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STRUCTURE OF MATTER
AND QUANTUM CHEMISTRY

Interaction of Polymer (Polyvinylpyrrolidone) with Azo Dye (Reactive Yellow): A Physicochemical Study

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Abstract—The influence of polymer, polyvinylpyrrolidone (PVP) on spectral properties of anionic azo dye, reactive yellow (RY) was investigated by UV–Vis spectroscopy in the temperature range of 298–313 K. The change in $\lambda_{\max}$ and absorbance indicated the presence of interaction between anionic dyes and polymer. The binding constant (K_b) of complexation was determined from the Benesi–Hildebrand plot. The K_b value increased with increasing dye concentrations and decreased with the rise of the temperature. The values of ΔG° for RY–PVP complexation were found to be negative and these negative values reduce with the enhancement of temperature which indicates that the binding process is more spontaneous at lower temperature. The negative values of ΔS° and negative values of ΔH° refer a process which is always enthalpy dominated. K_b values showed significant change with the change of pH. The K_b value enhances with the rise of the carbon chain length of the alcohol and reduces with increasing percentages of alcohol. The K_b value decreases at higher electrolyte concentrations and also with the increase of the size of the anion of the electrolyte. The removal of dye from the waste water by the interaction of dye with polymer in the presence of surfactant and salt of higher concentration has also been studied.

Keywords: reactive yellow (RY), polyvinylpyrrolidone (PVP), binding constant (K_b), complexation, thermodynamic parameters

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INTRODUCTION

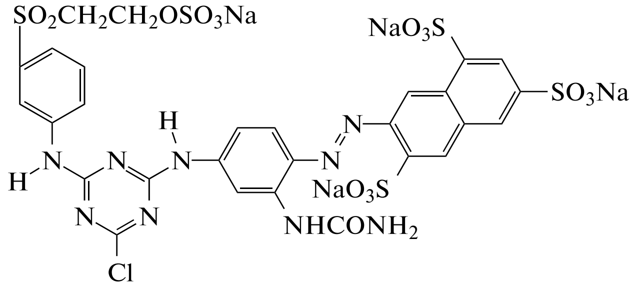
Among various dye–polymer mixtures, oppositely charged or similar charged systems have been studied widely. Dyes and polymer are two important classes of organic compounds with wide industrial uses. These molecules play a crucial role in many areas including such diverse fields as pharmaceuticals [1], foodstuffs [1], textiles [1–3], cosmetics and industrial as well as much biological process [4]. The aggregation of such molecules into larger definite structure in solution having specific order is an important process in science. The aggregation of detergent molecules is the best example of micelle formation. The lipid bilayer structure formation by phospholipids is one of the most important aggregation phenomena which is essential for animal life [5]. The dye-polymer interactions are important for industrial applications e.g., various dyeing processes such as textile dyeing, photography and ink and also in fundamental research area such as in the field of biochemistry, analytical chemistry and pharmaceutical application [6]. The principal utilization of dye is in the coloration of different substrate especially in the textiles. In order to get higher longevity, synthetic fibers require surfactant, polymer or other ordered aggregation e.g., micelles, vesicles or layers. Thus the research on the utilization of these auxiliary will probably be continued in the coloration of substrates in order to develop the fiber science and technology. As soon as surfactants or some amphiphilic drugs are placed in aqueous or organic solutions, they form micelles [1, 7–9] beyond the critical micelle concentration (CMC) [10–12], and all further surfactants/ amphiphilic drugs added to the solution go into the micelles [1].

According to the structures of dye and substrate, polymer used as leveling agents operates by different mechanisms. Dye molecules contain chromophore and auxochromes in its structure. Chromophores are the unsaturated groups which shift the absorption spectrum of the dye from the region of UV to the visible. The color of dye is modified by auxochromes and it helps the dye for the attachment to fibers. The investigation of such systems provides more information about effect of electrostatic as well as hydrophobic interaction on the dye–polymer complexation in aqueous medium. The experimental results allow the direct determination of the binding constant (K_b) and relative thermodynamic parameters of dye–polymer complex by UV–Vis spectroscopic method.

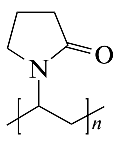
The effluents coming up from the textile industries are highly colored and cause water pollution. Thus they must be purified before disposal into environment. Most important methods for purification of water are biodegradation [13], flocculation–coagulation [14], oxidation [15] and adsorption [16]. Herein, the purification of water was studied by precipitation method utilizing electrolyte and alcohol in the presence of polymer.

EXPERIMENTAL

PVP having mass fraction purity 0.98 was obtained from BDH (England) and reactive yellow from China. All chemicals were used without further purification. $NaNO_3$, cetyltpyridinium chloride (CPC) and Na_2CO_3 having mass fraction purity 0.98, 0.98, and 0.985 respectively were purchased from Merck (Germany). Sodium alginate (mass fraction purity 0.98) was purchased from Across Organic. NaOH (mass fraction purity 0.98) and HCl (mass fraction purity 0.99) were obtained from Merck (India). Methanol (mass fraction purity 0.99), ethanol (mass fraction purity 0.98) and propanol-1 (mass fraction purity 0.99) were purchased from Fisher (UK), Keru & Co. (Bangladesh) and Merck (Germany), respectively. In all cases, stock solution of dyes was prepared in distilled and deionized water. Molecular structures of reactive yellow and PVP are represented below:



Scheme 1. Molecular structure of reactive yellow (RY).



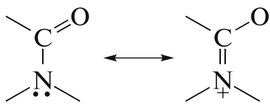
Scheme 2. Molecular structure of PVP.

UV–Vis spectroscopic method was used to study the interaction between RY and PVP. PVP solution (5 mL) of different concentrations were added to 5 mL 5×10^{-5} M RY solution taken in reagent bottles. The mixtures were then properly mixed and kept in an electrical shaker for about one hour with constant stirring at desired temperature. The absorbance of the mixture was measured using 1800PC UV-visible spectrophotometer (Shimadzu, Japan) at $\lambda_{max} = 416$ nm. All the experiments were carried out at various temperatures (298.15, 303.15, 308.15, and 313.15 K). The desired temperature of cell was maintained using temperature controller (Shimadzu-TCC-240A) in the temperature range of 280.15–333.15 K with accuracy of ±0.5 K.

RESULTS AND DISCUSSION

Binding Phenomenon of RY with PVP

The UV-absorption spectra obtained by addition of increasing amounts of PVP solution to a 5×10^{-5} M RY solution show that absorbance and the amplitude of the band of dye-polymer system were increased with the increase of concentration of PVP which illustrate the existence of interaction between the dye and polymer. The effective chromophore in the molecular structure of PVP is the lactam carbonyl with the resonance hybrid structures **I** and **II**:



(I) **(II)**

As lactam carbonyl is +E-type substituent [17, 18], a partial positive charge develops on nitrogen atom and partially negative charge develops on oxygen atom due to resonance. Thus PVP can effectively solvate anions by hydrogen bonding. However, substituents or any change in microenvironment influence the energy systems by changing charge distribution on electron excitation [19]. The reactive yellow dye (RY) in aqueous medium exist as anionic form [20, 21] and therefore the electrostatic interaction between anionic dye and N (positively charged due to resonance) of the lactam carbonyl bring them close proximity and so hydrophobic attraction must appear at the same time between the hydrophobic part of the polymer and dye. H-bonding is also possible between the polymer and dye. The steric hindrance prevents the involvement of nitrogen atom in the intermolecular interaction which makes the carbonyl group more feasible for hydrogen bonding to the dye molecule and thus dye–polymer complex might be formed. It was evident from the spectra (Fig. 1) that with increasing concentration of PVP, absorption was increased. So interaction between dye and polymer might be weak interactions such as hydrogen bonding or electrostatic interaction.

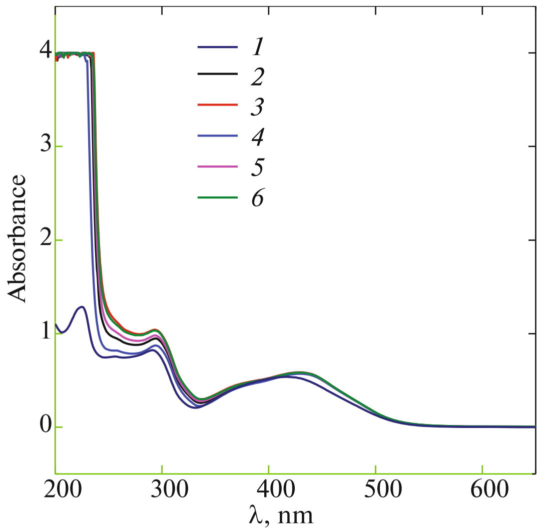


Fig. 1. The UV spectra of RY (5×10^{-5} M) in the presence of different concentration of PVP (*1*—0, *2*—1, *3*—2, *4*—3, *5*—4, *6*—5%) at 303.15 K.

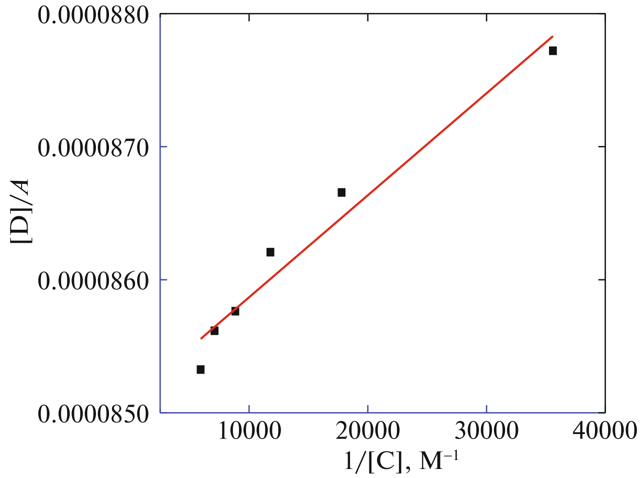


Fig. 2. The Benesi–Hildebrand plot for RY–PVP complex at 303.15 K.

The binding constant (K_b) *i*s readily obtained from Benesi–Hildebrand equation [22, 23],

$$[D]/A = 1/K_b\epsilon[C] + 1/\epsilon, \qquad (1)$$

where [D] and [C] elicits the initial concentration of dye and polymer respectively, A is the absorbance, and ϵ is the molar absorption coefficient of the dye–polymer complex at its given particular wavelength and K_b, the formation constant was obtained from the ratio of intercept and slope. Table 1 shows the values of K_b for dye–polymer complex having different concentration of RY with PVP. The result shows that with increasing concentration of RY binding constant increased which is the evident of more binding at higher concentration. The values of K_b for RY–PVP system at different temperatures are summarized in Table 2. The K_b values were found to decrease with increasing temperatures for all the RY–PVP complexes having same concentration of RY. At higher temperatures the tendency of ion pair formation reduces as equilibrium constants decrease with the rise of temperature [24]. The binding affinity of reactive yellow to the PVP might also significantly decrease with increasing temperature due to thermal agitation [25].

Effect of Different Alcohols on the Binding Behavior between RY and PVP

The absorbance of the aqueous solution of dye (RY) was measured in occurrence of amphiphilic polymer (PVP) in $H_2O–CH_3OH$, $H_2O–CH_3CH_2OH$, and $H_2O–CH_3CH_2CH_2OH$ mixed solvent in order to study the interaction between PVP and dye. To study the influence of cosolvent on the binding behavior of PVP and dye, similar experiments were performed in certain concentration of various alcohols and different concentration of same alcohol and subsequently binding constant between dye and polymer were estimated with the help of Benesi–Hildebrand equation. The executed magnificence of the binding constant is profiled in Table 2.

On addition of alcohol to the solution of dye/dye-amphiphilic substance, it interacts with dye and also with the amphiphilic molecules which causes some significant effects such as alter the tendency of ion pair formation, reduce the dielectric constant of the

Table 1. Binding constants and thermodynamic parameters of RY + 1% PVP system at different temperatures

$C_{\text{Dye}} \times 10^5$, M	T, K	$K_b \times 10^5$, L mol^{-1}	$-\Delta G$, kJ mol^{-1}	$-\Delta H$, kJ mol^{-1}	$-\Delta S$, J mol^{-1} K^{-1}
1.0	298.15	6.978	33.354	65.799	108.819
	303.15	4.471	32.792	46.982	46.809
	308.15	3.773	32.898	34.973	6.736
	313.15	2.871	32.720	44.548	37.770
3.0	298.15	10.169	34.288	49.665	51.575
	303.15	7.267	34.016	44.606	34.932
	308.15	5.672	33.942	61.515	89.480
	313.15	3.334	33.109	86.641	170.947
5.0	298.15	15.595	35.348	50.308	50.177
	303.15	11.096	35.083	44.850	32.220
	308.15	8.671	35.029	59.502	79.418
	313.15	5.222	34.278	82.687	154.589

Table 2. Binding constants of RY + 1% PVP system in different solvents

Solvent	$K_b \times 10^5$, L mol^{-1}	Solvent	$K_b \times 10^5$, L mol^{-1}
Water (pH 7.3)	11.096	0.001 M Na-alginate	5.673
Methanol (10%)	10.998	0.01 M $NaNO_3$	15.626
Ethanol (10%)	15.531	0.1 M $NaNO_3$	19.116
Propanol-1 (10%)	17.004	Acidic (pH 2.30)	5.283
Methanol (20%)	8.756	Acidic (pH 4.46)	7.684
Methanol (30%)	6.848	Basic (pH 8.53)	15.595
0.001 M $NaNO_3$	13.274	Basic (pH 10.31)	19.232
0.001 M Na_2CO_3	12.298	Basic (pH 12.59)	22.160

medium with the enhancement of the concentration of alcohol [26]. The dielectric constant of the medium varies with the divergence of the chain length of the alcohol as well as with the change of the concentration of the alcohol. The estimated binding constant of dye-polymer systems rises with the augment of the chain length of the alcohols (Table 2). The dielectric constant of H_2O, CH_3OH, CH_3CH_2OH, and $CH_3CH_2CH_2OH$ are 80, 33, 24.55, and 18, respectively [27]. Thus, with the addition of alcohol the dielectric constant of the medium decreases, which is the cause of greater attractive force between the water and alcohol molecules. Normally, upon addition of small quantity of alcohol to water, it acts as water structure maker and breaks the iceberg structure of the water with the addition of higher concentration of alcohol [28, 29].

It necessary to consider many factors e.g., changing water structure, preferential solvation of dye, change in dielectric constant of the medium, cohesive energy, change in micellar size and micellar properties due to incorporation of the co-solvents to the micelle core etc. in order to explain the influence of co-solvents on dye–amphiphilic polymer interaction. Besides the factors mentioned above, the interaction of dye with co-solvent might be considered in order to estimate the efficiency of the co-solvent. In the presence of water structure breaker solutes, it may disrupt the organization of water created by dissolved hydrophobic group which is cause of less availability water molecules to solvate amphiphilic substance (PVP) [27] and therefore PVP bind easily to dye i.e., binding constant increases chain length of the alcohol at lower concentration (Table 2). Again it was observed that the magnificence of binding constant reduces with the augment of the concentration of the alcohol (Table 2). The reduction of the binding constant between dye and amphiphilic substance with the rise of concentration is due to reduced dielectric constant. Similar result was also reported in the literature for dye surfactant interaction [27, 30]. Modified hydrophobic interaction in the presence of alcohol can be involved in order to explain the reduction in binding constant. The hydrophobic interaction between dye and PVP reduces with the rise of the concentration of same alcohol due to deleterious action of alcohol on the iceberg structure of H_2O around the hydrophobic parts of dye and PVP [26, 31] and consequently decreases the binding constant.

Effect of Electrolyte on the Binding Behavior between RY and PVP

The observed values of binding constant for the RY-PVP complex were attained to be higher in occurrence of $NaNO_3$ as compared to the value obtained in water. Again the values of binding constant for the RY–PVP complex increase with the subsequent rise of the concentration of $NaNO_3$ (Table 2). The higher value of binding constant illustrates the stronger complexation in the presence of salt, $NaNO_3$ [32]. In presence of electrolytes, the water molecules are tied up to the ions due to electrostatic attraction between the charged ion and dipole moment of the water molecules thus water molecules are less available in the vicinity of the amphiphilic substance (PVP) consequently decrease the solubility of PVP in presence of salt, $NaNO_3$ which is termed as salting out effect. The salting out of PVP in the presence of $NaNO_3$, makes PVP more available to dye which results in rising binding constant. In presence of $NaNO_3$, the hydrated shell around PVP is broken and surface charges consent the particles to settle to smaller volume which is the cause of more availability of dye to PVP consequently forms stronger binding. This effect is enhanced with the rise of the concentration of $NaNO_3$ thus binding constants raises with the augment of the concentration of $NaNO_3$. Again the binding constant of RY–PVP complex were observed to be decreased with the rise of size of anion of the electrolytes studied. The order of ionic size of alginate, carbonate and nitrate is as follows:

$$C_6H_7O_6^- > CO_3^{2-} > NO_3^-.$$

The magnitudes of binding constants of RY–PVP system in different electrolytes are viewed in Table 2. The reduction in the binding constant of RY–PVP system can be explained in terms of enhanced salting in effect with the increased size of the anion.

Effect of pH on the Binding Behavior between RY and PVP

In order to study the pH dependent of binding constant of RY–PVP system the experiment were performed at different pH ranging from 2.30 to 12.59. The desired pH of the medium was sustained utilizing either by HCl or by NaOH in order to avoid the interaction with buffer solutions. The estimated values of binding constant at different pH are illustrated in Table 2. It was observed that the values of binding constant enhance with the increment of the pH of the medium which is in well harmony with the literature [27]. In acidic medium i.e., at pH <7, the dye molecule (RY) exist as protonated form (HRY) whereas in basic medium i.e., at pH >7, RY exist as deprotonated form (RY^-). In neutral medium (aqueous medium) dye molecules remain as zwitterionic form and show a resonance structure in between two forms mentioned earlier. The electrostatic interaction between dye and polymer increases with the rise of effective charged of the dye molecules. As dye molecules exist as protonated form, the charged site is occupied by proton and hence binding between dye (RY) and polymer (PVP) due to electrostatic interaction is reduced in acidic medium and hydrophobic interaction predominates here. On the other hand, electrostatic interaction is predominant in basic medium as RY exist as anionic form. At pH >7, the positive charge is developed in the lactam carbonyl of PVP due to resonance interact electrostatically with the negative charge of the dye molecules (RY) and bring them closed to each other consequently hydrophobic interaction must align simultaneously between the hydrophobic moiety of dye and polymer [20]. Thus the binding constant between RY and amphiphilic substance (PVP) is more at higher pH which is well harmony with the literature [27]. In neutral medium, the electrostatic interaction as well as hydrophobic interaction lie between that present in acidic and basic medium as RY exist in zwitterionic form. Therefore the binding constants in neutral medium lie in between that in acidic and basic medium.

Thermodynamics of Binding between RY and PVP

The magnificence of Gibbs free energy change, ΔG° of dye polymer complexation can be evaluated from the attained values of binding constant (K_b) by means of the following equation [33]:

$$\Delta G^\circ = -RT\ln K_b. \tag{2}$$

In the above equation R and T expound the molar gas constant and temperature in Kelvin scale. The estimated magnitudes of Gibbs free energy change of dye-polymer complexation are viewed in Table 1. Again the standard enthalpy change of the complex formation between dye and polymer can be estimated utilizing the modified Van't Hoff equation [34–36]:

$$\Delta H^\circ = RT^2\partial\ln K_b/\partial T. \tag{3}$$

In order to evaluate the value of ΔH° solving the above equation, the magnitudes of $\ln K_b$ was plotted against the experimental temperature (T). At each temperature a tangent was drawn and the slope of the tangent was taken as $\partial\ln(K_b)/\partial T$ at corresponding temperature [34–36]. For the measurement of the standard entropy change of RY–PVP complex formation subsequent equation was utilized [37–41]:

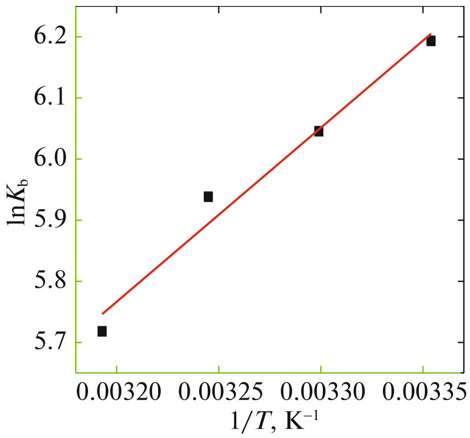


Fig. 3. (Color online) The representative Plot of $\ln K_b$ vs. $1/T$ for the calculation of ΔH°.

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}. \tag{4}$$

The estimated values of various thermodynamic parameters for RY–PVP complexation are viewed in Table 1. The estimated values of ΔG° for RY–PVP complexation were attained to be negative in all cases which signify that complex formation is spontaneous [42]. The negative magnificence of ΔG° decreased with the enhancement of temperature indicating more spontaneous complexation process at inferior of temperature.

The magnitudes standard enthalpy changes ΔH° changes for RY–PVP system in water was estimated utilizing the obtained the slope of $\ln K_b$ versus $1/T$ plot (Fig. 3) and the magnitudes standard enthalpy changes of ΔH° were obtained to be negative at each temperature which reveals that complexation phenomenon is exothermic. The negative value of ΔH° were obtained to be reduced with the enhancement of the temperature up to certain level and reach to minimum and then increased sharply with the subsequent rise of the temperature signifying that complexation between RY and PVP is highly exothermic at elevated temperature. The magnitudes of standard entropy changes, ΔS° of complexation were found to be negative at each temperature. The large negative magnitudes of ΔH° along with the negative values of ΔS° signifying that complexation phenomenon is enthalpy dominated process. The positive values of ΔH° and ΔS° are the characteristic of hydrophobic interaction while negative values of ΔH° and ΔS° arise due to hydrogen bonding and electrostatic interactions [43, 44]. The obtained values of ΔH° as well as ΔS° were negative which reveal that binding interaction between

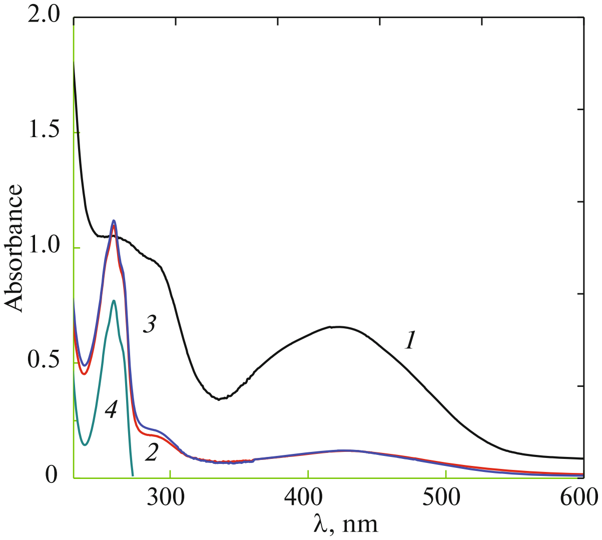


Fig. 4. The UV-Spectrum of RY solution before treatment and RY–PVP system in presence of 0.2 mM CPC and 0.1 M Na-alginate after treatment at different time intervals: *1*—0, *2*—24 h, *3*—48 h, *4*—7 days.

RY and PVP are mainly due to hydrogen bonding and electrostatic interactions.

Removal of Dye from Water by Precipitation Technique

Lots of industrial processes utilize various synthetic dyes for different purposes. The effluents secreted from these industries are highly colored which is cause of major environmental problems. Normally, the dye molecules contain complex aromatic moieties, which are more stable as well as more difficult to biodegrade and very difficult to treat. Reactive dyes are azo-based chromophores that contain various types of reactive groups such as vinylsulfone, chlorotriazine, trichloropyrimidine, diflurochloropyrimidine. The existence of dye even of very low concentrations (less than 1 ppm) in the effluent is highly visible and considered as undesirable [23]. Thus these effluents need to be treated before disposing into environment.

In this study, various concentration of CPC with PVP were treated with 5×10^{-5} M dye in methanol and 0.1 M Na-alginate then shacked for 60 min and allowed to settle. Then precipitation took place and thus absorbance was decreased. The progress of precipitation was monitored by recording spectral changes at different time intervals (Fig. 4). The absorbance almost systemically decreased with the progress of time. The degree of purification can be estimated utilizing the absorbance of the solution recorded by means of UV-spectrophotometer with the help of subsequent equation [32, 45]:

$$P,\ \% = \frac{A_0 - A}{A_0} \times 100\%. \qquad (5)$$

In the above equation A_0 and A expound the absorbance's of the solution before and after treatment respectively.

The dye solution before treatment (Fig. 5a) with surfactant and electrolyte as well as after treatment is viewed in Figs. 5b–5d.

Table 3 and Fig. 6 show maximum purification occurs at CPC concentration of 0.1 mM. With increasing concentration of CPC from 0.1 mM decreases the precipitation and maximum at 0.1 mM. Again, without PVP and surfactant (CPC), no precipitation takes place. With the enhancement of the settle down time dye removal from the water also increases (Fig. 6). When CPC is added, each sulfonic group of the dye bound to the opposite ion of CPC. With

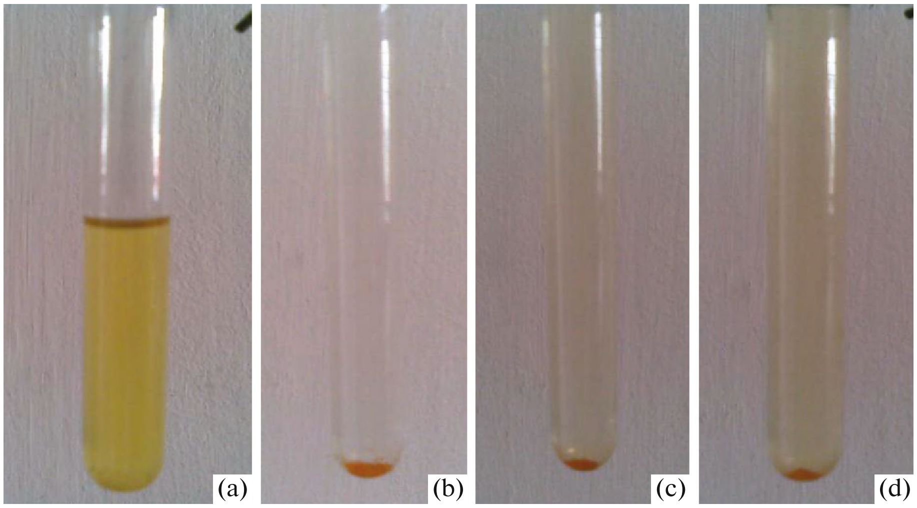


Fig. 5. (Color online) Precipitation of RY in presence of 0.1 M Na-alginate (a) before treatment and (b–d) after treatment with 1% PVP and various concentration of CPC (0.1 (b), 0.2 (c), and 0.3 mM (d)) after 48 h.

Table 3. Data for purification (%) of water using 0.1 M Na-alginate at 1% PVP with various concentration of CPC (C)

C, mM	Purification after		
	24 h	48 h	7 days
0.1	92.38	97.56	100.00
0.2	86.59	93.90	100.00
0.3	81.86	81.71	100.00
0.4	75.00	75.30	100.00
0.5	72.26	71.95	100.00
0.6	66.92	66.77	85.52
0.7	63.72	61.89	60.52

increasing CPC concentration all dye molecules are encapsulated into the CPC. Dye–surfactant complexes at certain level are water insoluble and thus precipitation take place (at concentration below CMC) but are solubilized in excess of surfactant [32, 46] and precipitation is lowered.

CONCLUSIONS

In this current study, we have investigated the interaction between textile dye, reactive yellow and amphiphilic polymer, PVP by means of UV–Vis spectroscopic method. The investigations were carried out in different solvent and pH. The estimated binding constant (K_b) increase with the enhancement of the concentration of RY, concentration of electrolyte studied and also with the rise of the carbon chain length of alcohol. The magnificence of K_b decreases with the rise of temperature and concentration of methanol. The binding of dye to the polymer studied is more favourable in basic medium. The RY–PVP complexation is exothermic at all temperature studied and thermodynamically spontaneous. The complexation phenomenon is enthalpy dominated process. The maximum water purification was obtained utilizing 0.1 mM CPC in presence of 1% PVP + 0.1 M Na-alginate. The dye removal enhances with the increase of the time for settle down.

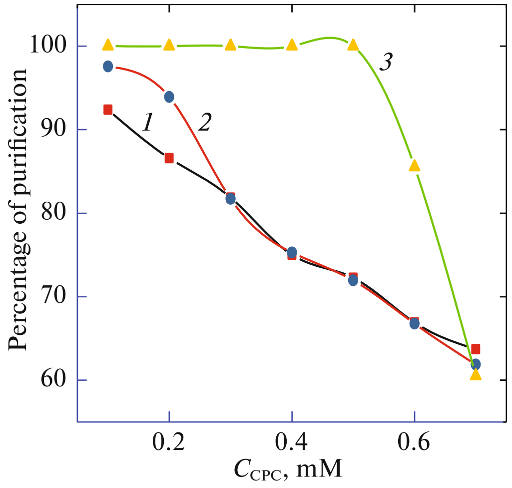


Fig. 6. Percentage of purification at different concentration of CPC with 1% PVP in 0.1 M Na-alginate at different times: *1*—24 h, *2*—48 h, *3*—7 days.

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