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Influences of NaCl and Na₂SO₄ on the Micellization Behavior of the Mixture of Cetylpyridinium Chloride + Polyvinyl Pyrrolidone at Several Temperatures

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Abstract: Herein, the conductivity measurement technique is used to determine the interactions that may occur between polyvinyl pyrrolidone (PVP) polymer and cetylpyridinium chloride (CPC) surfactant in the presence of NaCl and Na₂SO₄ of fixed concentration at variable temperatures (298.15–323.15 K) with an interval of 5 K. In the absence or presence of salts, we observed three critical micelle concentrations (CMC) for the CPC + PVP mixture. In all situations, CMC₁ values of CPC + PVP system were found to be higher in water than in attendance of salts (NaCl and Na₂SO₄). Temperature and additives have the tendency to affect counterion binding values. Various physico-chemical parameters were analyzed and demonstrated smoothly, including free energy (ΔG_m^0), enthalpy (ΔH_m^0) and entropy change (ΔS_m^0). The micellization process is achieved to be spontaneous based on the obtained negative ΔG_m^0 values. The linearity of the ΔH_m^0 and ΔS_m^0 values is excellent. The intrinsic enthalpy gain (ΔH_m^{0*}) and compensation temperature (T_c) were calculated and discussed with logical points. Interactions of polymer hydrophobic chains or the polymer + surfactant associated with amphiphilic surface-active drugs can employ a strong impact on the behavior of the gels.

Keywords: polyvinyl pyrrolidone; critical micelle concentration; cetylpyridinium chloride; thermodynamics; conductivity measurement

1. Introduction

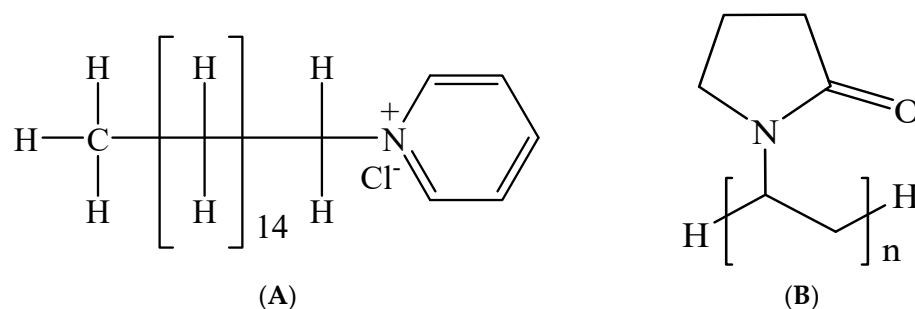
Surfactants are substances that can reduce the surface tension of a solvent. Aggregation behavior of amphiphilic substances, which is basically a non-covalent interaction, is a normal and spontaneous phenomenon [1]. The structural configuration of surfactant molecules, and the presence of polar and non-polar portions, helps them to be self-assembled in an aqueous medium at a certain concentration which is termed as critical micelle concentration (CMC) [2]. Micelles can easily incorporate feebly soluble drugs, organic chemicals, or polymers inside their hydrophobic core and facilitate the solubility of various substances and bioavailability as well [3,4]. However, surfactants act as a good recipient regarding drug delivery systems. Studies have suggested that insertion of external substances may impact on the physical properties of aggregates such as adding or departure of counter ion binding, reaction rate, and catalytic activity [5,6]. Gelation is the gel preparation process from a system through polymers. Functions of gels are established by their drug-loading

ability, rheological behavior, and the mechanisms and kinetics of drug discharge. The integration of small ratios of surfactants, which can elevate or impede intra/interchain polymeric bonds, can change these assets and be a valuable tool for emerging gel-based dosage forms [7,8].

It is inevitable that this aggregate nature of surfactant molecules has made it a perfect candidate for its versatile potential applications. In the case of pharmaceutical research, cosmetics and perfumes industries, antiseptics, and disinfectants, surfactants are used due to their good chemical and anti-microbial properties [5]. Surfactants can be utilized to prepare antibacterial hydrogels. Shunji Yunoki et al. [9] studied that cetylpyridinium chloride (CPC) and polyvinyl alcohol (PVA) based antibacterial hydrogels showed excellent antibacterial properties where interaction between the used surfactant and polymer was significant. Dye-surfactant interaction for formulation in textile and various coloring industries deserves a remarkable role [10]. Recent research revealed that rinsing the oral captivity can restrain and counteract the menace of transmission of SARS-CoV-2 [11,12]. A recent publication anticipated that CPC has capability to destroy viral capsids [13] and can become active against different enveloped viruses such as coronaviruses [14]. CPC is a quaternary ammonium salt and cationic surfactant and its structure made it a perfect component for numerous applications for humans such as dental plaque and gingivitis can be reduced by using 0.05% CPC [15]. Mukherjee et al. [16] and Popkin et al. [17] found that CPC exhibits potent, effective, and rapid antiviral response towards influenza and can decrease the duration and severity of the disease.

Investigation of interaction amid surfactants and polymeric substances is very important because these substances are used in many industries such as lubricants, food, sanitizations, detergents, coatings, paints, adhesives, and cosmetics. In a mixture of polymer and surfactant, they individually provide instinct properties such as rheological and interfacial properties, respectively [18]. Polymer and surfactant interaction is important to reduce interfacial areas between non-polar polymeric segments and water when they are linked with non-polar moieties of surfactants to create micelles [19].

Our previously published paper [20] and some other publications have delineated [21,22] the interactions between CPC and polymers/biopolymers in an aqueous medium, but examination of interaction of CPC (Scheme 1A) and polyvinyl pyrrolidone (PVP) (Scheme 1B) in presence of salts at various temperatures, such as in this present work, is rarely studied. Sodium chloride (NaCl), generally known as salt, is a necessary component of our bodies ability to absorb and transport nutrients, regulate blood pressure, and maintain fluid balance. On the other hand, an electrolyte replenisher, sodium sulfate in anhydrous form is used in isosmotic solutions to ensure that delivery does not disrupt normal electrolyte balance or cause water and ion absorption or excretion. Due to the greatest role of these two sodium salts to our body, we have selected these salts. Therefore, in this current work conductivity technique has been used to examine the interaction between the chosen surfactant (CPC) and polymer (PVP) with/without presence of salts (NaCl and Na₂SO₄). On the other hand, three different values of CMC, fraction of counter ion binding (β), thermodynamic parameters such as ΔG_m^0 , ΔH_m^0 , ΔS_m^0 and ΔC_m^0 for the aggregation behavior of CPC + PVP mixture in water, and electrolyte solutions, are calculated, expressed, and analyzed thoroughly.



Scheme 1. Molecular structure of (A) CPC and (B) PVP.

2. Experimental

2.1. Materials

The materials used in this study were of analytical grade and used without further purification. The chemical names, purity, CAS numbers, mass fraction, and other information are mentioned in Table 1.

Table 1. Information of used materials.

Name of the Materials	Sources	Purity in Mass Fraction	CAS Number	Molecular Weight (g/mol)
CPC	Sigma-Aldrich, st. louis, MAUSA	0.99	124-03-8	340
PVP	Sigma-Aldrich, st. louis, MAUSA	0.99	9003-39-8	360,000
NaCl	Merck, Gurgaon-12, India	0.99	7647-14-5	58.44
Na ₂ SO ₄	Merck, Mumbai, India	0.99	7757-82-6	142.04

2.2. Solution Preparation and Conductivity Measurement

CPC + PVP solutions, both in water and salts media, were prepared using distilled-deionized water considering molal concentrations. The specific conductivity of used distilled-deionized water was 1.7–2.0 $\mu\text{S cm}^{-1}$ maintaining temperature range 298.15–323.15 K. Electric balance machine (Mettler Toledo, Greifensee, Switzerland) and 4510 conductivity meter (Jenway, Staffordshire, UK) were used for taking the weight of samples and measuring specific conductivity (κ) for preparing different solutions. The conductivity meter had a glass cell electrode specifying cell constant 0.97 cm^{-1} and to calibrate the meter, appropriate concentration of freshly collected KCl solution was employed. Throughout the whole work of conductivity measurement, alternate current (AC) having a frequency of 60 Hz was maintained. In terms of explaining the procedure, initially, 25 mmol kg^{-1} aqueous solution of CPC in PVP was prepared and subsequently, this solution was inserted into the 20 mL solution of PVP at specific temperature both in attendance/non-attendance of salts. Then, salts solutions were also prepared and added to observe the impacts of salts during conductivity study. After every addition of solution, time was maintained to achieve temperature equilibration and conductivity value was recorded; then, this process was employed for every system. Our process of conductivity technique has good matching with others [6,23–25]. The RM6 Lauda circulating water bath was used and the error of temperature within ± 0.2 K was considered. The values of CMC were calculated from the intersection points of κ versus concentration of CPC plots for the CPC + PVP assembly by using Origin software.

3. Results and Discussion

3.1. The CMC and β for the Aggregation of CPC + PVP Mixture in Aqueous and Salts Media

The aggregation of surfactants has been investigated by different distinguished research teams applying a number of experimental techniques such as surface tension, conductivity, density, viscosity and ultrasound velocity measurements, fluorescence spectroscopy, NMR Spectroscopy, etc. [26,27]. Among these techniques, conductivity technique is a simple, trustworthy, and broadly used method to evaluate CMC for ionic amphiphiles.

Ionic surfactants ionize into ions in H₂O; consequently, specific conductivity has the tendency to increase with enhancing of surfactant contents. Nevertheless, the incremental increase in conductivity undergoes deviation from the initial trend when a certain concentration of surfactant is developed. Such behavior was detected by many researchers in their studies which is mainly owing to the micelle creation [6,20,28–30]. The dependence of the specific conductivity, κ , on surfactant concentration is shown in Figure 1.

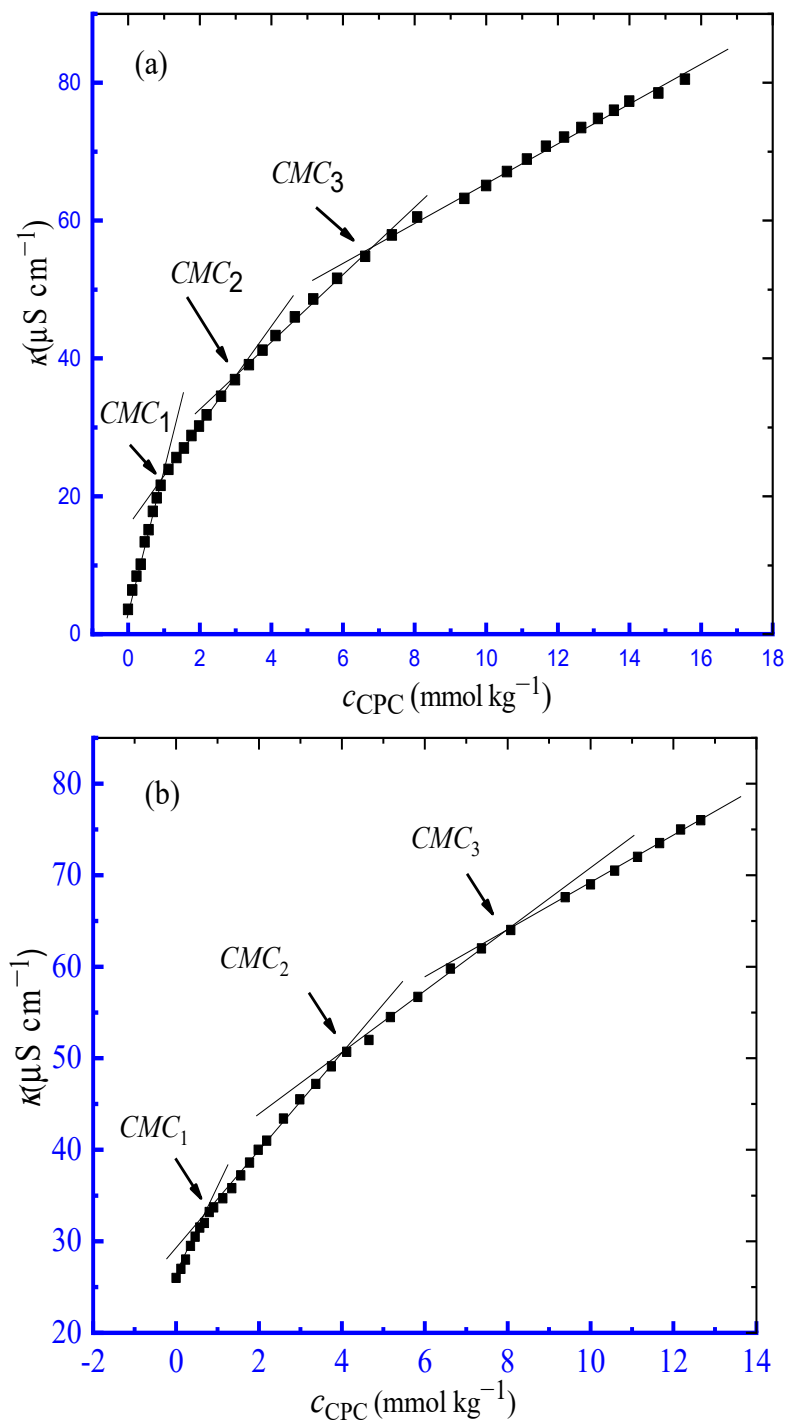


Figure 1. Specific conductivity (κ) versus CPC concentration plot for the CPC + 0.1% (*w/v*) PVP mixture in (a) water and (b) aq. 1.50 mmol kg⁻¹ NaCl solution at 303.15 K.

For all the cases of CPC + PVP mixed system, three break points were obtained. The concentration of surfactant achieved at the break point has been taken as the CMC, and

the successive CMC values were expressed as CMC_1 , CMC_2 , and CMC_3 , respectively. The CMC_1 can be associated with the formation of the PVP (polymer): CPC complex (critical aggregation concentration); the CMC_2 corresponds to free CPC micellization (critical micelle concentration in the presence of PVP), and the third break point (CMC_3) refers to the structural modifications in micelles as a sphere to rod transition [31]. The third critical micelle concentration indicates that the spherical micelle turns into a rod shape. Chakraborty et al. [32] described three CMCs (critical aggregation concentration (CAC), polymer saturation concentration (c_s), and free micellization concentration (c_m^*)) for the assembly of the mixture of SCMC and CTAB. Bhattarai has achieved three CMC values for the aggregation of the CTAB + sodium polystyrene sulfonate mixture [33]. In spite of the existence of multiple CMC for an association of polymer + surfactant mixture, a single CMC is also stated in the literature [34–37]. Chai et al. [38] investigated the interaction amid PVP and a gemini surfactant by NMR in a D_2O medium at 298 K. They confirmed the CMC, CAC, and additive saturated concentration (C_2) by measuring chemical shift and self-diffusion coefficients, respectively. Mukhim and Ismail [39] reported CMC values of 0.841 and 0.75 mmol kg^{-1} for the micellization of CPC in water and 0.32 mmol kg^{-1} NaCl solution, respectively, at 298 K by means of surface tension measurement technique. The decrease in CMC values in NaCl solution compared to water medium has good agreement with the current study. Varade et al. [40] investigated the impact of electrolyte (NaCl and NaBr) on the CMC value of CPC using different techniques (surface tension/conductance/viscosity/dynamic light scattering (DLS)/small angle neutron scattering). From surface tension and conductivity techniques, Varade et al. [40] stated that CMC value of CPC was found to be 0.98 and 0.95 mM, respectively at 303 K and obtained a decrease in CMC value in the occurrence of salt. The DLS study showed that, in presence of electrolytes, the repulsive interactions will cause a rise in the diffusion coefficient and therefore a reduction in the apparent diameter of the micelles, i.e., a decrease in CMC of CPC was observed [40].

The extent of micelles dissociation, α , has been computed from the ratio of the slopes corresponding to the linear regions below and above CMC. If S_1 and S_2 are the slopes below and above CMC_1 , respectively, then S_2 and S_3 are the slopes below and above CMC_2 , and S_3 and S_4 are the slopes below and above CMC_3 , respectively. Then, α_1 , α_2 , and α_3 can be determined from the ratios S_2/S_1 , S_3/S_1 , and S_4/S_1 , respectively. The fraction of bound counter ions, β , at CMC can be obtained by subtracting the α value from unity, i.e., $\beta = (1 - \alpha)$.

The effect of PVP on the CPC aggregation has been investigated considering the five different concentrations of PVP in the range 0.01–0.10% (w/v). The CMC values for the CPC + PVP system in H_2O having several concentrations of PVP at 303.15 K are depicted in Table 2. The CMC values initially tend to upsurge with the increase in PVP content, attain optimum value, and then undergo decline with the increase in PVP content. Sardar et al. [41] investigated the interactions between PVP and cationic surfactant (both conventional/gemini) while they achieved the enhancement of CAC and CMC values with the rise of PVP contents [40]. The change of CMC values for the CPC + PVP aggregation as a function of PVP content indicates the survival of interaction between CPC and PVP. Additionally, the micelle development phenomenon is a delayed process in the manifestation of PVP.

Table 2. The CMC values of CPC + PVP assembly in H_2O having different concentrations of PVP at 303.15 K.

c_{PVP}	CMC_1	CMC_2	CMC_3
% (w/v)	mmol kg^{-1}	mmol kg^{-1}	mmol kg^{-1}
0.01	0.67	2.27	6.06
0.03	0.74	2.68	6.22
0.05	0.83	2.88	6.47
0.10	1.12	3.49	7.44

All the *CMC* values for the CPC + PVP aggregation in aq. NaCl and Na₂SO₄ solution have been obtained to be lower in magnitudes in comparison to aqueous medium (Table 3). The reduction in *CMCs* is due to the decreased electrostatic repulsions between the charged head group of the amphiphiles [39]. The effect is much more pronounced in aq. Na₂SO₄ solution than in case of aq. NaCl solution. Sulfate ion is multicharged and exists left in the Hoffmeister series compared to the single charged anion Cl⁻. Therefore, the salting out tendency might be more pronounced in case of sulfate which reduces *CMC* to a greater extent at the identical ionic strength [42]. Barbosa et al. [43] achieved three *CMC* values for the SDS +PEO mixture in aq. salts solution including NaCl and Na₂SO₄. They also obtained a decreasing trend of *CMC* in the manifestation of these salts. They described that, although NaCl could not interact with PEO, the counter ions of surfactant interact with micelles and macromolecules, which allows the increase in the surfactant's chemical the potential, and thus the effect of NaCl results in the reduction in both *CAC* and *CMC* values. Akhlaghi and Riahi [44] reported the effect of different salts on the *CMC* of TX-100, and they obtained greater effect of NaCl in reducing *CMC* in comparison to Na₂SO₄.

Table 3. The *CMC* values of the CPC + 0.1% (*w/v*) PVP mixture in H₂O, H₂O + NaCl, and H₂O + Na₂SO₄ media at different temperatures.

Media	<i>I</i> _{salts} mmol kg ⁻¹	<i>T</i> K	<i>CMC</i> ₁	<i>CMC</i> ₂	<i>CMC</i> ₃
			mmol kg ⁻¹	mmol kg ⁻¹	mmol kg ⁻¹
H ₂ O	0	298.15	0.92	3.03	7.31
		303.15	1.12	3.49	7.44
		308.15	1.16	3.71	7.71
		313.15	1.23	3.95	7.81
		318.15	1.26	3.82	7.62
		323.15	1.32	3.32	7.13
H ₂ O + NaCl	1.50	298.15	0.78	4.29	8.01
		303.15	0.73	4.06	7.73
		308.15	0.57	3.15	7.66
		313.15	0.71	2.97	7.43
		318.15	0.77	2.49	7.45
		323.15	0.83	2.36	7.54
H ₂ O + Na ₂ SO ₄	1.50	298.15	0.43	4.65	8.51
		303.15	0.55	5.31	8.22
		308.15	0.51	4.81	8.11
		313.15	0.48	4.47	8.48
		318.15	0.44	4.27	9.02
		323.15	0.39	3.98	9.09

3.2. Effects of Temperature on the Association of CPC and PVP Mixture

As the surfactants are used broadly in the applied purposes, its aggregation process experiences an alteration of temperature depending on the seasonal time and applied regions. To understand the impacts of temperature on the aggregation of CPC + PVP mixture, we have selected a range of temperature 298.15–323.15 K in the current investigation, which also covers both room temperature and body temperature. The conductivity and *CMC* values of the CPC + PVP mixture experience a dependency on the temperature variation. The *CMC* values of the CPC + 1% (*w/v*) PVP mixture in H₂O, H₂O + NaCl, and H₂O + Na₂SO₄ media at several temperatures are shown in Table 3.

In aqueous medium, the *CMC*₁ values for the aggregation of CPC + PVP mixture undergo an enhancement with the rise of temperature while the *CMC*₂ and *CMC*₃ values primarily experience an upsurge with the escalation of temperature, reach an optimum value, and then undergo reduction with the gradual growth of temperature. For the aggregation of CPC + PVP mixture in H₂O + NaCl medium, the *CMC*₂ values suffer a fall with the rise of temperature while the *CMC*₁ and *CMC*₃ values primarily experience a reduction with the increase in temperature, reach the least value, and then experience

an increase with the gradual intensification of temperature. In H₂O + Na₂SO₄ medium, the CMC₂ values undergo a fall with the rise of temperature, while the CMC₁ and CMC₃ values primarily experience a reduction with an increase in temperature, touch the lowest value, and then experience a rise with the gradual intensification of temperature.

3.3. Energetics of the Aggregation of CPC + PVP Mixture in Aqueous and Salts Media

The feasibility of the aggregation process can be understood from the knowledge of standard free energy change (ΔG_m^0). It also signifies the spontaneity of the corresponding phenomena. The values of ΔG_m^0 for CPC + PVP mixture in water and aq. salts solution have been assessed using the following equation [45–51].

$$\Delta G_m^0 = (1 + \beta)RT \ln X_{CMC} \tag{1}$$

The symbols R , T , and X_{cmc} in the above equation imply the universal gas constant, study temperature (in Kelvin), and mole fractional value of CMC, respectively. The values of X_{cmc} were computed from the ratios of the number of moles of amphiphiles at CMC and the overall number of moles existing in the CPC + PVP mixture in H₂O/aq. salts solutions. The number of moles of H₂O was considered equal to the ratio of one kilogram and mol. wt. of H₂O.

The extent of free energy of transfer ($\Delta G_{m,t}^0$) for CPC + PVP mixture to shift from H₂O to H₂O + salts media was evaluated applying the subsequent Equation (2) [45,52,53]:

$$\Delta G_{m,t}^0 = \Delta G_m^0 (H_2O + salts) - \Delta G_m^0 (H_2O) \tag{2}$$

The changes in free energy (ΔG_m^0) values were determined only considering the CMC₁. The values of $\Delta G_{1,m}^0$ are depicted in Table 4. The $\Delta G_{1,m}^0$ values are negative in H₂O and aq. salts solution. In all the studied media, the negative ΔG_m^0 values increase with the growth of experimental temperature. The negative ΔG_m^0 values slightly increase in presence of NaCl while the values experience a fall in aq. Na₂SO₄ solution. As can be observed, the $\Delta G_{1,m}^0$ values are negative, indicating that micelles have formed spontaneously in the study solutions. Additionally, the enhanced negative $\Delta G_{1,m}^0$ values in aq. NaCl solution refer to the increase in the spontaneity for the micelle formation tendency.

Table 4. Values of β_1 , free energy change ($\Delta G_{1,m}^0$), and free energy change of transfer ($\Delta G_{1,t}^0$) for CPC + 0.1% (w/v) PVP mixed systems in H₂O and aq. solution of NaCl/Na₂SO₄.

Media	I_{salts}	T	$X_{CMC} (\times 10^5)$	β_1	$\Delta G_{1,m}^0$	$\Delta G_{1,t}^0$
	mmol kg ⁻¹	K			kJ mol ⁻¹	kJ mol ⁻¹
H ₂ O	0	298.15	1.658	0.67	-36.99	
		303.15	2.018	0.65	-37.08	
		308.15	2.090	0.65	-37.54	
		313.15	2.216	0.64	-37.87	
		318.15	2.270	0.63	-38.34	
		323.15	2.379	0.62	-39.00	
H ₂ O + NaCl	1.50	298.15	1.406	0.69	-37.05	-0.0599
		303.15	1.315	0.68	-37.60	-0.5124
		308.15	1.027	0.68	-38.26	-0.7106
		313.15	1.279	0.67	-38.78	-0.9095
		318.15	1.388	0.65	-38.91	-0.5689
		323.15	1.496	0.64	-39.23	-0.2351
H ₂ O + Na ₂ SO ₄	1.50	298.15	0.775	0.35	-29.39	7.596
		303.15	0.991	0.34	-29.78	7.304
		308.15	0.919	0.39	-31.45	6.096
		313.15	0.865	0.50	-34.31	3.554
		318.15	0.793	0.51	-34.85	3.494
		323.15	0.703	0.53	-35.83	3.165

This is a common occurrence for the aggregation of surface active materials [25,51]. A similar pattern was reported by Masalci [54], where the ΔG^0 values follow the trend we

noticed. It is also reported by Masalci [54] that ΔG^0 is shown to fall to higher negative values as the temperature rises when the polymer is increased in quantity. In the absence of electrolytes in the solution, $\Delta G^0_{1,m}$ values become more negative as the temperature rises, eventually remaining nearly constant. The drops of $\Delta G^0_{1,m}$ values as the temperature rises indicate that the surfactant's hydrophilic group has desolvated [55]. Sharma et al. [56] reported ΔG^0_m value of $-16.98 \text{ kJ mol}^{-1}$ for the assembly of 0.1% (*w/v*) PEG-4000 and CPC mixture, and the ΔG^0_m experienced an upsurge with the escalation of temperature. The ΔG^0_m value of $-29.03 \text{ kJ mol}^{-1}$ for the aggregation of PVP + cationic gemini (16-5-16) surfactant at 303 K was stated by Azum et al. [57] and the negative values of their investigation were increased with enhancing temperature. A decrease in spontaneity for the aggregation of the mixture of bovine serum albumin and CPC in aq. glycerol and dimethyl sulfoxide solutions has been achieved by Sharma et al. [58]. In the current study, the free energy of micellization for CMC_2 and CMC_3 were also negative, which revealed the spontaneous occurrence of the processes (not given in tabular form).

The ΔG^0_t values are negative in the present investigation for the shift of CPC + PVP system from H_2O to $H_2O + NaCl$ medium. The $-\Delta G^0_t$ values were also obtained for the mixture of TTAB and promethazine hydrochloride in $H_2O + NaCl$ medium [59]. Similar characteristics of PVP + CPC system on the basis of the values of ΔG^0_t have been published for the SCAP + PVP and SDS + PVP system [19,60]. For the aggregation of CPC in aq. 0.05 to 0.5% PVP solutions, Sood obtained ΔG^0_t values of -0.49 to $-0.64 \text{ kJ mol}^{-1}$ while the $-\Delta G^0_t$ values enhanced slightly with the growing concentration of PVP [19]. The average value of ΔG^0_t for CPC + PVP (mol. wt. 40,000) for variation of C_{PVP} from 0.05 to 0.5% and CPC + PVP (mol. wt. 3, 60,000) for variation of C_{PVP} range 0.01 to 0.07% is comparable with our observed data [31]. Azum et al. [53] obtained negative transfer free energy for the micellization of PVP + cationic gemini surfactant, and they obtained no specific trend with temperature. The $-\Delta G^0_t$ values disclose the feasibility of the interactions between the components present in the system.

Anand and Yadav [61] achieved the negative values of $-\Delta G^0_t$, and the negative values increased and underwent a fall with the enhancing of PVP contents and temperature of the study, respectively. In the case of sodium sulfate solutions, the ΔG^0_t values are positive, which indicates that the surfactant system prefers to stay in the aqueous medium than the salt solution.

The enthalpy (ΔH^0_m) and entropy (ΔS^0_m) changes involved in the aggregation of CPC + PVP mixture were determined using the following equations [45–51].

$$\Delta H^0_m = -(1 + \beta)RT^2 \left(\frac{\partial \ln X_{CMC}}{\partial T} \right) \quad (3)$$

$$\Delta S^0_m = (\Delta H^0_m - \Delta G^0_m)/T \quad (4)$$

The $\ln X_{CMC}$ is dependent on temperature and can be described as by Equation (5) [62–65].

$$\ln X_{CMC} = A + BT + CT^2 \quad (5)$$

A second-order polynomial fitting of $\ln X_{CMC}$ vs. T plot was achieved nonlinear (Figure 2). The values of fitting parameters (A , B , and C (regression constants)) have been exposed in Table 5. The enthalpy (ΔH^0_m) has thus been computed applying the following Equation (6):

$$\Delta H^0_m = -(1 + \beta)RT^2(B + 2CT) \quad (6)$$

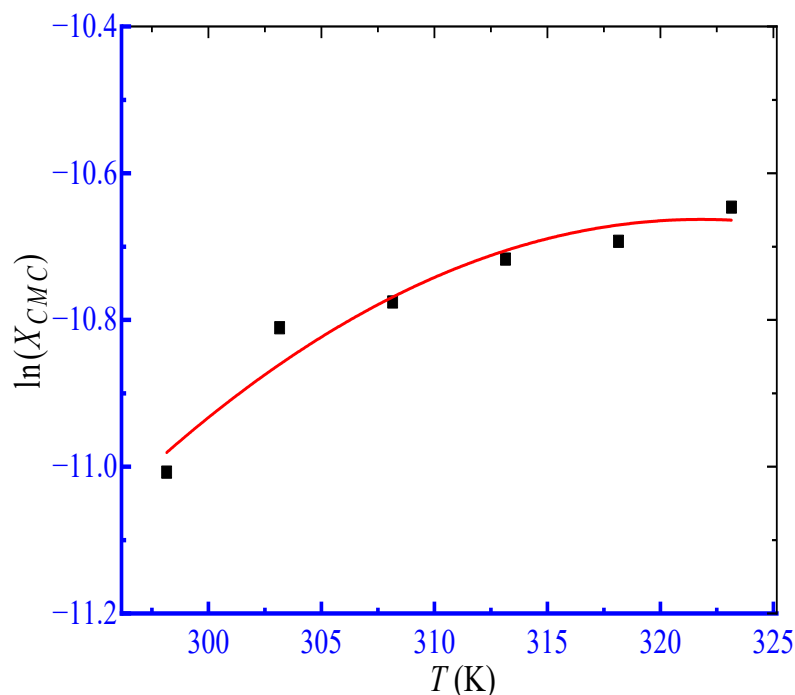


Figure 2. A second-order polynomial fitting of $\ln X_{CMC}$ vs. T plot for the assembly of CPC + 0.1% (w/v) PVP systems in water.

Table 5. The values of A , B , and C for the aggregation of CPC + 0.1% (w/v) PVP mixed system.

Media	I_{salts} mmol kg^{-1}	A	B	C
H ₂ O	0	−69.463	0.3654	−0.0006
H ₂ O + NaCl	1.5	126.7	−0.8927	0.0014
H ₂ O + Na ₂ SO ₄	1.5	−139.01	0.8273	−0.0013

The ΔH_m^0 and ΔS_m^0 values achieved in the current study are not exposed in the table, but these values are used to determine the ΔH_m^0 - ΔS_m^0 compensation. The enthalpy–entropy compensation (Figure 3) has been calculated from a linear connection amid ΔH_m^0 and ΔS_m^0 with R^2 value in the range of 0.9989–0.9992 using the following equation [66–75]:

$$\Delta H_m^0 = \Delta H_m^{0,*} + T_c \Delta S_m^0 \quad (7)$$

The compensation temperature, T_c , and the intrinsic enthalpy gain, $\Delta H_m^{0,*}$ are represented by the slope and intercept, respectively. Table 6 shows the values of $\Delta H_m^{0,*}$ and T_c for the CPC + 0.1% (w/v) PVP systems in H₂O and aq. salts solution.

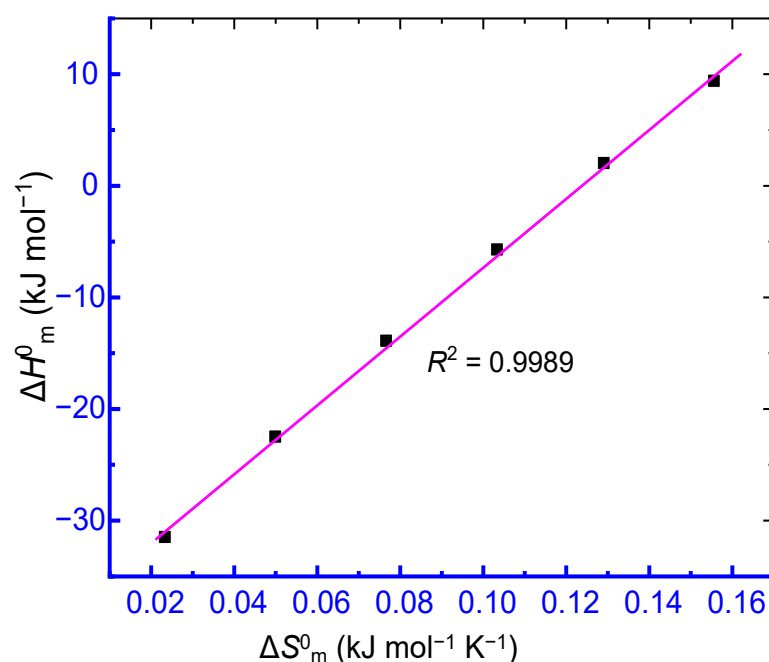


Figure 3. Enthalpy change vs. entropy change plot for the aggregation of CPC + 0.1% (w/v) PVP mixed system in water.

Table 6. Enthalpy–entropy compensation parameters for CPC + 0.1% (w/v) PVP systems in H₂O and aq. salts solution.

Media	I_{salts} mmol kg ⁻¹	$\Delta H_m^{0,*}$ kJ mol ⁻¹	T_c (K)	R^2
H ₂ O	0	−38.05	309.06	0.9989
H ₂ O + NaCl	1.50	−37.32	305.62	0.9992
H ₂ O + Na ₂ SO ₄	1.50	−35.66	324.90	0.9991

According to Equation (7) above, the R^2 value in the range of 0.9989–0.9992 was given in Table 6. The T_c and $\Delta H_m^{0,*}$ describe the solute–solute and solute–solvent interactions, respectively, for the self-assembly process of amphiphiles [75]. The greater negative $\Delta H_m^{0,*}$ value indicates that micellization is preferred even when $\Delta S_m^0 = 0$ [70,71]. If entropy change value becomes zero, ΔH_m^0 becomes equal to $\Delta H_m^{0,*}$ which refer the solute–solute interactions and the contribution of solvent effect might be ignored [73]. T_c values in this study were achieved in the range of 305.62–324.9 K. Shi et al. reported the T_c values of 312–321 K for the micellization of anionic/cationic/zwitterionic/nonionic amphiphiles. Koya et al. achieved the T_c and $\Delta H_m^{0,*}$ values of 220 K and -36.6 kJ mol⁻¹ for the micellization of CPC in 0.1 mol L⁻¹ glycine solution [74]. With a few exceptions, the T_c values for CPC + PVP were found to be nearly comparable to biological fluid [72]. Sugihara and Hisatomi [70] discovered a similar compensatory effect for the aggregation of charged amphiphiles in H₂O medium. The T_c values have been described as the proof of hydrophobic interaction between the studied components [71]. García-Mateos et al. suggested the presence of hydrophobic interactions between CPC and PVP [31]. On the basis of higher negative $\Delta H_m^{0,*}$ and greater T_c values, Shi et al. reported that zwitterionic surfactants form more tighter and stable micelles compared to the anionic/cationic and nonionic amphiphiles [73].

4. Conclusions

The conductivities of PVP + CPC mixed systems were measured in H₂O/H₂O + NaCl/H₂O + Na₂SO₄ solutions at various temperatures to insight into the interaction between PVP and CPC. The degree of interaction was determined by the values of CMC, β ,

and certain thermodynamic factors. Both the micellization of PVP + CPC mixed systems and β values were temperature dependent in aqueous and electrolytes media. At all temperatures, the values of ΔH_m^0 and ΔS_m^0 indicate the presence of hydrophobic interaction between PVP and CPC in aqueous and electrolytes media. The $\Delta G_{1,m}^0$ values show that, the spontaneity of self-aggregation is almost similar in case of water and aq. NaCl medium whereas the negative values are lower in aq. Na₂SO₄ solutions. The values of $\Delta H_m^{0,*}$ vary from -35.66 to -38.05 kJ.mol⁻¹, indicating that the micelle produced is stable. The T_c values are very similar to those of a biological system. Here, investigation of the interaction of surfactant and polymer in presence of low molecular weight electrolyte was carried out because low to moderate amphiphiles concentrations are used to form hydrogels, as self-assembly makes several approaches to attain gelation available.

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