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RESEARCH ARTICLE

EFFECTS OF POLYMER CONCENTRATION AND TEMPERATURE ON MICELLIZATION OF CETYLTRIMETHYLAMMNIUM BROMIDE (CTAB) IN AQUEOUS PVP-CTAB MIXED SYSTEM

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ABSTRACT

Polymeric micelles supply an environment, which can be cautiously regulated for drug delivery. The self-assembly of polymeric micellization is dynamic. Micellization thermodynamic describes how the system defines the formation of micelles. The present study enables the micellization behavior of the surfactants in the presence of polymer to be examined by conductometric and tensiometric methods. The effects of polymer concentration and temperature on the micellization thermodynamics of a neutral soluble polymer and cationic cetyltrimethylammomium bromide (CTAB) surfactant mixture in aqueous medium were investigated. To examine polymer-surfactant interaction, critical micellar concentration (CMC) and thermodynamic parameters such as standard free energy ΔG, enthalpy ΔH and entropy ΔS are calculated by using a pseudo-phase model. Based on CMC, ΔG, ΔH and ΔH, the dependence of the compensation temperature on the polymer effect is discussed. This advanced work to understand micelle stability and compatibility can be comprehensively feasible in polymeric systems.

Keywords: Polymer-surfactant interaction, Micellization, Thermodynamic parameters, Entropy

1. INTRODUCTION

The features of the aqueous solutions with surfactants and polymers are different from those with either one of them [1]. Mechanism of interaction between the surfactants with self- assembly property in water and large polymers with many molecules has long been of attention paid by interdisciplinary researchers who study in both experiment and calculation [2]. Practices of surfactant-polymer systems have been increased as industrial products by studying and better understanding their physical and chemical characteristics. Fields of use for such mixtures are quite extensive including detergents, painting and plating material, cosmetic and medicinal industries, mineral and oil refinery processes [3-7]. Although numerous studies [8-10] have been performed on interaction of pure surfactants with polymers, complex structure of such an interaction has yet to be thoroughly conceived [11, 12].

Interactions between polymers and surfactants in aqueous environment cause formation of association structures, thereby altering solution and interface properties [13, 14]. The morphology of the association compounds depends on the molecular properties of the polymer and the surfactant. In general, the combined presence of polymer and surfactant molecules changes the rheological properties of solutions, the adsorption properties of solid-liquid interfaces, the stability of colloid dispersions, their solubility in water for low-soluble molecules and their liquid-liquid interface tensions. The ability of surfactant and polymer molecules to influence the solution and interface properties is controlled by the formation in aqueous solutions [15]. In addition, micellar solubilization is a strong option for dissolving hydrophobic drugs in aqueous media [16]. It is seen in many studies that polymeric micelles have significant contributions to drug delivery [17].

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The behavior of the solution in water includes many complex interactions, which are essentially various water- water, water- solute molecule and soluble molecule- solute molecule ones. In the systems with surfactants and self- assembly nature, these interactions are grouped into those of 1) hydrophobicity of alkali chains 2) hydrophility of head groups 3) electrostatic character of head groups for ionic surfactants. Hydrophobicity of organic compounds is associated with the energy that the chemicals want to avoid aqueous phase needed for the purpose [18].

Surfactant substances aggregate together in groups to form micellar structures thanks to their self-assembly property in water, which is as a value called critical micellar concentration (CMC) [19]. When the surfactant has been dissolved in water to form micellar structures, conformational changes could occur if there are polymers as well due to the interaction between polymer and surfactant chains. Such changes may modify micellar properties of the surfactant [20-22]. The most agreeable model was proposed by Cabane for complex formations between water soluble polymers and surfactants [23, 24]. With the addition of surfactants to the aqueous solution of the polymer, surfactant molecules begin to aggregate anywhere near the polymer segment. The value of concentration at the beginning of the aggregation is less than that of CMC and referred to as critical aggregation concentration (CAC). As the surfactant concentration increases, there happens an increase at the surfactant that has formed an aggregate along the polymer chain with regular micelles at C2 point [25, 26].

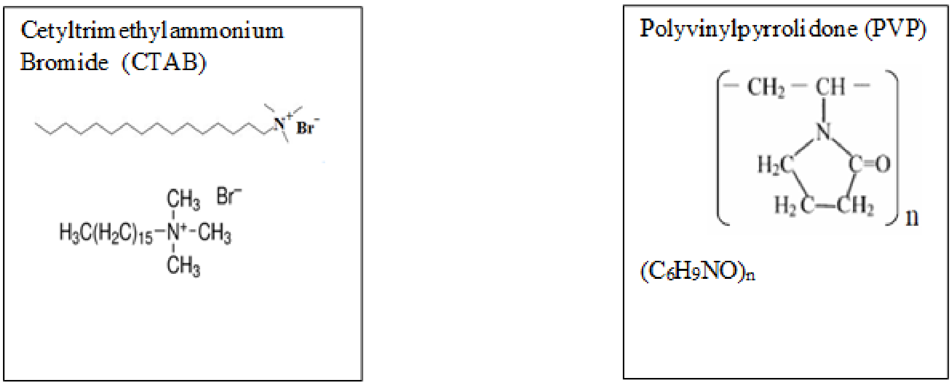
Polyvinylpyrrolidone (PVP) is a nonionic water-soluble polymer and can be applied in a variety of fields owing to the following advantages. It is present in several viscosity grades, ranging from low to high molecular weight. The low molecular weight-polymers have narrower distribution curves of molecular entities than high molecular weight compounds. PVP is a bulky and non-toxic polymer with C=O, C–N and CH_2 functional groups. The PVP molecule has a strongly hydrophilic component (the pyrrolidone moiety) and a significantly hydrophobic group (the alkyl group). PVP is a water-soluble nonionic polymer, which has beneficial uses such as cosmetics, biomedicine, food industry biocompatibility and biodegradability due to its nontoxicity [27, 28]. CTAB is a cationic surfactant and a bactericidal soluble in water. It is widely used for isolation of DNA [29].

The literature involves some studies, which handle interactions between Polyvinylpyrrolidone (PVP), a neutral and water soluble polymer and CTAB, a cationic surfactant. The study by Bali and Masalci [30] compared thermodynamic parameters upon the addition of chaotrope CTAB surfactant and cosmotrope CTACI surfactant into the solution including 1% PVP (w/V) in order to examine the counterion effect. On the other hand, our current study aims to investigate the effect of the polymer contribution on the system and polymer solutions with different concentrations were therefore used. The main purpose of the study by N Sardar et al. [31] was to examine the impact of the surfactants and it was thus different from our study. In addition, CTAB- PVP interaction was examined by electroconductivity method using the solutions with polymers less than 1% PVP (w/V). Our present study employed the solutions including 0,5 - 1-1,1.5 -2 %PVP (w/V). That is, contribution of the polymer greater than 1% PVP was explored by both electroconductivity and surface tension methods. Moreover, unlike other studies, the present study calculated enthalpy and entropy values as well.

2. MATERIAL AND METHODS

2.1. Materials

The current study used Cetylmethylammoniumbromide 99 % (molecule weight: 364.45 g/mol) (CTAB) as the surfactant and PVP 99% (molecule weight: 10000 g/mol) as the polymer. CTAB (SIGMA H-5882) and PVP (SIGMA PVP10) were purchased from Sigma-Aldrich and directly employed in the experiments without any given processes. Electrical conductivity of the deionized water used as the solvent in the samples was measured to be 6μS/cm at 25 ° C (298 K). Figure 1 presents chemical formulas and structures of the chemical materials used as CTAB and PVP.



(a) **(b)**

Figure 1. Structures and chemical formula of (a) CTAB and (b) PVP

An AND HR- 120 of 10^{-4} precision model scales was used to measure the amount of the surfactant determined during preparation. Twenty different samples at concentrations variable between 0.2mM and 5mM for the purpose of studies. Critical micellar concentration (CMC) was then determined using electrical conductivity and surface tension methods at 25°C - 30°C - 35°C - 40°C and 45°C.To study effect of polymer on aggression, four different polymer-water solutions of 0.5 % ,1.5 % ,1% , 1.5 % and 2 % were prepared by w/V ratio. Later, each solution was supplied with different CTABs at the concentrations determined above to constitute new solution sets. Newly prepared individual samples with polymer-surfactant mixtures in each was brought to an equilibrium temperature first then measurement of electrical conductivity and surface tension per each was made involving the above temperatures. CAC and C2 concentrations were found by means of fracture points at graphics of electrical conductivity and surface tension drawn by surfactant concentrations. The experiments were repeated at least 3 times.

2.2. Methods

2.2.1. Surface tension measurements

The present study examined surface tensions of the samples with Plate method using KrüssEasyDyne tensiometer. Plate method is a static process used to measure changes on surface tensions, in which one measures change of force needed to keep the plate stable in free immersion as the surface tension varies during its immersion in water. All the related measurements were made after equilibrium temperature had been achieved. To bring the samples to the equilibrium temperature required, PHYWE trade mark thermostat system was used and TTT-ECHNI-C TM902C trade mark thermocouple device employed to measure the temperature. Calibration of the tensiometer was tested using pure deionized water and ethyl alcohol.

2.2.2. Conductivity measurements

WTW inolab Level 3 module and its compatible TetraCon 325 probe made electrical conductivity measurements. The probe that we used to measure the temperature are made of graphite and include four electrodes. The temperature at which the probe could be used and the conductivity for the measurement ranged from -5 to 100° C and from 1μS/ cm to 2 S/cm, respectively. The probe measures the temperature at the precision of an integrated graphite - made NTC(30 kΩ/25 °C). Because the probe performs it by a total of four electrodes with two currents and two voltages, precision in measurement of conductivity depends on magnitude of conductivity being 0,5 % .

Prior to measurement experiments for electrical conductivity, a calibration adjustment was made using 0.5 mol/ l KCL calibration liquid under the procedure in the user guide.

3. RESULTS AND DISCUSSION

The present study examined changes of the surface tension (Figure 2) and specific conductivity (Figure 3) based on surfactant concentrations.

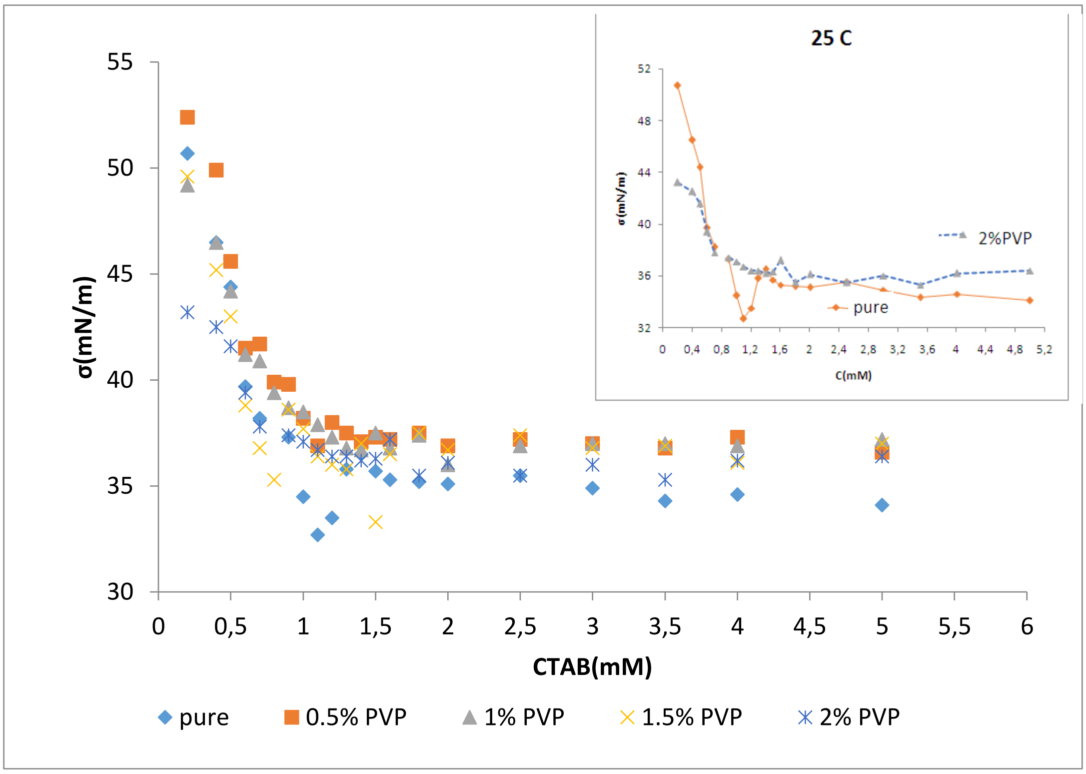


Figure 2. CTAB concentration change of the surface tension at T=25 ^{o}C

Figure 2 illustrates the variation of surface tension with surfactant concentration. As the surfactant concentration increases, the value of surface tension decreases rapidly as seen in the figure. Following the given low value, surface tension just increases a little then stabilizes. When the surface tension has been minimum, surfactant molecules begin to aggregate together to form micelles. The concentration of micelles formation as CMC value is thus experimentally determined [32-34]. In the presence and absence of PVP, change curves showed various differences. With the addition of 0.5 % PVP, the orientation of the curve almost resembles the previous position. Only one changing point is observed in the curve. In other words, in the presence of low polymer, it is the only interaction between the surfactant and polymer changes which is the concentration value when micellar formation has started. The study by N Sardar et al [31] observed the similar result. That is, at low concentrations of PVP exists CMC point only. As polymer concentration increases, a decrease of surface tension at 1% PVP value shows a change of two different slopes. The decrease is rapid first then slope of the curve decreases after a given fracture point, upon which a small instable region is observed and the surface tension remains almost stable. Therefore, in the curve appear three different characteristic regions and two fracture points, which are experimentally determined when PVP concentration are 1% - 1.5 % and 2 % with the former being called CAC the latter C2. At CAC value, the surfactant begin to aggregate around polymer chains only without formation of micelles yet, while micellar formation has begun as it is known at C2.

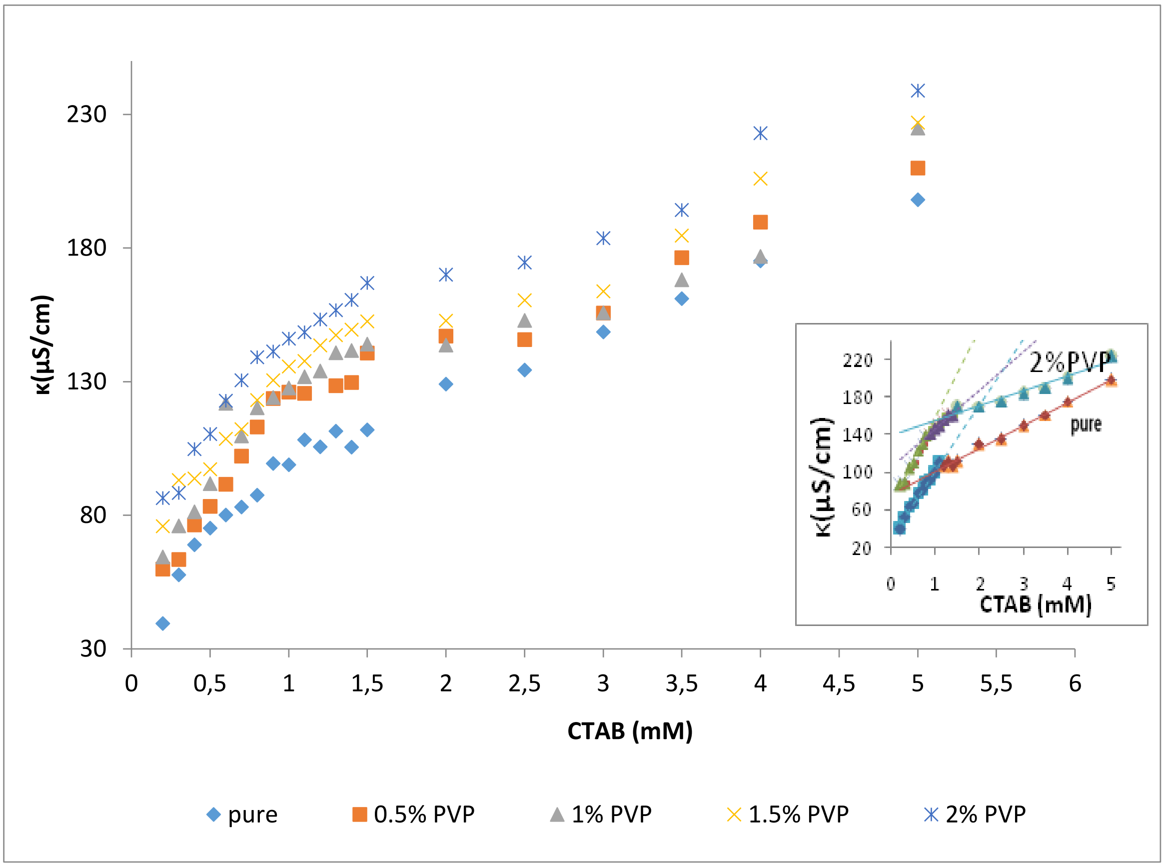


Figure 3. CTAB concentration change of specific electrical conductivity at T=25 ºC

Figure 3 shows change in specific conductivity with surfactant concentration. As the surfactant concentration increases , the specific conductivity elevates as in the figure. In the presence and absence of PVP, various differences were observed in the curves of changes [30]. Without PVP, the specific conductivity increases at certain concentrations, which is called CMC as the point when the course has begun to vary. With the addition of 1% PVP emerge two fracture points at specific conductivity, the former being called CAC and the latter C2. At CAC value, surfactant molecules begin to aggregate around polymer chains but micelles have not appeared yet. At C2 value, however, micellar formation has begun, as it is known. As PVP concentration was 1.5% and 2%, two different fracture points were experimentally observed in the specific conductivity changes. Experimentally found CMC, CAC and C2 points are presented in table 1.

Table 1. Micellar parameters; CMC, CAC, C2, standard free energy ΔG, enthalpy ΔH and entropy ΔS of CTAB in Aqueous PVP-CTAB Mixed System

%PVP	**Temp (ºC)**	**CMC (mM)**	**CAC (mM)**	**C2 (mM)**	**ΔG (kJmol^{-1})**	**ΔH (kJmol^{-1})**	**ΔS (kJmol^{-1})**
0	25	0.93			-48145.1	-90897.4	-143.39
	30	0.98			-56046.2	-84786.9	-94.81
	35	1,06			-59782.8	-92549.5	-106.33
	40	1.13			-60755.5	-96125.0	-112.95
	45	1.20			-61310.5	-99086.5	-118.74
0.5	25	1.00			-46215.9	-63657.3	-58.50
	30	1.02			-46360.8	-65046.8	-61.64
	35	1.13			-46514.2	-66972.9	-6639
	40	1.15			-46746.7	-68511.9	-69.50
	45	1.21			-47997.6	-71809.9	-74.85
1.0	25		0.68	1.30	-45951.87	-25855.20	67.40
	30		0.70	1.32	-45306.14	-16281.20	95.74
	35		0.86	1.28	-44526.13	-6680.42	122.82
	40		0.85	1.33	-44049.76	3157.91	150.75
	45		0.82	1.38	-44497.63	13334.66	181.78
1.5	25		1.0	1.45	-43133.1	-2472.24	136.38
	30		1.0	1.52	-42684.4	2296.20	148.38
	35		1.2	1.52	-41649.4	7142.57	158.34
	40		1.14	1.64	-40470.9	11761.98	166.80
	45		1.2	1.77	-40694.8	16942.31	181.16
2	25		0.76	1.39	-40983.6	14597	186.42
	30		0.76	1.45	-40413.2	19386.5	197.26
	35		0.77	1.48	-38477.6	23460.8	201.00
	40		0.71	1.47	-37267.7	25531.6	200.54
	45		0.70	1.55	-37379.0	31148.2	215.39

Thermodynamic parameters have significant roles to play in understanding mechanism of the micellar process [35-37]. To observe the effects of structural and environmental factors on CMC, CAC and C2 values and simultaneously determine new structural and environmental deviations, it is necessary to calculate values of the thermodynamic parameters such as standard free energy ΔG°_{m}, enthalpy ΔH°_{m} and entropy ΔS°_{m}. In this case, the widely used pseudo-phase model could be used in energetic interpretation of micellization [38, 39].

The following equation is employed to calculate the standard free energy of micellization ΔG°_{m}

$$\Delta G_{m}^{o} = (2-\propto)RT\ln X_{cmc} \tag{1}$$

Where R is the gas constant (8.314 J/mol K), X_{cmc} the cmc expressed in mole fraction unit, T temperature in Kelvin scales. Micelle ionization degree (α) can be calculated by proportioning the slope of the curve below CMC value to that above it and vice versa.

Other thermodynamic parameters such as enthalpy ΔH°_{m} and entropy ΔS°_{m} can be calculated as follows;

$$\Delta H_{psi}^{o} = -(2-\propto)RT^{2}\left(\frac{\partial \ln X_{cac}}{\partial T}\right) \tag{2}$$

$$\Delta S_{psi}^{o} = \frac{\Delta H_{psi}^{o} - \Delta G_{psi}^{o}}{T} \tag{3}$$

The following equation can be used to calculate the standard free energy emerging based on surfactant-polymer interactions when the polymer has been added to the binary system.

$$\Delta G^{o}_{psi} = (2-\propto)RTlnX_{cac} \quad (4)$$

where X_{cac} is the mole value of experimentally found. Values of ΔH^{o}_{psi} and entropy ΔS^{o}_{psi} needed to understand surfactant-polymer interactions can be calculated by using the equations below.

$$\Delta H^{o}_{m} = -(2-\propto)RT^{2}(\frac{\partial lnX_{cmc}}{\partial T}) \quad (5)$$

$$\Delta S^{o}_{m} = \frac{\Delta H^{o}_{m} - \Delta G^{o}_{m}}{T} \quad (6)$$

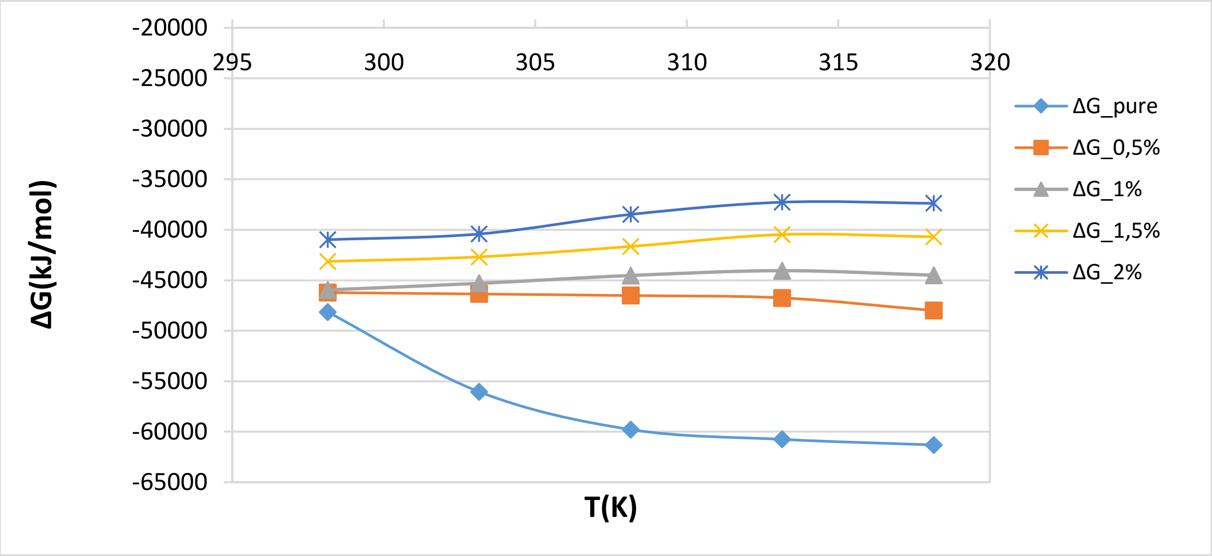


Figure 4. Change of standard free energy with the temperature

Figure 4 exhibits variation of ΔG with temperature. As can be seen, the values are negative, which shows that micelles have formed in the solution by themselves. This is an expected phenomenon for the molecules including surface active material [39]. In the absence of polymer in the solution, as the temperature increases, ΔG values go more negative to finally remain almost constant. The fact that ΔG decreases as the temperature increases shows that desolvation has occurred in hydrophobic group of the surfactant [40]. Once the polymer has been added to the medium, the trend of ΔG becomes differentiated though it is negative. Low addition of polymer (0.5 % PVP) tends to show that as the temperature increases ΔG goes negative only with a deceleration. When the polymer has been increased in quantity and with the addition of 1% PVP, ΔG is shown to go to less negative values as the temperature increases. High polymer concentrations of 1.5 % PVP and 2 % PVP have been shown to make ΔG to increase more significantly with the temperature.

As the medium has polymer and surfactant, bonding of the surfactant to the polymer is exothermic phenomenon while spreading of the polymer in the aqueous medium is an endothermic process, which shows a competition between the two [41]. As the polymer has been added to the medium, presence of polymer chains likely to spread in it increases and the value of free energy becomes less negative (it comes closer to zero).

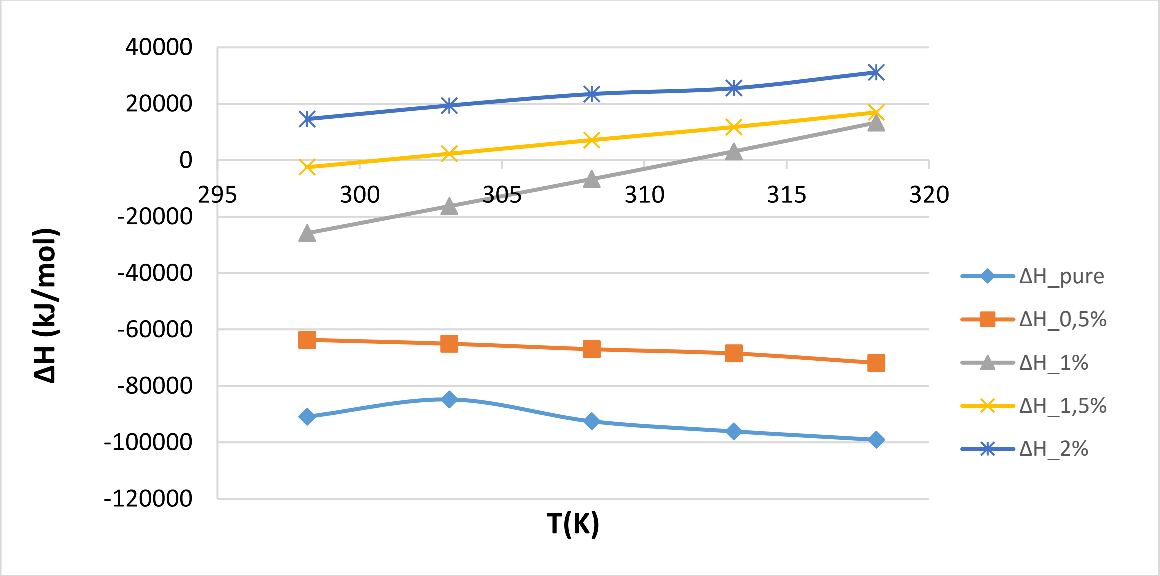


Figure 5. Change of enthalpy value with the temperature

Figure 5 illustrates the variation of ΔH with temperature. As can be seen, in the absence of polymer and presence of low polymer, ΔH values are negative. Without polymer and as the temperature increases, ΔH decreases. However, ΔH increases for 1%, 1.5 % and 2 % PVP as the temperature increases.

Beginning from 1%PVP value, the presence of polymer in the environment affected the trend of change of ΔH depending on temperature, ΔH starts to increase with temperature instead of decreasing. The fact that ΔH is negative in value shows that $\Delta H < 0$ micellization is an exothermic process [42]. With polymer concentration, increasing, negative value of ΔH is observed to increase. ΔH becomes positive ($\Delta H > 0$) for 1%,1.5 % and 2% PVPs at high, low and all temperatures respectively. That is, micellization turns to an endothermic process. For ΔH to be positive requires that either structured H_2O should be severed or its hydrogen bonds be broken in hydrophobic region as the result of hydrophobic interactions [43]. Increase of polymer concentration in the medium has led to the fact that both effects possibly occur together ΔH becomes positive. On the other hand, the fact that enthalpy is negative ($\Delta H < 0$) in the presence of low polymer at low temperature implies that London dispersion force is dominant during the aggregation [43, 44].

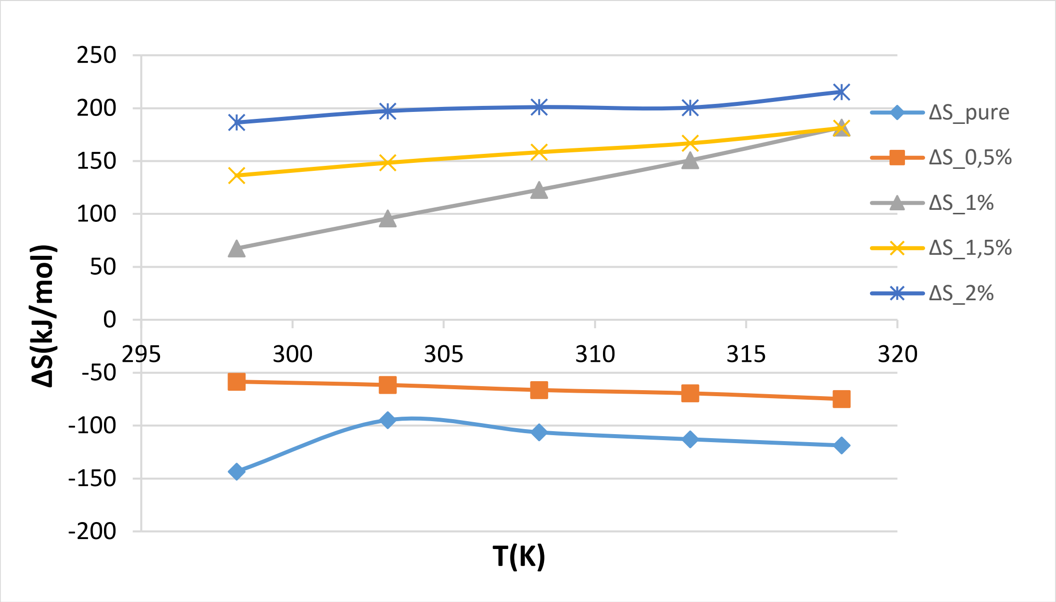


Figure 6. Change of entropy value with the temperature

Figure 6 shows change of ΔS with temperature. As can be seen, in the absence of polymer and in the presence of low polymer, ΔS has negative values but from 1% PVP upwards values of ΔS turns positive and increases with temperature as seen in the graph. Enthalpy is found negative (ΔH <0) and entropy seen positive (ΔS>0) in the absence of polymer and in the presence of low PVP (05% PVP) at all temperatures, which shows that micellization has been under enthalpy controlled. Negative values of ΔH and ΔS show the presence of hydrogen bonds between the constituents [45]. As the amount of PVP for 1% PVP at low and medium temperatures, enthalpy (ΔH<0) is negative and entropy (ΔS>0) positive, which implies that micellization has been enthalpy + entropy controlled. As the temperature increases and at high temperatures, enthalpy turns positive (ΔH>0) and entropy (ΔS>0) positive, implying that micellization has been under entropy.

When the amount of PVP is 1.5% PVP, at low temperatures, enthalpy is negative (ΔH<0), and entropy positive (ΔS>0), which shows that micellization has been enthalpy+ entropy controlled. As the temperature increases, both enthalpy and entropy become positive and thus micellization has been entropy controlled. At high polymer concentration and for 2%PVP, both enthalpy and entropy are positive and thus micellization has been entropy controlled. ΔS positive value for mixed surfactant micelles could be caused by two factors, one of which is that nonpolar chains of the surfactant might have slipped from the aqueous medium to the center of the micelle in nonpolar nature as the result of breakdown of iceberg structure of water. The other factor could be the shooting of freedom of hydrophobic chains in micellar interior as compared with the aqueous medium [30, 45].

4. CONCLUSION

Using surface tension and conductivity methods, we examined contribution of PVP, a neutral polymer to micellization machinery of CTAB, a cationic surfactant. CMC, CAC and C2 values were experimentally determined by two different methods. It follows from the results that temperature hardly effects the values but has a much greater impact on thermodynamic parameters.

ΔG values are negative at all examined temperatures. That is, micelles form in the solution spontaneously, which shows that interactions are voluntary. The sign of ΔH informs us on the nature of micellization mechanism, in other words on whether it is endothermic or exothermic [46]. Positive ΔH value may emphasize importance of hydrophobic interaction while negative ΔH value shows that the major attraction force for micellization exhibits London dispersion interaction [47].

In the absence of polymer or in its little presence, enthalpic contribution is of greater importance. Enthalpic contribution causes hydrogen bonds among water molecules to begin to break. As PVP concentration increases and due to temperature, enthalpy +entropy contributed micellization process can be seen. As the amount of PVP in the solution, micellization mechanism becomes entropy-contributed. Such assessments show that at low temperatures and polymer amounts, combination of electrostatic and hydrophobic interactions is effective but hydrophobic interactions are dominant at high temperatures and in low polymer amounts.

When we look at other studies examining the interactions between surfactant-polymer [17, 21, 25, 30, 48], it is seen that the interactions are enthalpy, enthalpy-entropy and entropy controlled depending on the ambient conditions. If the interaction between CTAB and PVP is improved and the thermodynamics of the surfactant-polymer is better understood, this system can be used as a solubilizing area for an active matter in drug delivery systems.

CONFLICT OF INTEREST

The author stated that there are no conflicts of interest regarding the publication of this article.

REFERENCES

[1] Bharswaj P, Kamil M, Panda M. Surfactant-polymer interaction :effect of hydroxypropylmethyl cellulose on the surface an solution properties of gemini surfactants. Colloid Polym Sci, 2018; 296: 1879-1889.

[2] Thiele MJ, Davari MD; Hoffmann I. Enzyme-Compatible Dynamic Nanoreactors from Electrostatically Bridged Like-Charged Surfactants and Polyelectrolytes. Angew Chem Int Ed, 2018; 57: 9402-9407

[3] Slastanova A, Campbell RA, Snow T, Mould E, Li P, Welbourn RJL, Chen M, Robles E, Briscoe WH. Synergy, competition, and the ‘‘hanging” polymer layer: Interactions between a neutralamphiphilic ‘tardigrade’ combco-polymerwith ananionicsurfactant at the air-water interface, J Colloid Interf Sci, 2020; 561: 81–194

[4] Kancharla S, Zoyhofski NA, Bufalini L, Chatelais BF, Alexandridis P. Association between Nonionic Amphiphilic Polymer and Ionic Surfactant in Aqueous Solutions: Effect of Polymer Hydrophobicity and Micellization. Polymers, 2020; 12: 1831

[5] Yang J, Pal R. Investigation of Surfactant-Polymer Interactions Using Rheology and SurfaceTension Measurements. Polymers, 2020; 12: 2302

[6] Bagheri A. Comparison of the interaction between propranolol hydrochloride (PPL) with anionic surfactant and cationic surface active ionic liquid in micellar phase. Colloids Surf, A Physicochem Eng Asp, 2021; 615: 126183

[7] Hu C, Du Z, Tai X, Mao X, Liu X. The property study of sodium dodecyl benzenesulfonate and polyvinylpyrrolidone complexes. Colloid Polym Sci, 2018; 296: 335–340

[8] Hansson P, Almgren M. Interaction of alkyltrimethylammonium surfactants with polyacrylate and poly (styrenesulfonate) in aqueous solution: phase behavior and surfactant aggregation numbers. Langmuir, 1994 ;10: 2115–2124.

[9] Pettersson E, Topgaard D, Stilbs P, Söderman O. Surfactant/nonionic polymer interaction. A NMR diffusometry and NMR electrophoretic investigation. Langmuir, 2004; 20: 1138–1143.

[10] Xu L, Yokoyama E, Satoh M. Specific interactions of poly(4-vinyl phenol) gel with cationic and anionic surfactants. Langmuir, 2005; 21: 7153–7160.

[11] Tajik B, Sohrabi B, Amani R, Hashemianzadeh SM, The study of polymer–surfactant interaction in catanionic surfactant mixtures. Colloids Surf, A Physicochem Eng Asp, 2013; 436: 890–897

[12] Zhang H, Deng L, Zeeb B, Weiss J, Solubilization of octane in cationic surfactant–anionic polymer complexes: Effect of polymer concentration and temperature, J Colloid Interf Sci, 2015; 450: 332–338

[13] Nagarajan R. Polymer-Surfactant Interactions. In New Horizons: Detergents for the New Millennium Conference Invited Paper Fort Myers, Fla, USA, 2001.

[14] Lindman B, Nylander T. Cosmetic Science and Technology, 1st ed. Elsevier, eBook, 2017.

[15] Kocakülah G, Algül G, Köysal O. Effect of CdSeS/ZnS quantum dot concentration on the electro-optical and dielectric properties of polymer stabilized liquid crystal. J Mol Liq, 2020;299:112182.

[16] Schreier S, Malheiros SVP, Paula E. Surface active drugs: self-association and interaction with mebranes and surfactants. Physicocehemical and biological aspects. Biochim Biophys Acta, 2000; 1508:210-234.

[17] Grimaudo MA, Pescina S, Padula C, Santi P, Concheiro A, Alvarez-Lorenzo C, Nicoli S. Topical application of polymeric nanomicelles in ophthalmology: a review on research efforts for the noninvasive delivery of ocular therapeutics. Expert Opin Drug Deliv, 2019;16:397-413.

[18] Hammer J, Haftka JJH, Scherpenisse P, Hermens JLM, De Voogt P. Investigation hydrophilic and electrostatic properties of surfactants using retention on two mixed-mode liquid chromatographic columns. J Chromatogr A, 2018;1571:185-192.

[19] Rangel-Yagui CO, Pessoa-Jr A, Tavares LC. Micellar solubilization of drugs. J Pharm Pharmaceut Sci, 2005; 8: 147-163.

[20] Chiappisi L, Leach SD, Gradzielski M, Precipitating polyelectrolyte–surfactant systems by admixing a nonionic surfactant – a case of cononsurfactancy. Soft Matter 2017; 13: 4988-4996.

[21] Sardar N, Kamil M, Kabir-ud-Din. Studies on Solution Behavior of Aqueous Mixtures of Nonionic Polymer in Presence of Cationic Surfactants. J Surfact Deterg, 2017; 20: 631–645.

[22] Rahman F, Ali MS, Al-Lohedan HA, Aazam E, Aldhayan DM, Rafiquee MZA. Influence of PVP-PEG mixed aggregates and electrolytes on the rate of alkaline hydrolysis of benzocaine in aqueous and surfactant medium. J Mol Liq, 2020; 317: 113963

[23] Cabane B. Structure of some polymer–detergent aggregates in water. J Phys Chem, 1977; 81: 1639–1645

[24] Gelgec U, Iscan M. Interactions of Polyglycol Ethers with Anionic Surfactants in Water. J Disper Sci Technol, 2010; 31:1667-1672

[25] Rauf A, Baloch MK, Khan A, Khan Z, Rauf S, Effect of Concentration and Molecular Mass of PEO on The Micellization and Thermodynamic Behaviour of Cetyltrimethylammnium Bromide(CTAB) in Aqueous PEO-CTAB Mixed System. J Chil Chem Soc, 2016; 61: 3013-3017

[26] Jönsson B, Lindman B, Holmberg K, Kronberg B. Surfactant and Polymers in Aqueous Solution. 1st ed. Chichester, England:John Willey& Sons, 1999.

[27] Chang H, Du Z, Tai X, Mao X, Liu X. The property study of sodium dodecyl benzenesulfonate and polyvinylpyrrolidone complexes. Colloid Polym Sci, 2018;23:296-335

[28] Higuchia A, Shiranoa K, Harashimaa M, Yoona BO, Haraa M, Hattorib M, Imamura K. Chemically modified polysulfone hollow fibers with vinylpyrrolidone having improved blood compatibility. Biomaterials, 2002;23:2659:2666.

[29] Barut KD, Coşkun Arı FF, Öner F. Development and Characterization of a Cationic Emulsion Formulation as a Potential pDNA Carrier System.Turk J Chem, 2005;29:27-40.

[30] Bali M, Masalci O. Interactions of Cationic Surfactants with Polyvinylpyrrolidone (PVP): Effects of Counter Ions and Temperature. J Mol Liq, 2020; 303: 112576

[31] Sardar N, Kamil M, Kabir-ud-Din. Interactions between Polyvinylpyrrolidone and Cationic Gemini/Conventional Surfactants. Chem. Eng. Comm, 2013;200: 1683-1700.

[32] Sanz MA, Granizo N, Gradzielski M, Rodrigo MM, Valiente M. Mixed micellar systems of octylβ,d-glucopyranoside with a nonionic surfactant and a water-soluble polymer. Colloid Polym Sci, 2005; 283: 646–652.

[33] Capalbi A, La Mesa C. Polymer Surfactant Interactions, J Therm Anal Calorim, 2001; 66: 233-241

[34] Singh R, Chauhan S, Sharma K, Surface Tension, Viscosity, and Refractive Index of Sodium Dodecyl Sulfate (SDS) in Aqueous Solution Containing Poly(ethylene glycol) (PEG), Poly(vinyl pyrrolidone) (PVP) and Their Blends. J Chem Eng Data, 2017;62: 1955−1964.

[35] Mahbub S, Molla MR, Saha M, Shahriar I, Hoque MA, Halim MA, Rub MA, Khan MA, Azum N. Conductometric and molecular dynamics studies of the aggregation behavior of sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) in aqueous and electrolytes solution. J Mol Liq, 2019;283: 263–275.

[36] Sultana S, Alam MDH, Shumon MAH. Physico-chemical study of the interaction between levofloxacin hemihydrate Drug with Cetylpyridinium chloride in aqueous medium: Conductometric and spectrophotometric investigation. Int J Chem Stud, 2020; 8: 15-26

[37] Ali A, Uzair S, Malik NA, Ali M. Study of interaction between cationic surfactants and cresol red dye by electrical conductivity and spectroscopy methods. J Mol Liq, 2014; 196: 395–403.

[38] Soni SS, Sastry NV, Aswal VK, Goyal PS. Micellar Structure of Silicone Surfactants in Water from Surface Activity, SANS and Viscosity Studies. J Phys Chem B, 2002; 106: 2606–2617

[39] Hoque MA, Patoary MOF, Rashid M, Molla MR, Rub MA. Physico-chemical Investigation of Mixed Micelle Formation Between Tetradecyltrimethylammonium Bromide and Dodecyltrimethylammonium Chloride in Water and Aqueous Solutions of Sodium Chloride. J Solution Chem, 2017; 46: 682–703.

[40] Khan Z, Malik MA, AL-Thabaiti SA, Alshehri A, Nabi F. Micellization and Thermodynamic Properties of Cationic Surfactant Cetyltrimethylammonium Bromide in non-Aqueous Mixture of Lauric Acid. Int J Electrochem Sci, 2017; 12: 4528–4542

[41] Gharibi H, Rafat AA, Feizollahi A, Razavizadeh BM, Safarpour MA. Thermodynamic studies of interaction between cationic surfactants and polyvinylpyrrolidone using potentiometric techniques. Colloid Surface A, 1998; 145: 47–60.

[42] Dubey N. CTAB aggregation in solutions of higher alcohols: Thermodynamic and spectroscopic studies. J Mol Liq, 2013; 184: 60–67.

[43] Rahman M, Hoque MA, Rub MA, Khan MA. Interaction of cetyltrimethylammonium bromide with cefixime trihydrate drug at different temperatures and compositions: Effect of different electrolytes. Chin J Chem Eng, 2019; 27: 1895-1903.

[44] Nusselder JJH, Engberts JBFN. Toward a better understanding of the driving force for micelle formation and micellar growth. J Colloid Interface Sci, 1992; 148 : 353-361

[45] Molla MR, Rub MA, Ahmed A, Hoque MA. Interaction between tetradecyltrimethylammonium bromide and benzyldimethylhexadecylammonium chloride in aqueous/urea solution at various temperatures: An experimental and theoretical investigation. J Mol Liq, 2017; 238: 62-70.

[46] Chauhan S, Singh R, Sharma K, Kumar K. Interaction Study of Anionic Surfactant with Aqueous Non-Ionic Polymers from Conductivity, Density and Speed of Sound Measurements. J Surfact Deterg, 2015; 18: 225-232.

[47] Chauhan S, Sharma K. Effect of temperature and additives on the critical micelle concentration and thermodynamics of micelle formation of sodium dodecyl benzene sulfonate and dodecyltrimethylammonium bromide in aqueous solution: A conductometric study. J. Chem. Thermodyn, 2014; 71: 205–211.

[48] Bao H, Li L, Gan LH, Zhang H. Interactions between Ionic Surfactants and Polysaccharides in Aqueous Solutions. Macromolecules, 2008; 41:9406-9412.