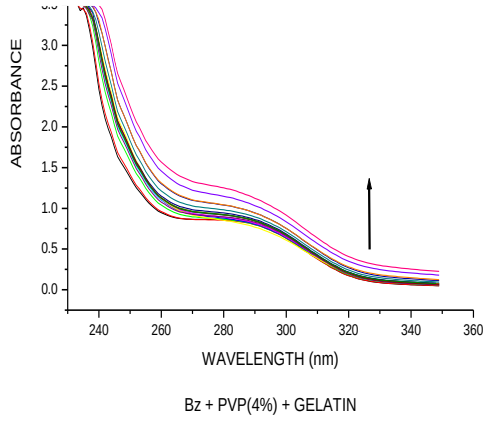

Fig. 3(a): Absorption spectra for solution with fixed benzocaine, PVP (4%) different [Gelatin].

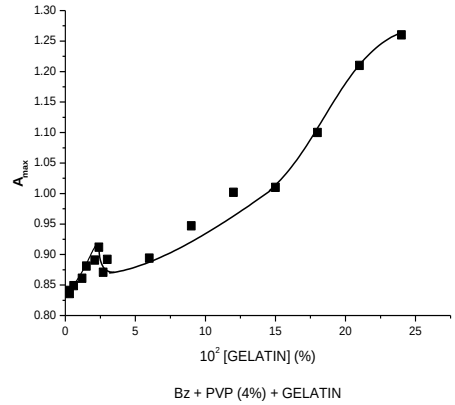

Fig. 3(b): A_{max} vs [PVP] plot for solution containing 3.0×10^{-3} mol dm^{-3} benzocaine and 2% PVP with different [Gelatin].

International Journal of Modern Agriculture, Volume 9, No.3, 2020
ISSN: 2305-7246

Interaction of benzocaine with PVP-Starch mixed system

The interaction of benzocaine (3×10^{-5}moldm^{-3})with PVP (2% and 4%)in presence of different [Starch] has been studied. The repetitive scans performed at different [Starch](ranging from 1.0×10^{-2} mol dm^{-3} to 8.0×10^{-1} moldm^{-3}) with fixed [Benzocaine](3×10^{-5} moldm^{-3})and [PVP] (2%) is shown in Fig. 4(a). The variation in absorption intensity at λ_{max}(284 nm) with the corresponding [Starch] in presence of 2% PVP is represented in Fig. 4(b). The graph shows a steady rise in A_{max} values from 35.0×10^{-2} to 80.0×10^{-2} mol dm^{-3} [Starch] followed by a crest at 10.0×10^{-2} mol dm^{-3}[Starch]. The PVP-Starch blend system show intermolecular associations by the formation of H-Bond between C=O groups in PVP and–OH groups in Starch and through weak intermolecular interactions between the hydrophobic -C-H groups present in both polymeric chains that were earlier confirmed by various techniques like FTIR, NMR etc [21].

Initial increase in A_{max} values from 1.0×10^{-2} to 10.0×10^{-2} mol dm^{-3}[Starch] in Fig. 4(a) indicates the dissolution of benzocaine molecules by the PVP-Starch associated complex formed between dilated and uncoiled PVP and Starch segments that supportelectronic transitions in benzocaine.The drop in A_{max} values from 20.0×10^{-2} to 30.0×10^{-2} mol dm^{-3} [Starch], suggest polymer-polymer interaction region of starch that favours intra-chain Starch-Starch interaction rather than PVP-starch interaction. Again the sudden rise in A_{max} from 35.0×10^{-2} to 80.0×10^{-2} mol dm^{-3} [Starch], indicates the formation of complex between the entangled starch chains with uncoiled PVP segments encasing the benzocaine molecules.

Similarly, the absorption spectra for the solution set containing benzocaine (3×10^{-5}moldm^{-3}) and PVP (4%)in presence of different [Starch] is traced in Fig. 5(a). The A_{max} versus [Starch] data is plotted in Fig. 5(b). The graph show similar behavior as for Bz + PVP (2%) + Starch but with more intense dig in the A_{max} values from 9.0×10^{-2} to 40.0×10^{-2} mol dm^{-3} [Starch].

The concentration of PVP taken in the following set i.e. 4% falls in polymer-polymer interaction region for PVP (Region II; Fig. 1(b)). It might be considered that the polymer-polymer interaction region for starch has its onset from 9.0×10^{-2} mol dm^{-3}and become maximum at 20.0×10^{-2} mol dm^{-3} (this concentration coincides with the one in Fig. 4(b); both show maximum fall in A_{max} value) . At this point the two polymers present in the system favours intra-chain PVP-PVP and Starch-Starch interaction over intra-chain PVP-starch interaction. The rupture in PVP-Starch complex solubilizing benzocaine molecule in these concentration ranges (9.0×10^{-2} to 40.0×10^{-2} mol dm^{-3})brings a downfall in A_{max} values. Thereafter the starch segments start forming entanglements with PVP-PVP interacted chains that encase the benzocaine molecules and favourenhancement in the π-electron delocalization and solubilization as suggested by rise in A_{max} in Fig. 5(b).

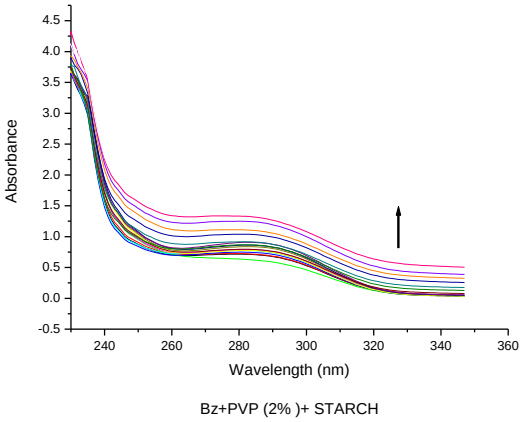

Fig. 4(a): Absorption spectra for solution containing fixed benzocaine, PVP (2%) at different [Starch].

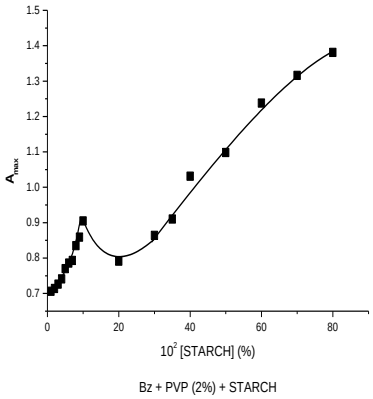

Fig. 4(b): A_{max} vs [PVP] plot for solution containing 3.0×10^{-3} mol dm^{-3} benzocaine and 2% PVP with different [Starch].

International Journal of Modern Agriculture, Volume 9, No.3, 2020
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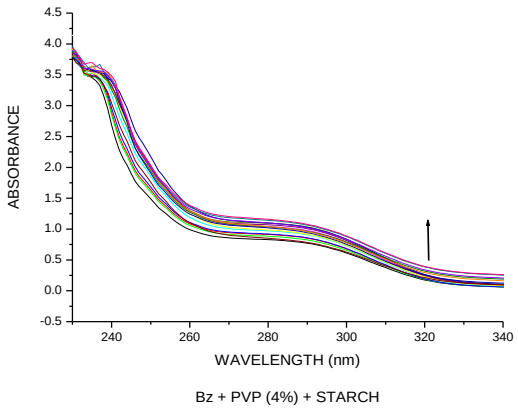

Fig. 5(a): Absorption spectra for solution containing fixed benzocaine, PVP (4%) at different [Starch].

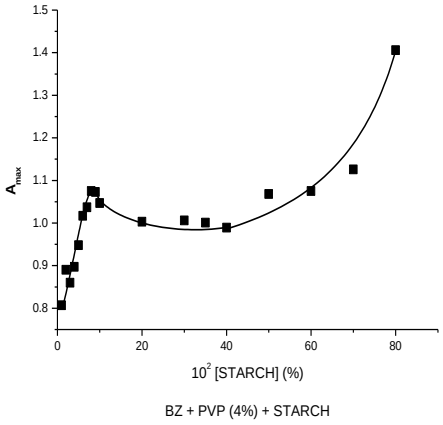

Fig. 5(b): A_{max} vs [PVP] plot for solution containing 3.0×10^{-3} mol dm^{-3} benzocaine and 4% PVP with different [Starch].

10.0×10^{-2} mol dm^{-3} at fixed[benzocaine] (3×10^{-5}moldm^{-3})and [PVP](2%).It is distinctly clear from Fig. 6(b)that the absorption intensity at λ_{max}(A_{max}) of the solution changes with the sucrose concentration variation. The dynamical behaviour of hydrophilic polymers in aqueous medium depends upon the water structure associated to them. Presence of electrolytes (like NaCl, KCletc) and non-electrolytes (Sucrose, Urea etc) alter the water structure and hence the affinity for water/ hydration capacity of these polymers in the medium. Sucrose falls in the category of water structure forming agent [22]. The U-shaped curve obtained in Fig. 6(b) suggests the decrease in the Benzocaine-PVP interaction due to the competence of PVP with sucrose for water up to 2.0×10^{-2} mol dm^{-3} [Sucrose] (sucrose is water-structure forming agent). Beyond that it is suggested that the sucrose starts acting as salting-out salt for PVP and decreases its affinity for water. Dilated PVP chains began coiling and encapsulating benzocaine and hence solubilisation of benzocaine starts increasing as indicated by the increase in A_{max} values.

Similarly the spectrophotometric scans were performed for solution containing fixed [benzocaine] (3×10^{-5}moldm^{-3}), [PVP](4%) with different [Sucrose] (2.0×10^{-3} mol dm^{-3} to 10.0×10^{-2} mol dm^{-3}) (Fig. 7(a)). The A_{max} versus [Sucrose] plot (Fig. 7(b)) shows rise in A_{max} at all [Sucrose]. The [PVP] in this set falls in polymer-polymer interaction region that were thought of capable enough to solubilize the benzocaine molecules. Moreover the presence of sucrose keeps on hampering the solubilising capability of PVP by decreasing its water affinity with increasing [Sucrose].

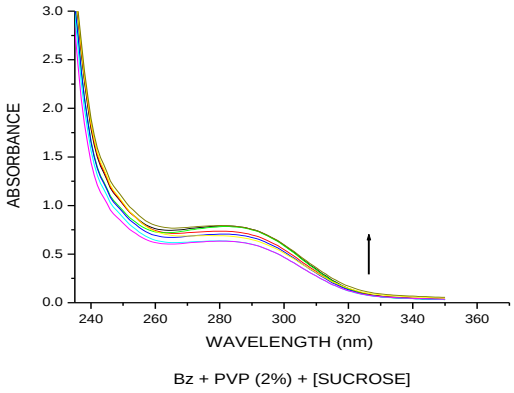

Fig. 6(a): Absorption spectra for solution containing fixed benzocaine (3.0×10^{-3} mol dm^{-3}), PVP (2%) at different [Sucrose].

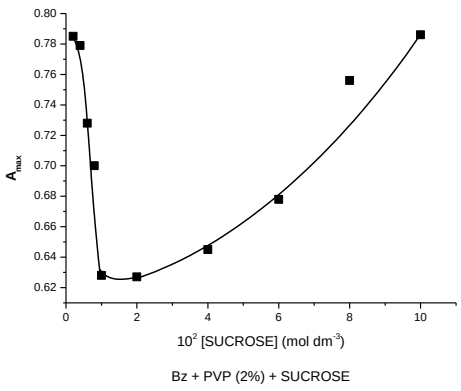

Fig. 6(b): A_{max} vs [PVP] plot for solution containing 3.0×10^{-3} mol dm^{-3} benzocaine and 2% PVP with different [Sucrose].

International Journal of Modern Agriculture, Volume 9, No.3, 2020
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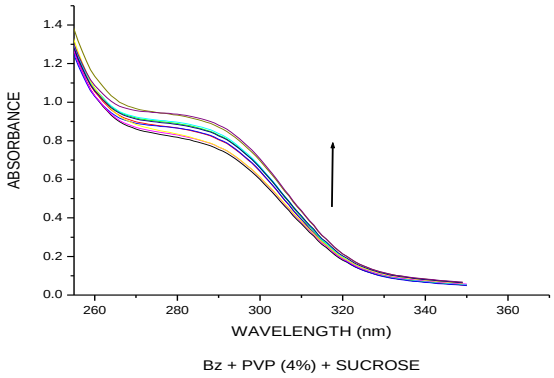

Fig. 7(a): Absorption spectra for solution containing fixed benzocaine, PVP (4%) at different [Sucrose].

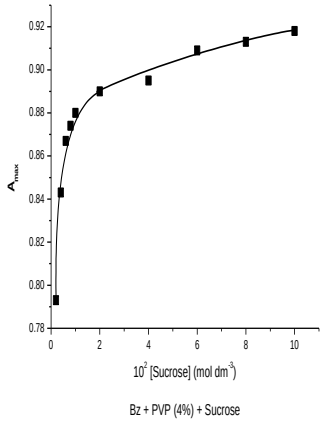

Fig. 7(b): A_{max} vs [PVP] plot for solution containing 3.0×10^{-3} mol dm^{-3} benzocaine and 4% PVP with different [Sucrose].

$^{-5}$moldm^{-3})and [PVP](2%) at a different [NaCl](varying from 2×10^{-2} mol dm^{-3} to 5×10^{-2} mol dm^{-3}) is traced in Fig. 8(a).Fig. 8(b) shows the variation in $A_{max}$with the change in [NaCl].The plot initially shows peak behavior and then gradual decrease in A_{max}. NaCl is regarded as weakly hydrated salt [23]. Its affinity for water to create a hydration shell around itself is considered to be comparatively lower than PVP. Initial addition of NaCl in the medium is thought to abstract some hydration sphere form PVP but is insufficient to disturb the PVP segments to contest for water.With increase in [NaCl] enough room has been created for benzocaine in PVP segments to get attached with and experience electronic transition in its structure. As a result the A_{max} plot attain maxima type curve in lower [NaCl]. Increase in [NaCl] the PVP segments start facing challenges to maintain its hydration sphere as earlier and start competing with NaCl molecules. As a result the morphology of the PVP segments start altering and its interaction with benzocaine keeps on decreasing as evidence from decrease in A_{max}Fig. 8(b).

Similar trend for A_{max} versus [NaCl] has been observed for solution of 3×10^{-5}moldm^{-3} benzocaine, 4% PVP at a different [NaCl] (varying from 0.2×10^{-2} mol dm^{-3} to 5.0×10^{-2}mol dm^{-3}) (Fig. 9(b)). The spectrum for the following set has been represented in Fig. 9(a). The decrease in A_{max} values at higher [NaCl] is more abrupt in present case as compared to the set containing 2% PVP. The reason for the obtained trend is thought to be same as in case of solution containing 2% PVP. The removal of hydration sphere from PVP-PVP interacted segments (4% PVP; polymer-polymer interaction region) at lower [NaCl] (upto10×10^{-2} mol dm^{-3})is not ample to disturb the morphology of polymer segments to disrupt its interaction with benzocaine. While at higher [NaCl], in order to maintain its hydration sphere, the PVP segments start contesting with NaCl. In doing so, the PVP-PVP interaction might get disturb and hence the compaction of PVP-PVP complexes accommodating benzocaine molecules start loosening up which brings about sudden decrease in A_{max} value.

International Journal of Modern Agriculture, Volume 9, No.3, 2020
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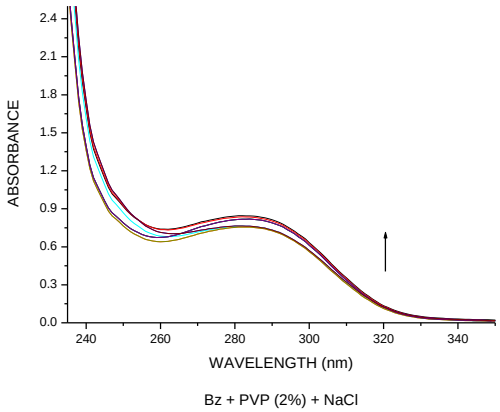

Fig. 8(a): Absorption spectra for solution containing fixed benzocaine (3.0×10^{-3} mol dm^{-3}), PVP (2%) at different [NaCl].

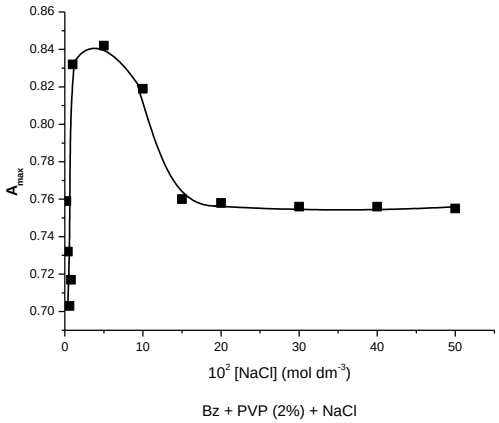

Fig. 8(b): A_{max} vs [PVP] plot for solution containing 3.0×10^{-3} mol dm^{-3} benzocaine and 2% PVP with different [NaCl].

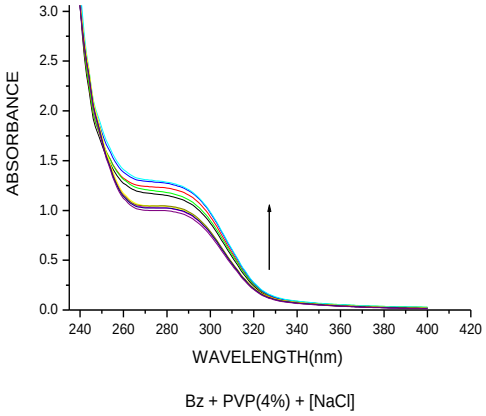

Fig. 9(a): Absorption spectra for solution containing fixed benzocaine (3.0×10^{-3} mol dm^{-3}), PVP (4%) at different [NaCl].

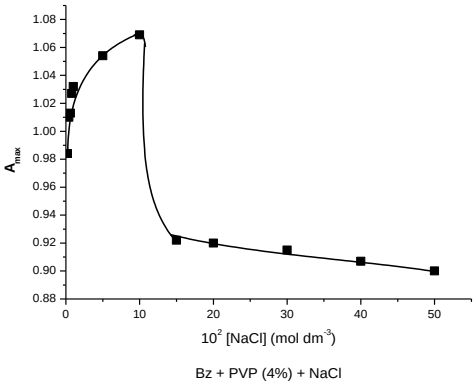

Fig. 9(b): A_{max} vs [PVP] plot for solution containing 3.0×10^{-3} mol dm^{-3} benzocaine and 4% PVP with different [NaCl].

Interaction of benzocaine with PVP in presence of Na_2SO_4

The cooperative pattern of benzocaine with PVP (2%) at varying [Na_2SO_4] is studied by tracing absorbance variation. The absorption spectrum of the solution is shown in Fig. 10(a). The figure shows the change in absorption intensity of the solution with the change in the concentration of Na_2SO_4. For more clear demonstration the plot for the A_{max} versus [Na_2SO_4] is presented in Fig. 10(b). The plot show a sudden downfall in A_{max} values from 0.2×10^{-2} mol dm^{-3} to 1.0×10^{-2}mol dm^{-3} and then an abrupt increase in same.$Na_2SO_4$is regarded as highly hydrated salt [24]. The addition of Na_2SO_4in the medium trigger an impact on PVP segments to maintain its hydrosphere due to which the PVP chains start widening up to attract more water molecules toward itself. Hence the morphology of the polymer segments is thought to acquire more relaxed confirmation that lessen up its contact with benzocaine molecules and decreases its solubilisation. Beyond 2.0×10^{-2} mol dm^{-3}

International Journal of Modern Agriculture, Volume 9, No.3, 2020
ISSN: 2305-7246

[Na_2SO_4],the concentration of Na_2SO_4might become enough high to abstract water from polymer segments and forcing it to acquire comparatively more confined morphology. Such a structure of PVP binds more of the benzocaine molecule with itself and increase the π electron transition in its structure which is accompanied by the increase in A_{max} value.

The repetitive scan of solution holding benzocaine (3×10^{-5} mol dm^{-3}) and PVP (4%) along with varying [Na_2SO_4] (from 0.2×10^{-2} mol dm^{-3} to 10.0×10^{-2}mol dm^{-3}) is shown in Fig. 11(a). The variation in A_{max} values with corresponding [Na_2SO_4] is plotted in Fig. 11(b). The graph shows an increase in A_{max} values with the increase in [Na_2SO_4]. Since the water molecules are associated with PVP by dipole-dipole interaction. On addition of highly hydrated salt like $Na_2SO_4$the PVP-water interaction lessen up and promote more of the intra-chain PVP-PVP interaction (the [PVP] (4%) choosen in the following set falls in the polymer-polymer interaction region; Fig. 1(b)). As a result the PVP-PVP complex become more compact with the increase in [Na_2SO_4] and in return its solubilizing capability for benzocaine increases as indicated by increase in A_{max} value in Fig. 11(b).

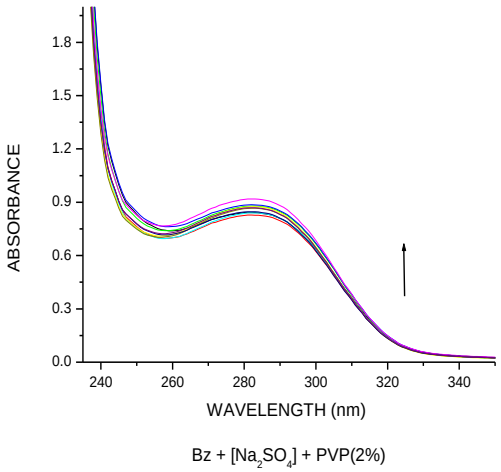

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Fig. 10(a):Absorption spectra for solution containing fixed benzocaine,PVP (2%) at different [Na_2SO_4].

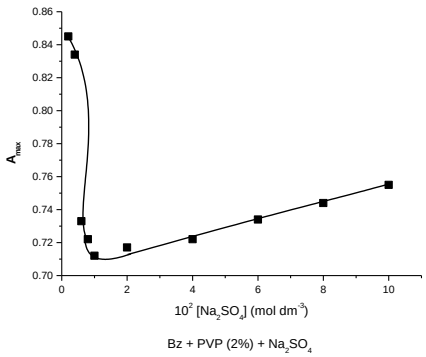

Fig. 10(b): A_{max} vs [PVP] plot for solution containing 3.0×10^{-3} mol dm^{-3} benzocaine and 2% PVP with different [Na_2SO_4].

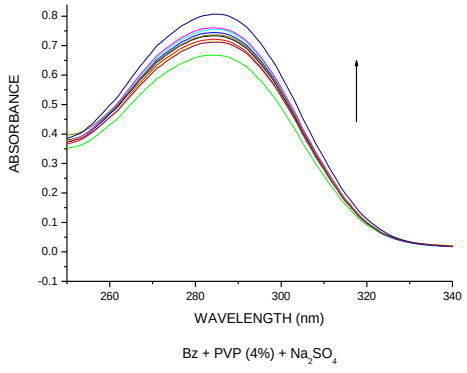

Fig. 11(a): Absorption spectra for solution containing fixed benzocaine, PVP (4%) at different [Na_2SO_4].

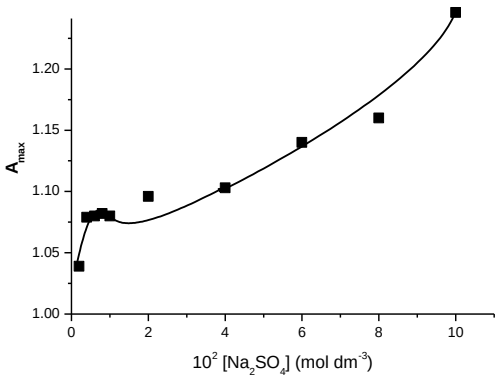

Fig. 11(b): A_{max} vs [PVP] plot for solution containing 3.0×10^{-3} mol dm^{-3} benzocaine and 4% PVP with different [Na_2SO_4].

International Journal of Modern Agriculture, Volume 9, No.3, 2020
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CONCLUSION

Benzocaine a local anaesthetic containing ester group is an UV-active molecule that undergoes π- electron transition on combining with suitable agent. Attempt has been made to exploit these effects of benzocaine to study the dynamical and morphological behaviour of PVP in presence of different additives. A diverse range in absorbance values at different concentrations of PVP were determined and correlated with other additives like electrolyte (sucrose, NaCl and Na_2SO_4) and non-electrolyte (Gelatin and Starch). PVP has propensity to amass in different morphologies in aqueous solution. Concentration of PVP and its aggregation relies on the presence of additives which influences the absorbance values of benzocaine. The absorption intensity undergoes alterations with the variation in concentration of PVP advocating the amount of electrostatic or hydrophobic interaction between the benzocaine and PVP. The delocalization of π electrons of benzocaine molecules is influences by variation in binding and hence results in change in absorbance intensity (A_{max}) at λ_{max}. Our results imply the occurrence of hydration states of PVP chain in aqueous medium with various morphological arrangement.

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CONFLICT OF INTEREST

No conflict of interest.

CONTRIBUTION OF AUTHORS

All authors have made substantial contribution to the work and approved it for publication.

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