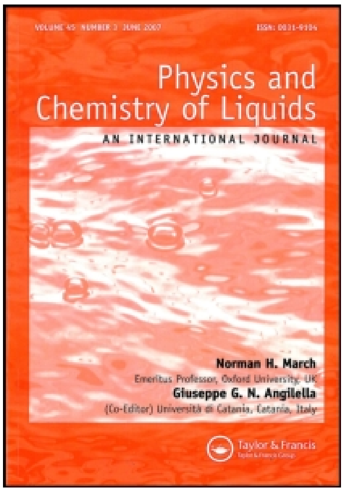

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Preparation, molecular weight determination and structural studies of (polyvinylpyrrolidone)-oximate silico-benzoyl glycine copolymer with IR spectroscopy at pH 7

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Preparation, molecular weight determination and structural studies of (polyvinylpyrrolidone)-oximate silico-benzoyl glycine copolymer with IR spectroscopy at pH 7

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Polyvinylpyrrolidone (PVP)-oximate silico-benzoyl glycine (POSBG), a glycine copolymer, has been prepared with PVP-oxime and benzoyl glycine in a 1 : 1 ratio, w/w, in ethanol medium. The ethanolic solution with silicic acid [$Si(OH)_4$] as binder in same ratio was refluxed for 2–3 h resulting in colloidal solution, which was further refluxed for 2 h and cooled to 37°C for 15 min. After this, a whitish solid material settled, which was separated by vacuum filtration followed by washing several times with aqueous ethanol at ordinary conditions. The average viscosity molecular weights ($\bar{M}_v$) of PVP-oxime and the copolymer were determined with their respective dilute aqueous solutions at pH 7. Primarily the calibration curves between the intrinsic viscosity [η] data and their respective molecular weights of PVOH (polyvinyl alcohol) (marker) have been obtained to determine the $\bar{M}_v$ of oxime. Similarly the $\bar{M}_v$ of the copolymer was determined with the [η] data of lysozyme (molecular weight = 24,000 $g\,mol^{-1}$), Egg albumin (40,000 $g\,mol^{-1}$) and Bovine Serum Albumin (BSA) (65,000 $g\,mol^{-1}$). The IR spectra of the PVP-oxime and copolymer were recorded in Nujol, which do not depict band frequency of –OH group of the binder. The 1602, 1688, 1182 and 1127 cm^{-1} stretching vibration frequencies noted in the spectra infer the presence of –C = N, –C=O, –Si–O–Si– and –Si–O–C– functional groups, respectively, in the copolymer.

Keywords: Average viscosity molecular weight ($\bar{M}$v); PVP-oxime; Silicic acid; Benzoyl glycine; Glycine copolymer; Stretching vibration frequencies

1. Introduction

Currently preparation of polymer materials [1] with several chemical moieties has been fascinating for the purpose of nanotechnological applications [2], especially weakly conducting synthetic biopolymers due to their tremendous applications in biochips, biophysics and drug delivery systems. However, the polymer composites have been an asset for multipurpose uses [3,4], but most of them are non-degradable materials and non-structural compounds without any specific trends of their physico-chemical properties. Thus a preparation of the copolymers with various applications in several

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fields have been urgent need of the hour; therefore, in the present work, the copolymer of polyvinylpyrrolidone (PVP)-oxime and benzoyl glycine assisted by silicic acid is prepared and structurally characterised with IR spectroscopy. The copolymer is supposed to be biocompatible as it has amino acid in its structural framework and also conducting material due to silicon. As a concept of developing silicon-based electronic copolymer has never been reported before, the preparation of oxime from PVP, benzoyl glycine and adjoining them with binder (silicic acid) and formation of copolymer is fundamentally a new concept to prepare the bindlex on the pattern of preparations based on condensation reactions. Such compounds are of current industrial interest and can open new channel in the fields of nanotechnology [5] as a biosensor [6] in the field of science and technology and semiconductors. The structural elucidation of such compounds has become an informatory approach for assessing the feasibility of their structure for structure-based applications like synthesis, etc. Such work might boost up the semiconductor and defense sciences for coded messages, optics [7], etc and facilitate the other allied sciences [8–10] emerging for specific applications in conducting materials. These have been the grounds to choose the present studies for developing the copolymer materials with silicon as hub of molecule that introduces the conducting properties in the material.

2. Experimental

The PVP (Merck), glycine (AR, Merck), tetraethylorthosilicate (TEOS; Merck) and benzoyl chloride (AR, Merck) were used as received. The preparation of the copolymer was undertaken via four-step procedure – firstly, the PVP-oxime was prepared by conducting the reaction of the PVP with hydroxylamine hydrochloride in a 1 : 1 ratio, w/w, in alkaline medium by adding aqueous 5 mL of 1 N NaOH. These contents were taken in 250 mL capacity RB flask and stirred on electric shaker for 15–20 min; during this, a white precipitate of PVP-oxime was formed [11]. It was filtered through Whatman filter paper no. 41 with vacuum pump followed with washing several times with 30% aqueous ethanol solutions. The substance was vacuum dried by keeping it in the vacuum chamber for 24 h.

Secondly, the benzoyl derivative of glycine was prepared where the chloride (Cl^-) atom of the benzoyl chloride reacts with amino ($–NH_2$) functional group of the glycine that protects the $–NH_2$ group exposing the $–COO^-$ group to react with the binder, $Si(OH)_4$. Their specific amounts were taken for reaction, as 5 g of glycine was dissolved in 100 mL of 10% aqueous sodium hydrogen carbonate ($NaHCO_3$) solution followed by adding 10 g of benzoyl chloride. This mixture was shaken vigorously in a stoppered flask for 10 min and refluxed for 10 min, it involves evolution of CO_2 in the reaction mixture; therefore the stopper was removed from time to time to ease out its pressure. Initially the reaction mixture gives an odour of the benzoyl chloride, which ceases with time, indicating the completion of the reaction for benzoyl glycine compound. Afterwards, the latter was acidified with dil. HCl to form insoluble compound, which filtered off. The residue, the desired product, was washed several times and recrystallised, with absolute alcohol, and the m.p. of the dried sample was determined and found to be 187°C. The sample was dried in P_2O_5-filled vacuum desiccator. The presence of the nitrogen was confirmed with Lassaigne's test and of $–COO^-$ with $NaHCO_3$ wet test, respectively, and also with CHN analyzer, the compound is referred to as benzoyl glycine in the text.

2.1. *Preparation of silicic acid TEOS*

Thirdly, the TEOS was hydrolysed using a sol-gel technique [7,8] by employing an ethanolic solution of TEOS in 1 : 2 ratio, v/v, in 250 mL RB flask. One millilitre of ethanolic TEOS solution was dissolved in 4 mL of 1N KOH in a 1 : 4 ratio, v/v, to hydrolyse the TEOS into silicic acid. These contents in RB flask were refluxed for 15 min using a water condenser of length 25 inches, thereafter the mixture was air cooled for half an hour. On cooling, a whitish solid precipitate was formed, which was filtered, washed and dried as of PVP-oxime to get the pure form of the silicic acid. Finally, the copolymer was prepared with the PVP-oxime, benzoyl glycine and silicic acid by admixing together in 1 : 1 : 1 ratio, w/w, in 500 mL RB flask and subjected to condensation for about 2.30 h resulting in the copolymer compound. The latter was filtered off and washed several times with 20% aqueous ethanol; the yield of the copolymer was found to be 7.5 g, i.e. 80.6%.

3. Results

The data for the average viscosity molecular weight determination were obtained with dilute solutions of the copolymer and are given in tables 1–3. The FTIR spectra of PVP-oxime, BDG and POSBG were recorded in the form of a thin film within a KBr disc using a Nicolet Protégé-460 Spectrometer and are depicted in figures 1, 2 and 3 respectively. Two physicochemical functions, viz. viscosity and density, are plotted as a function of concentration in figure 4(a) and (b), respectively for physicochemical characterization.

4. Discussion

The vibration frequencies of the PVP-oxime (figure 1) confirm the presence of –C=N stretching at 1643.17 cm^{-1} and –C–N stretching at $-1469.28\,\text{cm}^{-1}$ (s), the –C–H stretching at 2989.22 cm^{-1} (b) confirms the side chain (polyvinyl chain). The stretching at 3400 cm^{-1} infers the presence of the –OH attached to N atom, which is attached to the C of the pyrrolodine ring. The vibration frequencies of BDG were noted at 3341.73 cm^{-1} (s) for –N–H stretching, at 1687.81 and 1602 cm^{-1} for –C=O, 1454 and 1421 cm^{-1} for –C–N stretching, 1325 cm^{-1} for –OH deformation and 707 cm^{-1} for $-(CH_2)_n$, respectively. The presence of the nitrogen was confirmed by wet Lassaigne's

Table 1. The reduced viscosities (η_{red}) and densities (ρ) of the PVP, PVP-oxime and copolymer in aqueous solutions at 298.15 K.

	PVP			PVP-oxime			Copolymer		
Conc. c (%)	ρ	η	η_{red}	ρ	η	η_{red}	ρ	η	η_{red}
0.01	0.99962	0.89754	0.74509	0.99923	0.92790	4.15355	0.99891	0.91288	2.46705
0.04	0.99966	0.90335	0.34942	0.99928	1.00161	3.10669	0.99941	0.94766	1.59272
0.07	0.99971	0.90917	0.29290	0.99933	1.00184	1.77889	0.99992	0.95624	1.04771
0.10	0.99976	0.91498	0.27029	0.99938	1.01971	1.44590	1.00042	0.99245	1.13987
0.14	0.99982	0.92273	0.25522	0.99944	1.01998	1.03493	1.00109	1.07231	1.45449

Units: $\rho \pm 6 \times 10^{-5}$ (g cm^{-3}), $\eta \pm 6.6 \times 10^{-5}$ ($\text{g cm}^{-1}\,\text{s}^{-1}$) and $\eta_{\text{red}} \pm 5 \times 10^{-5}$ (mL g^{-1}).

Table 2. The viscosities (η) and densities (ρ) of the Bovine Serum Albumin, egg albumin and lysozyme (used as markers) aqueous solutions at 298.15 K.

Conc. c in %	$\rho \pm 10^{-5}$ (g cm^{-3})	$\eta \pm 10^{-5}$ (10 g cm^{-1} s^{-1})
Bovine Serum Albumin		
0.0010	0.99641 ± 6.2	0.7895 ± 6.6
0.0014	0.99622 ± 6.2	0.7992 ± 6.6
0.0018	0.99619 ± 6.2	0.8085 ± 6.6
Egg albumin		
0.0010	0.99625 ± 6.2	0.7614 ± 6.6
0.0014	0.99623 ± 6.2	0.7769 ± 6.6
0.0018	0.99623 ± 6.2	0.7917 ± 6.6
Lysozyme		
0.0010	0.99634 ± 6.2	0.8039 ± 6.6
0.0014	0.99621 ± 6.2	0.8041 ± 6.6
0.0018	0.99607 ± 6.2	0.8065 ± 6.6

Table 3. Limiting densities (ρ^0) with slope values (S_d) and intrinsic viscosities [η] with slope values D for the markers in aqueous solutions at 298.15 K.

Protein	ρ^0 (g cm^{-3})	S_d (g^2 cm^{-3} mol^{-1})	[η] (mL g^{-1})	D (g mol^{-1})^2
Bovine Serum Albumin	0.9964	−0.2764	−32.58	22,606.0
Egg albumin	0.9963	−0.0220	−96.01	51,987.0
Lysozyme	0.9967	−0.3383	8.45	−1698.1

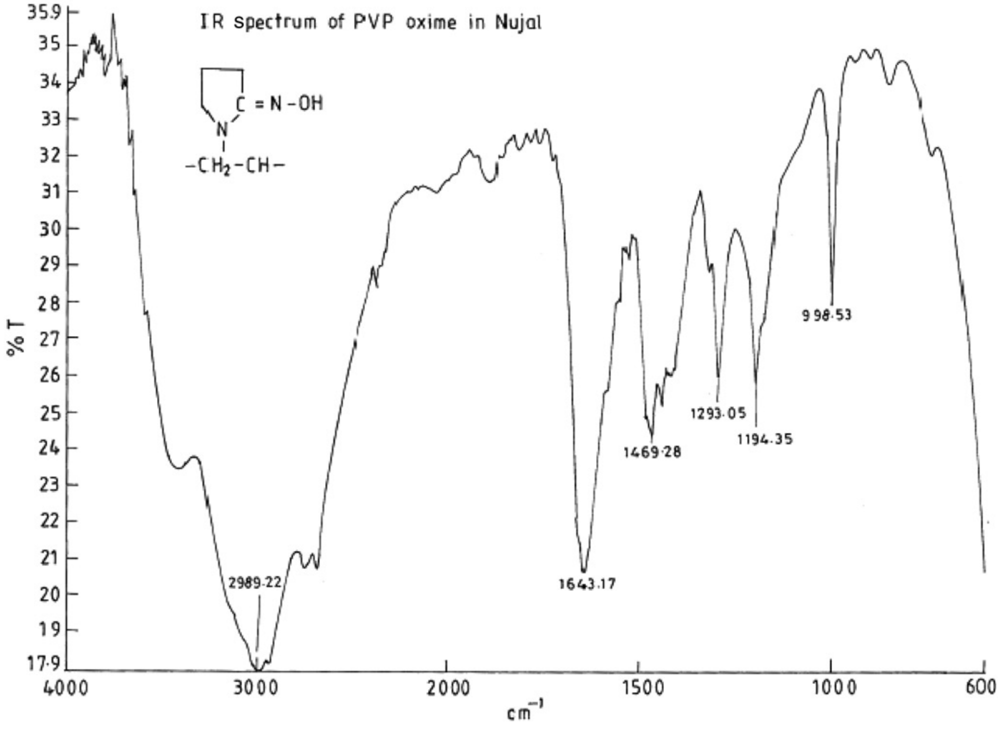

Figure 1. IR spectra of PVP-oxime in Nujol with stretching frequencies.

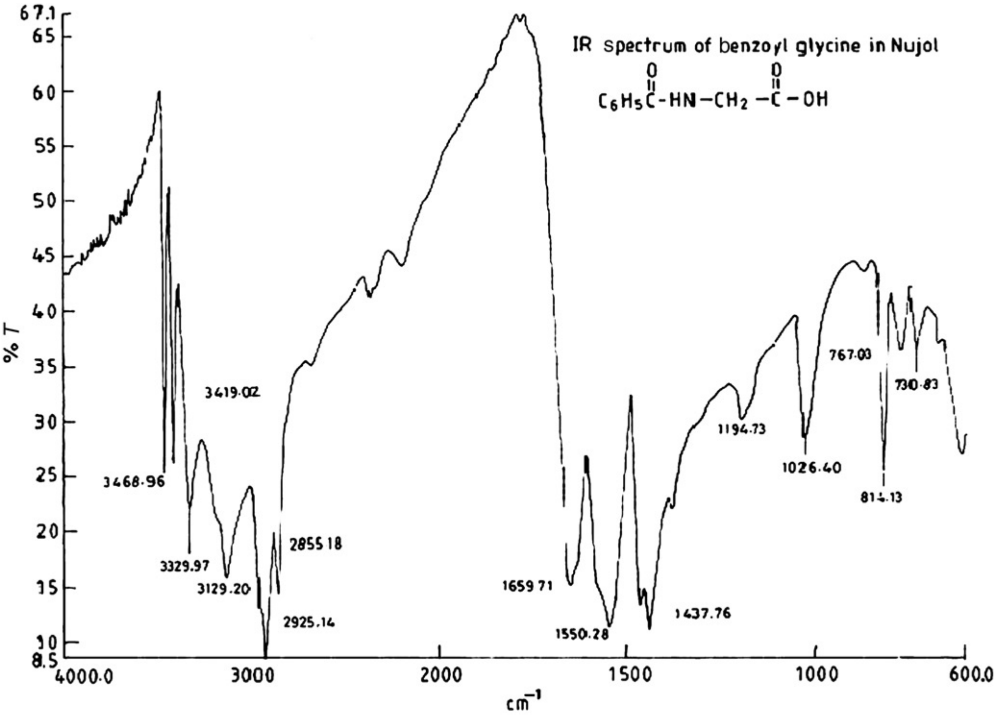

Figure 2. IR spectra of benzoyl glycine in Nujol with stretching frequencies.

test; the copolymer was found soluble in water. The vibration frequencies for POSBG confirm the –C–H strec at 2924.28 cm^{-1} for side chain, at 1688.96 cm^{-1} for –C=O strec, at 1602–1582 cm^{-1} for –C=N strec, 1454 cm^{-1} for –C–N strec, at 1182 and 1127 cm^{-1} for –Si–O–Si strec and –Si–O–R (R = ethoxy alkyl group) asymmetric stretching, respectively.

4.1. *Molecular weight determination of prepared molecule*

Viscometeric measurement [12] on the dilute aqueous solutions of the PVP-oxime and the copolymer has been made at 298.15 K for molecular weights determination. The viscosity (η) values are the functions of the size and shape of the polymeric molecules, the PVP-oxime is found linear, and the copolymer spherical in shape, where head to tail or head to head fashion arguments seem to be less prominent. As the alternative attachments of the PVP-oxime and benzoyl glycine, units with silicon atom seem to be the most appropriate. The 0.005–0.050% aqueous solutions, at an interval of 0.005%, each of the PVP-oxime and copolymer, w/v, were prepared separately for measurements of times for flow viscous for 10.1 mL each of solution and solvent, respectively, with Survismeter [13] having capillary of 0.5 mm internal diameter, under constant experimental conditions. The η values were calculated with $\eta/\eta_0 = \eta_r = (t/t_0) \cdot (\rho/\rho_0)$ relation; the η and η_0 functions represent the values of viscosities, t and t_0 the flow times and ρ and ρ_0 the densities of solution and water, respectively, and the η_r parameter denotes the value of the relative viscosities. Triple distilled, deionised and degassed

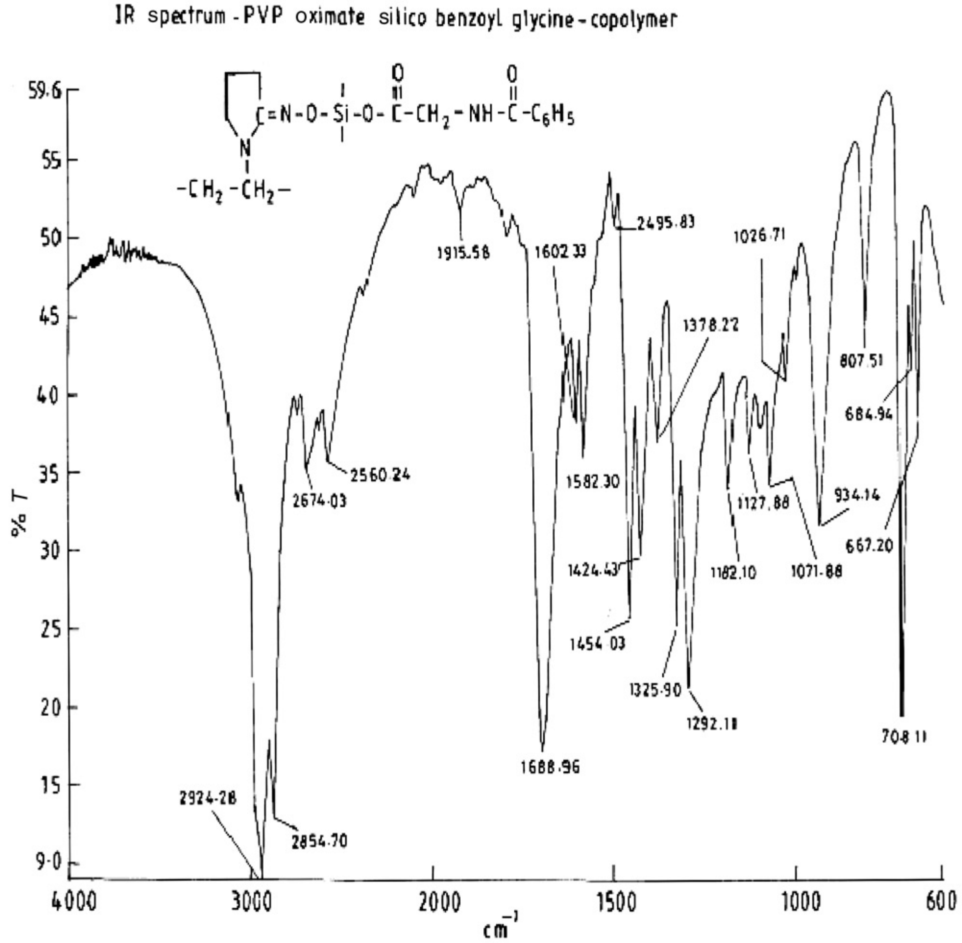

Figure 3. IR spectra of PVP-Oximate silico benzoyl glycine copolymer in Nujol with stretching frequencies.

water, of $1 \times 10^{-6}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ conductivity, was used as a reference solvent and for solution preparation, respectively.

The B/t and kinetic correction (k) for Survismeter were obtained from the relation $\eta = (k - B/t)$ with solution of known η values, and the B/t and k values are found to be -0.1821×10^{-4} and 1.8977×10^{-4}, and -0.20508×10^{-5} and 2.32647×10^{-5} at 298.15 and 303.15 K, respectively. Survismeter constant B with distilled water is calculated from $\eta/\rho = Bt - V/8\pi rLt$, where V is the total volume of water that flows, r the radius and L is the length of the capillary. The densities were measured with a $20 \times 10^{-3}\,\mathrm{dm}^3$ bicapillary pycnometer [14] with 0.01mg analytical balance model 100DS (Instruments Pvt. Ltd., Calcutta, India) under constant experimental conditions. Prior to weighing the solutions with pycnometer, they were separately thermostated for about 30 min in water bath; before weighing, the pycnometer was absolutely dried with tissue paper. The densities (ρ) were calculated with $\rho = ((w - w_0/w_0 - w_e))\rho_0 + 0.0012\,(1-(w - w_0/w_0 - w_e))$ equation, ρ_0 is the density of water, $0.0012(1 - (w - w_0/w_0 - w_e))$ buoyancy correction in weights in air, the w_e, w_0 and w are weights of empty

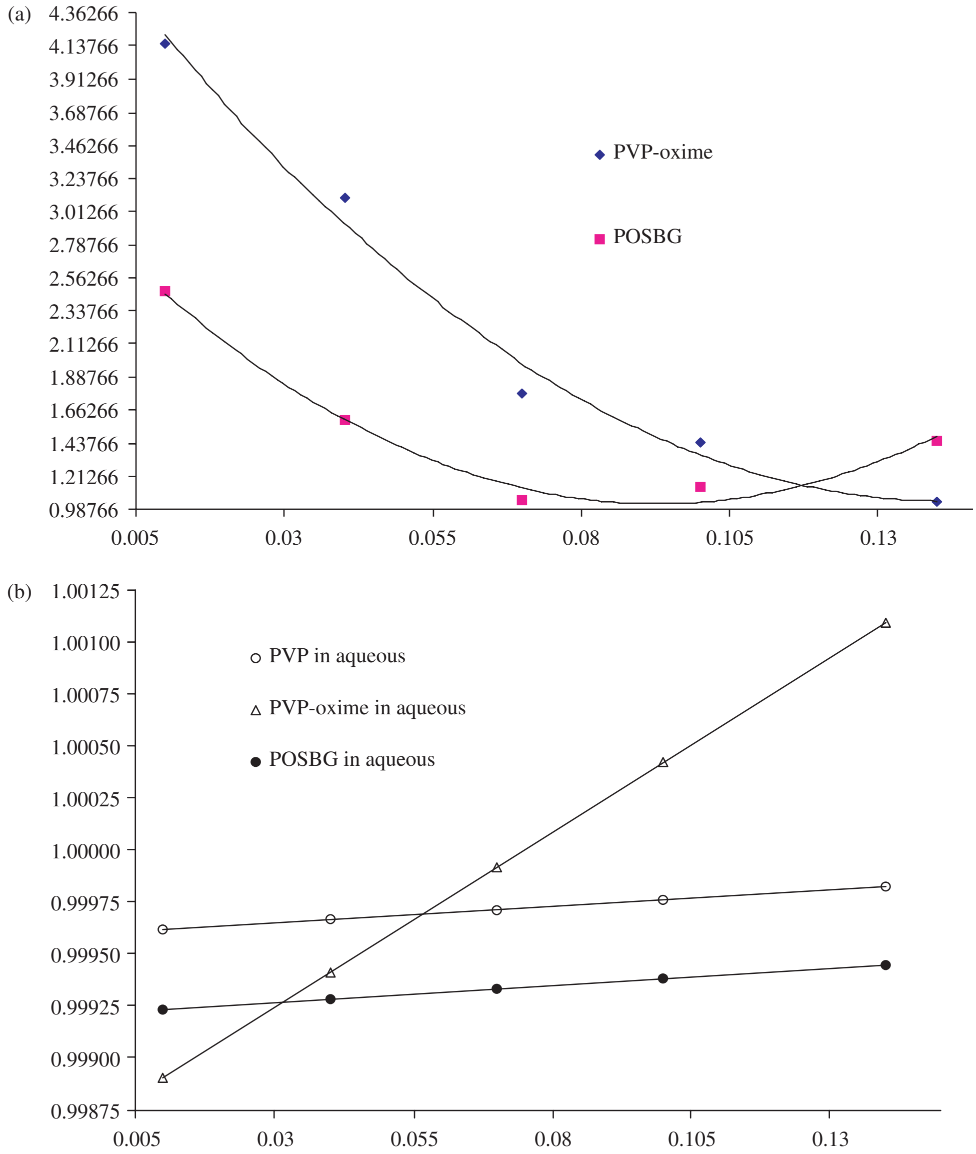

Figure 4. (a) *Y*-axis denotes the η_{red} values and *X*-axis the concentrations *c* in percent for aqueous PVP-oxime and copolymer solutions. (b) *Y*-axis depicts the density values and the *X*-axis, the concentration in percent. POSBG denotes the copolymer.

pycnometer, solvent- and solution-filled, respectively.The molecular weight can be obtained with end group analysis and osmometry but the intrinsic viscosities $[\eta]$ are assumed as an effective technique for its determination. The PVP-oxime and copolymer were found soluble in water, thus the η_r values were measured for 0.005–0.050 g per 100 mL solutions at 298.15 K. The $[\eta]$ values derived from the η_r values were fitted to Mark–Houwink equation for the $\bar{M}_v$ values [4]. The η_{sp} denotes the values of the specific viscosity which are calculated from the $\eta_{sp} = (\eta_r - 1)$ relation, and the reduced viscosity ($\eta_{red} = \eta_{sp}/c$) values compute the $[\eta]$ values according to:

$$\eta_{red} = \frac{\eta_{sp}}{c} = [\eta] + Dc. \tag{1}$$

Thus the η_{sp}/c *versus* c values are plotted and the values of the $[\eta] = \eta_{sp}/c,\ _{c \to 0}$, the c is composition in g/100 mL and the D denotes the slope values. Several solutions of different compositions of PVOH of different molecular weights were prepared for the viscosity data. Similarly the $[\eta]$ values for each solution of PVOH of 45,000, 50,000, 65,000 and 70,000 g mol^{-1} for calibration curve were determined. The PVOH is feebly hydrolysed and develops hydrogen bonding with water; thereby its aqueous solutions behave as standard for $[\eta]$ values for PVP-oxime. Thus the $[\eta]$ values were determined for PVP-oxime and fitted on the calibration curve; it gave 40,042 g mol^{-1} molecular weight of PVP-oxime.

4.2. *Gel permeation chromatography (GPC)*

The GPC for PVOH was run in 45 cm length with 3 cm inner diameter borosil glass column with packing of fine glass wool at its lower end and silica (SiO_2) gel slurry in water as stationary phase. The gel phase was maintained completely wet. Firstly, the 0.005–0.150 g per 100 mL solution of each sample of PVOH of known molecular weights was run at 1 mL min^{-1} followed by elution with water. The η_r values for each elution volume (V_e) was measured for $[\eta]$ data and plotted against V_e to determine constants 'K' and 'a' according to the Mark–Houwink equation below:

$$\log[\eta] = \log K + a \log M. \tag{2}$$

Here, M is the molecular weight, the experimental values of K and a for PVOH were calculated to be 1.987×10^{-4} and 0.7606, respectively, against 2×10^{-4} and 0.76, as shown in literature [4]. The column was washed several times with water, and the aqueous PVP-oxime solutions were run with PVOH solutions, the $[\eta]$ data were determined for each V_e and put on the calibration curve. A perpendicular on its abscissa gave the values 38,721 g mol^{-1} for oxime, i.e. 3.3% lower than those estimated with $[\eta]$ method. The molecular weight of benzoyl glycine, 179 g mol^{-1}, was calculated with its molecular formula as the –COOH group of glycine; it was protected from polymerisation by maintaining slightly acidic medium to overcome the common ion effect on the proceeding of benzoylation reaction that releases HCl. The $\bar{M}_v$ of copolymer is found to be 80,297.13 g mol^{-1}. The optical densities for very dilute aqueous solutions of the PVP-oxime and copolymer in solutions have shown their uniform distribution. Thus, Einstein correlated the η_{sp} values with the shape and size of the molecules using the v/V data. Here, v is the volume occupied by all the spheres and V the total volume of solution taken in the Survismeter bulb; thus, the v/V value calculated with η_{sp} values was found as $v/V \leq 2.5$ for the copolymer molecule.

Einstein [11] reported a v/V value <2.5 for spherical particles and $v/V > 2.5$ for nonspherical. For copolymer, the v/V values-derived viscosity data are found to be $v/V \leq 2.5$, which remain almost constant supporting the copolymer molecule to be nearly spherical in shape with no change on viscous flow without any preferential orientation.

The $[\eta]$ data were calculated with the following relation.

$$[\eta] \equiv \lim_{c \to 0} \frac{\eta_{\mathrm{sp}}}{c} = \lim_{c \to 0} \left(\frac{1}{c} 2.303 \log \eta_{\mathrm{r}} \right) \tag{3}$$

where c is the% concentration in 100 g of solutions. The plots of η_{sp}/c *versus* $1/c$ (2.303) log η_{r} show a linear behaviour that infers the properties of the copolymer as those of the polymeric molecules. The negative slopes of the $1/c$ (2.303) log η_{r} *versus* c data further ensure the similarities of the copolymer molecule with those of the polymers, as for structure and properties. The obtained data suggest a rational relation between volume and molecular weights; thus, monomer of our copolymer molecule along with markers show properties like macromolecules in aqueous solution. The intercept of η_{sp}/c *versus* $1/c$ (2.303) log η_{r} plot at zero concentration illustrates the degree of rotation around their bonds and configuration around successive carbon atoms along with the PVP-oxime-propagating chain. Thus, for very dilute solutions, the number of molecules in a prescribed weight of the copolymer molecule reported to be inversely proportional to the molecular weight. It facilitates an evaluation of volume occupied by molecules in a given weight as $v_{\mathrm{m}} = cVM^{1/2}$ relation, the v_{m} values are the volumes occupied by molecules in a given weight. Thus the Mark–Houwink–Sakurada equation is relevant for their molecular weight determination with respect to the viscous flows.

The a and K were found to be 0.2645 and 0.0174, respectively, reportedly the a value for very coiled rigidly rod-like molecules ranges 0.5–1.7. Flory [15] found K and a values 2.0×10^{-4} and 0.76, respectively, by taking monodispersive specimens of PVOH having different molecular weight. The densities measured for different compositions of the copolymer are noted as PVP-oxime in H_2O > PVP in H_2O > copolymer in H_2O, except densities of PVP-oxime at around lower compositions. The ρ of the PVP-oxime for lower composition are found to be lower than those of the PVP alone and copolymer, but for higher composition the increment is greater than those of the remaining two compounds (tables 1–3). This infers greater PVP-oxime intermolecular forces than that of the copolymer and reveals the fact that the large-sized molecule causes weaker intermolecular forces. But the ρ values of the PVP-oxime and the copolymer systems are found to be lower than those of the PVP in aqueous and copolymer in water. It predicts weaker molecular interactions of the oxime and the copolymer with the water molecules (figure 4a and b). The viscosity values of the copolymer are found to be higher than those of the PVP-oxime at 298.15 K. It demonstrates that there are various forces like potential, electronic and transnational are participating, which makes the copolymer geometry steric. This reveals that copolymer is more branched causing larger steric forces on viscous flow (figure 4a and b). Hence, the copolymer is non-linear and constituted by amino acids so correlated by different markers. The intrinsic viscosities of PVP-oxime and copolymer depicts that PVP-oxime has higher value of intrinsic viscosity than that of the copolymer. The PVP-oxime has a maximum reorientation with stronger hydrodynamic forces while the solution of same concentration of copolymer is showing the lower hydrodynamic volume. Interestingly, with compositions the viscosities of both of the substances meet at a common point depicting similar molecular activity and intermolecular interactions [16]. This predicts that pairwise interactions in both are of same order; where the action of PVP-oxime has slightly lower slope values than the copolymer. At almost 0.115% composition, both the molecules acquire the same value of hydrodynamic volume and forces (Newtonian forces). After this composition the PVP-oxime starts showing maximum hydrodynamic volume with stronger torque while the copolymer been decreased with respect to these parameters.

5. Conclusion

The presence of –Si–O–Si– and –Si–O–R frequencies confirms the binding of the electronic site in copolymer. The absence of the frequencies for the –OH group confirms the replacement of –OH group. Also, the v/V values found almost very slightly lower than 2.5 confirming its shape near to spherical molecule. It shows the lowest activity with composition of the PVP-Oximate silico benzoyl glycine copolymer.

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