



Influence of some added electrolytes on the surface and thermodynamic properties of cetylpyridinium chloride in aqueous medium

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The effect of some added electrolytes, viz. NaCl, CaCl₂ and AlCl₃, on the critical micelle concentration (CMC), maximum surface excess concentration (Γ_{\max}) and minimum area per molecule (A_{\min}) at air-liquid interface of a cationic surfactant cetylpyridinium chloride (CPC) in aqueous solutions have been studied at 288.15, 293.15 and 298.15 K using tensiometric method. The effect of an added electrolyte on decreasing CMC of CPC is found to be in the order (AlCl₃) > (CaCl₂) > (NaCl), which falls in the same order as of the moles chloride ions furnished by each mole of the added electrolyte. The Γ_{\max} decreases with increasing temperature and electrolyte concentration leading to an enhanced available area per molecule at the air-liquid interface. The process of micellization and adsorption of CPC at air-liquid interface are both favoured by exothermic enthalpy change as well as entropy gain. The observed features such as lowering of CMC, higher thermodynamic micellar stability, more relaxed surfactant molecules at the interface, due to an added electrolyte, may be exploited for improving the efficiency of the surfactant as a detergent, solubilizing agent, froth floatation process for concentrating ores, petroleum oil recovery and oil spill management.

Keywords: Surface properties, Thermodynamic properties, Cetylpyridinium chloride, Added electrolytes

Surfactants are a unique class of versatile amphiphilic compounds with spatially distinctive polar hydrophilic head and non-polar hydrophobic tail groups. Owing to their amphiphilic nature and characteristic features such as tendency to decrease interfacial tension and aggregation to form micelles in the bulk, surfactants are widely employed as individual care products, domestic cleaners and in food handling. Besides these, surface active compounds also find their applications in pharmaceuticals¹, agriculture, enhanced petroleum oil recovery^{2,3}, emulsifying^{4,5}, solubilizing⁶ and wetting agents⁷, metallurgical processes^{8,9} and nanotechnologies¹⁰. Several reports have appeared on different physico-chemical properties of surfactants in aqueous solutions. Naskar et al.¹¹ investigated the counter-ion effect on micellization of an anionic surfactant, sodium dodecyl sulfate (SDS) and a cationic surfactant, dodecyltrimethylammonium bromide. Suhail & co-workers¹ have reviewed the classification of surfactants, their mechanism of action, antimicrobial functions, their role in pharmaceutical product development, gene therapy and personal care products. Dominguez & Berkowitz¹², while performing molecular dynamics simulation on SDS monolayer at the

water/carbon tetrachloride and water-vapour interfaces observed that surfactant tails are less ordered at the water/vapour interface, while at the water/carbon tetrachloride interface the amphiphilic molecule is less inclined to the surface normal. Sukul et al.¹³ studied interaction between the polymer polyvinyl pyrrolidone (PVP) and an anionic surfactant SDS using excited state proton transfer of 1-naphthol as a probe. They inferred the existence of two kinds of environment in the SDS-PVP aggregates and also recorded that the critical association concentration of SDS for the PVP-SDS system is 10 times lower than the critical micelle concentration (CMC) of SDS. Watry & Richmond¹⁴ compared molecular structures of dodecanesulphonate and dodecyl benzenesulphonate adsorbed at organic/water interface (CCl₄/Water) and air/water interface employing vibrational sum frequency spectroscopy. They observed that change in aromatic ring orientation as a function of surface concentration is quite different for dodecylbenzene sulphonate at the air/water interface relative to that at CCl₄/water interface. Mukherjee et al.¹⁵ studied physicochemistry of micellization of binary mixtures of a cationic surfactant cetylpyridinium chloride (CPC) and a non-ionic surfactant Triton X-100

and determined micellar composition and their mutual interaction using Rubingh regular solution theory elucidating synergistic behaviour of the two surfactants. Heinz et al.¹⁰ have reviewed covalent and non-covalent interactions of surfactants with nanomaterials of metals, metal oxides, layered materials, and polymers. The surface modified nanomaterials have found applications in therapeutics, sensors, catalysis, classical detergents energy conversion and storage and purification systems.

However, reports on physicochemical and thermodynamic studies of surfactants in electrolyte aqueous solutions are limited¹⁶⁻¹⁹. Partap & Yadav¹⁷ studied the effect of inorganic ions on surface properties of a non-ionic surfactant iso-octyl phenoxy polyethoxy ethanol in water and aqueous Na₂SO₄ and Na₃PO₄ solutions. They found that the micellization process despite being endothermic, becomes feasible due to dominating entropy gain. Hoque et al.¹⁸ from conductometric measurements studied interactions between two cationic surfactants, tetradecyltrimethylammonium bromide and dodecyltrimethylammonium chloride, in water and in aqueous solution of NaCl. They analyzed the data in terms of Rubingh's model within the framework of the pseudophase separation model. Recently, Wołowicz & Staszak¹⁹ have studied surface and adsorption characteristics of SDS at the liquid-air interface in the presence of hydrochloric acid and heavy metal ions. They found that both hydrochloric acid and heavy metal ions cause decrease in CMC of the surfactant and the SDS adsorption is controlled by diffusion.

To the best of our knowledge no report exists, at present, on the effects of added electrolytes, comprising halides associated with varying metal ion's valency, on the surface and thermodynamic properties of CPC in aqueous medium. Derived from the tensiometric measurements, we report here, CMC, surface excess concentration (Γ_{\max}), minimum area per molecule (A_{\min}) at the air-liquid interface, surface pressure at CMC (π_{cmc}), and thermodynamic parameters of micellization as well adsorption of CPC aqueous solutions in the presence of chlorides of metals with varying cation valencies on the above physico-chemical properties at 288.15, 293.15 and 298.15 K.

Materials and Methods

Chemicals

Sodium chloride (NaCl, M.W. 58.44 g mol⁻¹); calcium chloride (CaCl₂, M.W. 110.98 g mol⁻¹), aluminum chloride (AlCl₃, M.W.: 133.34 g mol⁻¹) and

CPC (C₂₁H₃₈ClN, M.W.: 339.99 g mol⁻¹) used were from SD Fine Chemicals. Molecular structure of CPC is given in Fig.1.

Methods

Surface tension measurement

Surface tensions of CPC aqueous solutions, with or without added an electrolyte, were measured by drop-weight method using a modified stalagmometer, described elsewhere²⁰. Different concentrations of aqueous CPC solutions were prepared by appropriately diluting 50 mM CPC stock solution using distilled water. However, for preparing varying CPC concentrations in case of CPC + electrolyte + water systems, dilutions were done using electrolyte solution of proper molarity. The stalagmometer was calibrated using standard liquids including benzene, carbon tetrachloride, *n*-hexane, acetophenone and water. Surface tensions were measured over a wide range of CPC concentrations and at temperatures 288.15, 293.15 and 298.15 K. using a thermostatic bath (Tempstar, Model KW 201 A) that ensured temperature control within ± 0.01 K. The reproducibility of measured surface tension values was within ± 0.2 m N m⁻¹.

Specific conductivity measurements

A digital conductivity meter (Model E.I. 601 E) equipped with conductivity cell having cell constant = 1.0 and pre-standardized using 0.1 M KCl, was employed for conductivity measurements of CPC aqueous solutions at temperatures 288.15, 293.15 and 298.15 K. Doubly distilled water (specific conductance 2.0×10^{-6} S cm⁻¹) was used for preparing different CPC aqueous solutions.

Calculation of maximum surface excess concentration

Maximum surface excess concentration (Γ_{\max}) at the air-liquid interface was obtained using Gibb's adsorption equation²⁶,

$$\Gamma_{\max} = -1/2.303 nRT(d\gamma/d(\log C))_T \quad \dots(1)$$

where, n is number of particles released per surfactant molecule in the solution; R is gas constant (8.314 J K⁻¹ Mol⁻¹) and C is molar concentration of the surfactant CPC. The $(d\gamma/d(\log C))_T$ represents the

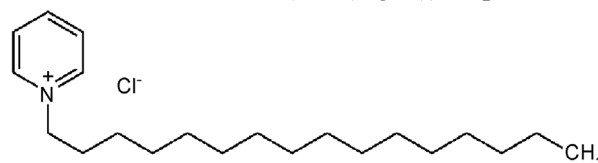


Fig. 1 — Molecular structure of cetylpyridinium chloride

slope of the plot for surface tension versus $\log C$ below CMC, at constant T (K) and these values are included in Table 1; for the ionic surfactant CPC, $n = 2$.

Calculation of minimum area per molecule at liquid–air interface

Minimum area (or area of exclusion) per surfactant molecule, A_{\min} , ($\text{nm}^2/\text{molecule}$) at the liquid–air interface has been calculated using the Eqn (2)²⁶,

$$A_{\min} = 10^{14} / N \Gamma_{\max} \quad \dots(2)$$

where, ‘ N ’ is Avogadro's number ($= 6.022 \times 10^{23}$ molecules per mole) and Γ_{\max} is maximum surface excess concentration at the air-liquid interface.

Calculation of surface pressure at CMC

Surface pressure at CMC (π_{cmc}), an index of the surface tension reduction at CMC, was obtained using the relation²⁶,

$$\pi_{\text{cmc}} = \gamma_0 - \gamma_{\text{cmc}} \quad \dots(3)$$

where, γ_0 = surface tension of water and γ_{cmc} = surface tension at CMC.

Calculations of thermodynamic properties of micellization

Standard Gibb's free energy of micellization (ΔG^0_{mic}) for CPC in aqueous solution, with or without an added electrolyte, was calculated using Eqn (4)²⁸,

Table 1 — Critical micelle concentration (CMC), surface excess concentration (Γ_{\max}), minimum area per molecule (A_{\min}) and surface pressure at CMC (π_{cmc}) for CPC + water system with or without an added electrolyte of different concentrations

[Electrolyte] mol dm ⁻³	Temp (K)	CMC x 10 ³ (mol dm ⁻³)	Γ_{\max} x 10 ¹⁰ (mol m ⁻²)	A_{\min} x 10 ² (nm ²)/molecule	π_{cmc} (mNm ⁻¹)		
CPC+H ₂ O	288.15	6.2 (6.2)*	2.18(-2.41)**	76.2	24.5		
	293.15	6.7 (6.8)*	2.06(-2.31)**	80.6	25.4		
	298.15	7.0 (7.2)*	1.92(-2.19)**	86.5	26.4		
CPC+NaCl	0.025	288.15	5.9	2.05	81.0	30.7	
		293.15	6.4	1.93	86.0	32.8	
		298.15	6.8	1.82	91.2	34.9	
	0.050	288.15	5.5	1.81	91.7	31.7	
		293.15	6.0	1.69	98.2	33.4	
		298.15	6.4	1.58	105.1	35.4	
	0.075	288.15	5.2	1.63	101.9	32.1	
		293.15	5.7	1.51	110.0	34.0	
		298.15	6.0	1.40	118.6	36.4	
CPC+CaCl ₂	0.025	288.15	5.6	2.13	77.9	32.3	
		293.15	6.1	2.03	81.8	34.4	
		298.15	6.6	1.88	88.3	36.4	
	0.050	288.15	5.3	2.04	81.4	32.7	
		293.15	5.8	1.87	88.8	35.2	
		298.15	6.3	1.73	95.9	37.4	
	0.075	288.15	5.0	1.92	86.5	34.5	
		293.15	5.5	1.76	94.3	36.9	
		298.15	6.0	1.62	102.5	39.4	
	CPC+AlCl ₃	0.025	288.15	5.2	1.80	92.2	32.5
			293.15	5.7	1.72	96.5	34.4
			298.15	6.2	1.65	100.6	36.2
		0.050	288.15	4.9	1.73	95.9	33.3
			293.15	5.3	1.67	99.4	35.2
			298.15	5.8	1.59	104.4	37.4
0.075		288.15	4.6	1.69	98.2	34.3	
		293.15	5.0	1.60	103.8	36.4	
		298.15	5.3	1.53	108.5	38.4	

*CMC values in parenthesis were obtained from conductance method; ** $(d\gamma/d \log C)_T$ values representing the slope of the plot for surface tension versus $\log C$ below CMC, at constant T (K) and used in the calculation of Γ_{\max}

$$\Delta G_{\text{mic}}^0 = (2 - \beta)RT \ln X \quad \dots(4)$$

where, β , is the fraction of micellar charge un-neutralized by the counterions or counterion binding of micelles and was determined from the ratio of post-micellar and pre-micellar slopes of specific conductance versus surfactant concentration plot; R and T are gas constant ($8.314 \text{ J K}^{-1} \text{ Mol}^{-1}$) and temperature (K), respectively; X_{cmc} represents the mole fraction of CPC at CMC and was calculated using the relation,

$$X_{\text{CMC}} = M_{\text{CPC}} / (M_{\text{CPC}} + M_{\text{Elc}} + M_{\text{H}_2\text{O}}) \quad \dots(5)$$

where, M_{CPC} , M_{Elc} and $M_{\text{H}_2\text{O}}$ are the number of moles of CPC, electrolyte and water, respectively, per litre of the solution. However, in the denominator the values of (M_{CPC} and M_{Elc} , are negligibly small compared to moles of water ($=55.56$) per litre of the solution. The standard state for surfactant is the solvated surfactant monomer at unit mole fraction referred to infinite dilute solution, and for micelle, the micelle itself is considered as its standard state. Entropy of micellization (ΔS_{mic}^0) and enthalpy of micellization (ΔH_{mic}^0) were obtained using Eqns (6) and (7), respectively²⁶.

$$\Delta S_{\text{mic}}^0 = -d(\Delta G_{\text{mic}}^0)/dT \quad \dots(6)$$

$$\Delta H_{\text{mic}}^0 = \Delta G_{\text{mic}}^0 + T\Delta S_{\text{mic}}^0 \quad \dots(7)$$

Calculation of thermodynamic parameters of adsorption

Standard free energy of adsorption (ΔG_{ad}^0) at the aqueous solution/air interface for surface-active solutes were obtained assuming a monomolecular layer of surfactant at zero surface pressure as the standard state for the adsorbed solute and can be given by the relation³⁰:

$$\Delta G_{\text{ad}}^0 = \Delta G_{\text{mic}}^0 - 6.023 \times 10^{-1} \pi_{\text{cmc}} \cdot A_{\text{min}} \quad \dots(8)$$

Standard enthalpy of adsorption (ΔH_{ad}^0) and standard entropy of adsorption (ΔS_{ad}^0) have been evaluated using Eqns (9) and (10), respectively,

$$\Delta S_{\text{ad}}^0 = -d(\Delta G_{\text{ad}}^0)/dT \quad \dots(9)$$

$$\Delta H_{\text{ad}}^0 = \Delta G_{\text{ad}}^0 + T\Delta S_{\text{ad}}^0 \quad \dots(10)$$

Results and Discussion

Critical micelle concentration (CMC)

CMC of CPC solutions with or without an added electrolyte at studied temperatures were obtained from the point of inflexion on their respective surface tension versus $\log [\text{CPC}]$ plots. For pure surfactant solutions, their CMCs were also obtained from the break point on specific conductance versus $[\text{CPC}]$ plots. Plots of surface tension versus $\log [\text{CPC}]$ and specific conductance versus CPC concentration (mM) for CPC+ H_2O system at 288.15, 293.15 and 298.15 K are presented in Fig. 2. The plots of surface tensions versus $\log [\text{CPC}]$ at varying electrolyte (NaCl/CaCl₂/AlCl₃) concentrations and studied temperatures are given in Figs 3 to 5 and the data are given in Table S1-S4 in Supplementary Data. The values of CMC, thus obtained, for the studied systems are presented in Table 1. The CMC values for CPC aqueous solutions at 298.15 K from surface tension measurements agree well with those obtained from the conductance method. The CMCs for the studied systems invariably increase upon raising the temperature. This may be due to (a) lowering of the dielectric constant of water at higher temperature causing enhanced ionic head group repulsions of the surfactant and (b) enhanced thermal agitation at an elevated temperature leading to a diminished charge density of counterion causing more ion-ion head group repulsion. Both these effects cumulatively shift the surfactant monomers \rightleftharpoons micelle equilibrium in favour of the monomers leading to

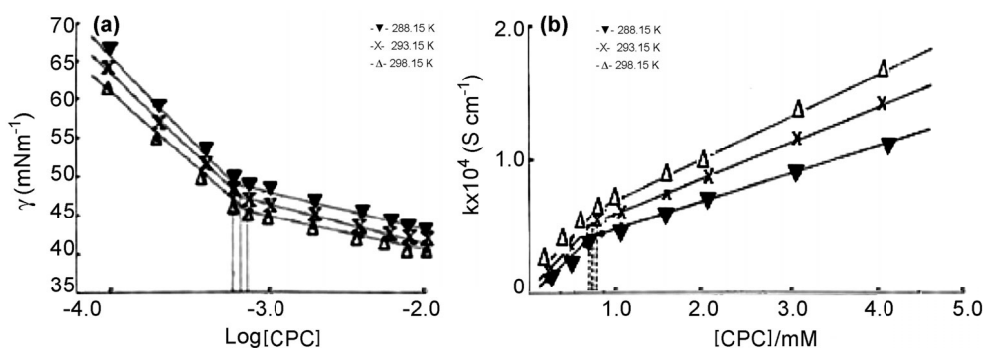


Fig. 2 — Plot of (a) surface tension as a function of $\log [\text{CPC}]$ and (b) specific conductance as a function of $[\text{CPC}]$ at 288.15, 293.15 and 298.15 K for CPC+ H_2O system

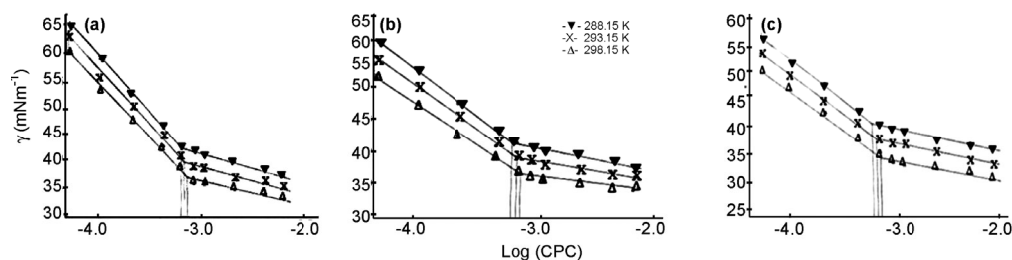


Fig. 3 — Plot of surface tension versus Log[CPC] for CPC + H₂O + NaCl system at 288.15, 293.15 and 298.15 K at different NaCl concentrations: (a) 0.025 M, (b) 0.050 M and (c) 0.075 M

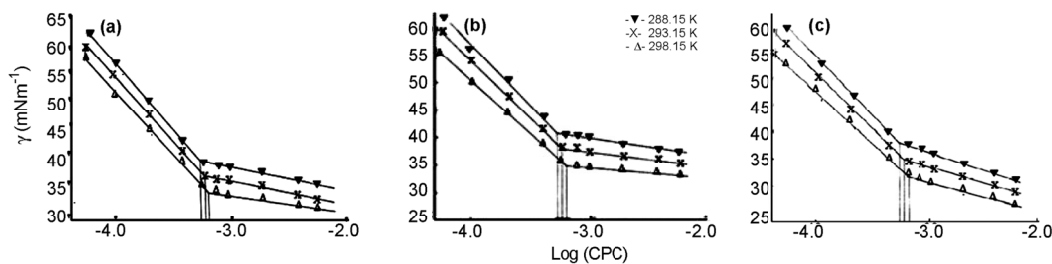


Fig. 4 — Plot of surface tension versus Log[CPC] for CPC + H₂O + CaCl₂ system at 288.15, 293.15 and 298.15 K at different CaCl₂ concentrations: (a) 0.025 M, (b) 0.050 M and (c) 0.075 M

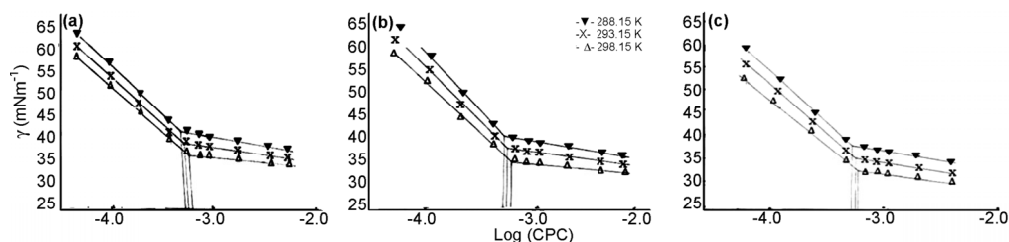


Fig. 5 — Plot of surface tension versus Log[CPC] for CPC + H₂O + AlCl₃ system at 288.15, 293.15 and 298.15 K at different AlCl₃ concentrations: (a) 0.025 M, (b) 0.050 M and (c) 0.075 M

higher CMC^{21, 22}. The CMC of CPC solutions decreases with an added electrolyte and the same becomes more pronounced upon mixing a metal halide with higher cation valence.

The observed decrease in CMC in the presence of an electrolyte can be attributed to (a) enhanced dielectric constant of aqueous medium which favours early formation of normal micelles and (b) increased charge density of CPC counterion causing a diminished intermolecular head-group repulsion leading to higher surfactant's association ability²³⁻²⁴. All these factors result in contracting electrical double layer around the micelle in the presence of an electrolyte resulting in the lowering of CMC of the surfactant²⁵. The effect of an added electrolyte on decreasing CMC was in the order: (AlCl₃) > (CaCl₂) > (NaCl) which falls in the same order as of chloride ions moles furnished by each mole of the added electrolyte. More the chloride ions present in the bulk, less would be the effective positive charge on the

surfactant (CPC) head group, resulting in diminished ion-ion repulsion and thus the lower CMC.

Maximum surface excess concentration

Maximum surface excess concentration (Γ_{\max}) at the air-liquid interface at varying electrolyte concentrations and studied temperatures for the studied systems are also included in Table 1. The Γ_{\max} values decrease with increasing temperature which may be due to the enhanced thermal agitation at higher temperature causing a partial shifting of surfactant monomers from the air-liquid interface to the bulk²⁷. The Γ_{\max} values further decrease upon mixing an electrolyte in CPC solution which may be to the displacement of a fraction of surfactant molecules at the air-liquid interface by the electrolyte ions.

Minimum area per molecule at the liquid-air interface

Minimum area (or area of exclusion) per surfactant monomer (A_{\min}) at the liquid-air interface are given in

Table 1. The A_{\min} values invariably show a positive dependence on temperature as well as the amount of the added electrolyte. It may be because at a higher temperature, due to the expansion of the liquid, the available free space per molecule at the interface is enhanced, while mixing of an electrolyte to a CPC aqueous solution, results in partial disruption of water-structure, enabling further relaxation of the surfactant molecules.

Surface pressure at CMC

Surface pressure at CMC (π_{cmc}) and an index of the surface tension reduction at CMC, are recorded in Table 1. The π_{cmc} values increase with increasing temperature as well as on mixing an electrolyte. It may be due to the fact that at higher temperature as

well as mixing an electrolytes in surfactant solution cause weakening of hydrogen-bonded water-structure in the bulk, thus cumulatively contribute to decrease in intermolecular interaction of water molecules and resulted in lowering of the surface tension i.e., π_{cmc} .

Thermodynamic properties of micellization

The thermodynamic properties of micellization are presented in Table 2. It may be seen that that the micelle forming process in aqueous media is favoured both by entropy gain as well as the exothermic enthalpy change. The ΔG_{mic}^0 values, in pure water as well as in surfactant + electrolyte solutions are negative and increase (become less negative) with increasing temperature. It suggests that though the CPC micellar formation in aqueous media is feasible,

Table 2 — Thermodynamic parameters of micellization / adsorption / transfer for CPC + water system with or without an added electrolyte of different concentrations

[Electrolyte] (mol dm ⁻³)	Temp (K)	$-\Delta G_{\text{m}}^0 / -\Delta G_{\text{ad}}^0$ (kJ mol ⁻¹)	$-\Delta H_{\text{m}}^0 / \Delta H_{\text{ad}}^0$ (kJ mol ⁻¹)	$\Delta S_{\text{m}}^0 / \Delta S_{\text{ad}}^0$ (kJ K ⁻¹ mol ⁻¹)
CPC+ H ₂ O	288.15	38.46 / 39.61		
	293.15	38.04 / 39.27	13.12 / 20.80	0.085 / 0.063
	298.15	37.61 / 38.98		
CPC+NaCl 0.025	288.15	35.94 / 37.44		
	293.15	35.47 / 37.16	7.62 / 21.33	0.095 / 0.054
	298.15	34.99 / 36.90		
0.050	288.15	36.16 / 37.91		
	293.15	35.67 / 37.65	6.94 / 23.29	0.098 / 0.049
	298.15	35.18 / 37.42		
0.075	288.15	36.80 / 38.31		
	293.15	35.83 / 38.06	6.52 / 28.38	0.100 / 0.033
	298.15	35.38 / 37.98		
CPC+CaCl ₂ 0.025	288.15	33.35 / 34.87		
	293.15	32.84 / 34.53	2.94 / 16.94	0.102 / 0.060
	298.15	32.33 / 34.27		
0.050	288.15	33.51 / 35.11		
	293.15	32.98 / 34.86	2.20 / 20.49	0.105 / 0.049
	298.15	32.46 / 34.62		
0.075	288.15	33.68 / 35.48		
	293.15	33.14 / 35.30	1.48 / 22.11	0.0108 / 0.045
	298.15	32.60 / 35.03		
CPC+AlCl ₃ 0.025	288.15	31.05 / 32.87		
	293.15	30.51 / 32.51	+1.44 / 11.40	0.109 / 0.072
	298.15	29.96 / 32.15		
0.050	288.15	31.23 / 33.15		
	293.15	30.71 / 32.82	+1.54 / 13.18	0.110 / 0.067
	298.15	30.13 / 32.48		
0.075	288.15	31.39 / 33.42		
	293.15	30.86 / 33.14	+1.97 / 17.31	0.112 / 0.054
	298.15	30.27 / 32.88		

however, upon increasing temperature the micellar stability decreases due to thermal agitation and endothermic desolvation of the surfactant hydrophilic head group at higher temperature²⁹.

The ΔG_{mic}^0 values increase (i.e., become less negative) upon mixing an electrolyte in a CPC solution, may be due to endothermic enthalpy change overweighing the entropy gain during disruption of hydrogen bonded water structure in an aqueous solution. The feasibility of micelle formation further decreases upon raising the electrolyte concentration as well as upon replacing a lower valence metal halide salt by higher valence metal halide in CPC solution as evident from the increasing ΔG_{mic}^0 in both the cases. The entropy of micellization ΔS_{mic}^0 values are invariably positive and increase with increasing temperature, for the studied CPC solutions. It is obvious since higher temperature and mixing an electrolyte both cause disruption of water structure resulting in entropy gain. Enthalpy of micellization (ΔH_{mic}^0) values for CPC+H₂O, CPC+NaCl+H₂O and CPC+CaCl₂+H₂O are exothermic and the exothermicity decreases with increasing temperature and addition of an electrolyte. However, in case of CPC+AlCl₃+H₂O system endothermicity is enhanced with increasing temperature as well as electrolyte concentration. These results can also be readily explained in terms of water-structure breaking effects of temperature and added electrolyte.

Thermodynamic parameters of adsorption

Standard thermodynamic parameters of adsorption i.e., ΔG_{ad}^0 , ΔH_{ad}^0 and ΔS_{ad}^0 are also included in Table 2. The observed lower values of ΔG_{ad}^0 compared to corresponding ΔG_{mic}^0 for CPC solutions, at studied temperatures and electrolyte concentrations, suggest that the process of adsorption of CPC monomers at the air-liquid interface is thermodynamically more feasible compared to their aggregation to form micelles. The higher entropies of adsorption (ΔS_{ad}^0) in comparison to ΔS_{mic}^0 may be due to higher degree of freedom of the surfactant monomers at the liquid-air interface compared to the cramped interior of micelles^{31,32}. Further, higher exothermic enthalpy of adsorption (ΔH_{ad}^0) compared to corresponding ΔH_{mic}^0 can be attributed to more degree of surfactant head group hydration in less structured water at the liquid-air interface than in the bulk. However, the observed lowering of exothermic ΔH_{ad}^0 at higher temperatures as well as upon adding an electrolyte may be due to

endothermic water structure disruption in both the cases and the same becomes more significant when an electrolyte comprised of higher cation valence is mixed in CPC solution.

Conclusions

This work reports the effect of three metal chlorides (NaCl, CaCl₂ and AlCl₃) on physico-chemical and thermodynamic properties of a cationic surfactant CPC in aqueous medium. The effect of an added electrolyte on decreasing CMC of CPC was in the order: (AlCl₃) > (CaCl₂) > (NaCl) which falls in the same order as of chloride ions moles furnished by each mole of the added electrolyte. However, upon increasing temperature, a reverse effect on the CMC is observed. Thermodynamic studies revealed that exothermic enthalpy change and entropy gain favours the micellization and the surfactants adsorption at the air-liquid interface is preferred over their aggregation in the bulk. The observed features such as lowering of CMC of CPC upon mixing a metal chloride which becomes more significant when the electrolyte producing more halide ions is added, may be exploited for improving the efficiency of CPC in its use as laundry detergent, solubilizing organic material in water, concentration of ores and enhanced petroleum recovery in the tertiary process.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at [http://nopr.niscair.res.in/jinfo/ijca/IJCA_60A\(04\)561-568_SupplData.pdf](http://nopr.niscair.res.in/jinfo/ijca/IJCA_60A(04)561-568_SupplData.pdf).

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References

- 1 Suhail M, Janakiraman A K, Khan A, Naeem A & Badshah S F, *J Pharma Pharmac*, 6 (2019) 72.
- 2 Abbas A, Sulaiman W R W, Jaafar M Z & Aja A A, *Recent Adv Petrochem Sci*, 1 (2017) 82.
- 3 Belhaj A F, Elraies K A, Mahmood S M, Zulkifli N N, Akbari S & Hussien O S, *J Pet Explor Prod Technol*, 10 (2020) 125.
- 4 Pegiadou-Koemtjopoulou S, Tsatsaroni E & Mylona M, *J Surfactants Deterg*, 1 (1998) 499.
- 5 Frenkel M, Krauz Z & Garti N, *J Disper Sci Technol*, 5 (1984) 35.
- 6 Randall K, Cheng S W & Kotchevar A T, *In Vitro Cell Dev Biol Anim*, 47 (2011) 631.

- 7 Shalaby M N & El-shamy O A A, *Tenside Surfactants Deterg*, 42 (2005) 373.
- 8 Shah H S, Rao K H, Forssberg K S E, Zhu B Y, Gu T, Zhao X et al., *Surfactants in Mineral Processing*, Mittal K L & Shah D O (Eds), Surfactants in Solution, (Springer, Boston) 1991, p 639.
- 9 Karavasteva M, *Min Proc Ext Met Rev*, 30 (2009) 122.
- 10 Heinz H, Pramanik C, Heinz O, Ding Y, Mishra R K, Marchon D, Flatt R J, Estrela-Lopis I, Llop J, Moya S & Ziolo R F, *Surf Sci Rep*, 72 (2017) 1.
- 11 Naskar B, Dey A & Moulik S P, *J Surfactants Deterg*, 16 (2013) 785.
- 12 Dominguez H & Berkowitz M L, *J Phys Chem B*, 104 (2000) 5302.
- 13 Sukul D, Pal S K, Mandal D, Sen S & Bhattacharyya K, *J Phys Chem B*, 104 (2000) 6128.
- 14 Watry M R & Richmond G L, *J Am Chem Soc*, 122 (2000) 875.
- 15 Mukherjee S, Mitra D, Bhattacharya S C, Panda A K & Moulik S P, *Colloid J*, 71 (2009) 677.
- 16 Partap R, Swaroop N, Tyagi D K & Yadav O P, *Indian J Chem*, 44A (2005) 719.
- 17 Partap R & Yadav O P, *Indian J Chem*, 47A (2008) 1524.
- 18 Hoque M A, Patoary M O F, Rashid M M, Molla M R & Rub M A, *J Solution Chem*, 46 (2017) 682.
- 19 Wołowicz A & Staszak K, *J Mol Liq*, 299 (2020) Article ID 112170.
- 20 Jain D V S & Singh S, *Indian J Chem*, 10 (1972) 629.
- 21 Jakubowska A, *Z Phys Chem*, 218 (2004) 1297.
- 22 Ma X, & Pawlik M, *J Colloid Interface Sci*, 298 (2006) 609.
- 23 Patra N, Ray D, Aswal V K & Ghosh S, *ACS Omega*, 3 (2018) 9256.
- 24 Liu Z, Cao M, Chen Y, Fan Y, Wang D, Xu H, & Wang Y, *J Phys Chem B*, 120 (2016) 4102.
- 25 Tennouga L, Mansri A, Medjahed K, Chetouani A & Warad I, *J Mater Environ Sci*, 6 (2015) 2711.
- 26 Rosen M J, Cohen A W, Dahanayake M & Hua X Y, *J Phys Chem*, 86 (1982) 541.
- 27 Sharma V K, Yadav O P & Singh J, *Colloids Surf A*, 110 (1996) 23.
- 28 Barry B W & Russell G F J, *J Colloid Interface Sci*, 40 (1972) 174.
- 29 McDonald C, *J Pharm Pharmac*, 22 (1970) 148.
- 30 Rosen M J & Aronson S, *Colloids Surf*, 3 (1981) 201.
- 31 Wertz D H, *J Am Chem Soc*, 102 (1980) 5316.
- 32 Rubingh D N, *Solution Chemistry of Surfactants*, Vol.1, K. L. Mittal (Ed), (Plenum, New York) 1979, p. 337.