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# Bulk-Solution Properties of CpyCl/CTABr a Mixed Surfactant System in the Presence of Nonionic Hydrotropes

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**Abstract:** The current research work centred on the micellization of binary system of Cetylpyridinium chloride (CpyCl) and cetyltrimethylammonium bromide (CTABr) in the absence and presence of nonionic hydrotropes (i.e urea and resorcinol) using conductometric technique. The critical micelle concentrations (CMC), at different mixed mole fraction of mixed surfactant were evaluated. Activity coefficient, ideal CMC, micellar mole fraction, interaction and thermodynamic parameters were obtained using theoretical Clint and Rubingh models. Addition of hydrotropes lowered the CMC values than the ideal CMC values and the individual components which is an indication of positive synergistic interaction in CpyCl/CTABr mixed micelle formation. The interaction parameter values were all negative, signifying strong interaction between the mixed surfactant. The evaluated thermodynamic parameters were all negative, indicating spontaneity and stability of the mixed micelle formed.

**Keywords:** Cetylpyridinium Chloride, Mixed Micelle, Hydrotrope, Cetyltrimethylammonium Bromide, Thermodynamic Parameter, Resorcinol

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## 1. Introduction

With the growing demands of industrial technology, a search for high performance surface active compounds is increasing [1-5]. One such attempt is the cationic-cationic surfactant mixtures which would be stable and superior on the application front compared to the pure systems. Investigation has shown that, the bigger the size of the polar head of cationic surfactant, the lesser (by a factor of 10%) the aggregation number, while the micellization degree (i.e critical micelle concentration) increases to the same extent [6]. Since interactions between ionic surfactants are generally governed by the electrostatic forces between their head groups [7], it would be expected that such interactions would be stronger for surfactants having two ionic groups as reported over the years in case of anionic/anionic [8-10], cationic/anionic [11-12] and cationic/cationic [13-14]

mixtures. Such observation is expected of the mixture of cetylpyridinium chloride and cetyltrimethylammonium bromide (CpyCl/CTABr) mixed micellar system both with the same chain length but different head group-couple with the same charge. Ghosh et.al reported that, binary system of CpyCl/CTABr shown minor decrease in CMC and repulsive interaction over all mole fraction of study, basically due the role played by different head group couple with similar positive head charge of the amphiphiles [15].

Surfactants are mixed for the purpose of better performance over single one. This is achieved when there is better interaction between the two surfactants leading to drastic decrease in cmc of the mixture [7]. Since there is minor interaction between CpyCl/CTABr as reported by Ghosh et.al [15], additive could be added to modify the interaction for better performance. The solubility behaviour (krafft point, cloud point), micellar characteristics (critical

micelle concentration (CMC), aggregation number), and adsorption at interfaces for a surface active agent could be altered in the presence of different additives. The effect of additive like hydrotropic salt on single phase surfactant have been extensively [16-19] studied. However, study on the effect of hydrotropes addition on mixed CpyCl/CTABr surfactants are not known. Hydrotropes are efficient solubilizers which could influence the formation of micelle and microemulsion [20]. Besides enhancing the solubilization of compound in water, they are known to exhibit influences on surfactant aggregation leading to micelle formation by affecting the packing colloidal association structures of amphiphiles.

In this paper, we introduce two nonionic hydrotropes to the binary mixtures of CpyCl/CTABr to extend our understanding on the interaction of cationic/cationic with the same chain length couple with different head groups which are known to show minor repulsive interactions according to the literature. Keeping in view of the ability of hydrotropes to drastically alter the solubility of other molecule in a medium, the purpose of the current study is to inspect the influence of nonionic hydrotrope on the overall combination of these

surfactant (i.e CpyCl/CTABr) vis-a-vis there physicochemical properties.

This was done using conductometric technique with the purpose of providing adequate information on the characterization of physicochemical properties of CpyCl/CTABr mixed surfactants system. The experimental data were analysed using established theory of Clint and Rubingh approach for the quantification of the interactive and thermodynamic parameter of micellization [21-22].

## 2. Experimental

### 2.1. Materials

Material, source and purity of all chemical employed in this study are shown in Table 1. All listed chemicals in Table 1 were used as obtained without further purifications. De-ionised double distilled water were employed to make stock solution of the surfactants and hydrotropes with conductivity not greater than  $3\mu\text{scm}^{-1}$  at  $25^\circ\text{C}$ . The structures of the material used are shown in Figure 1 below;

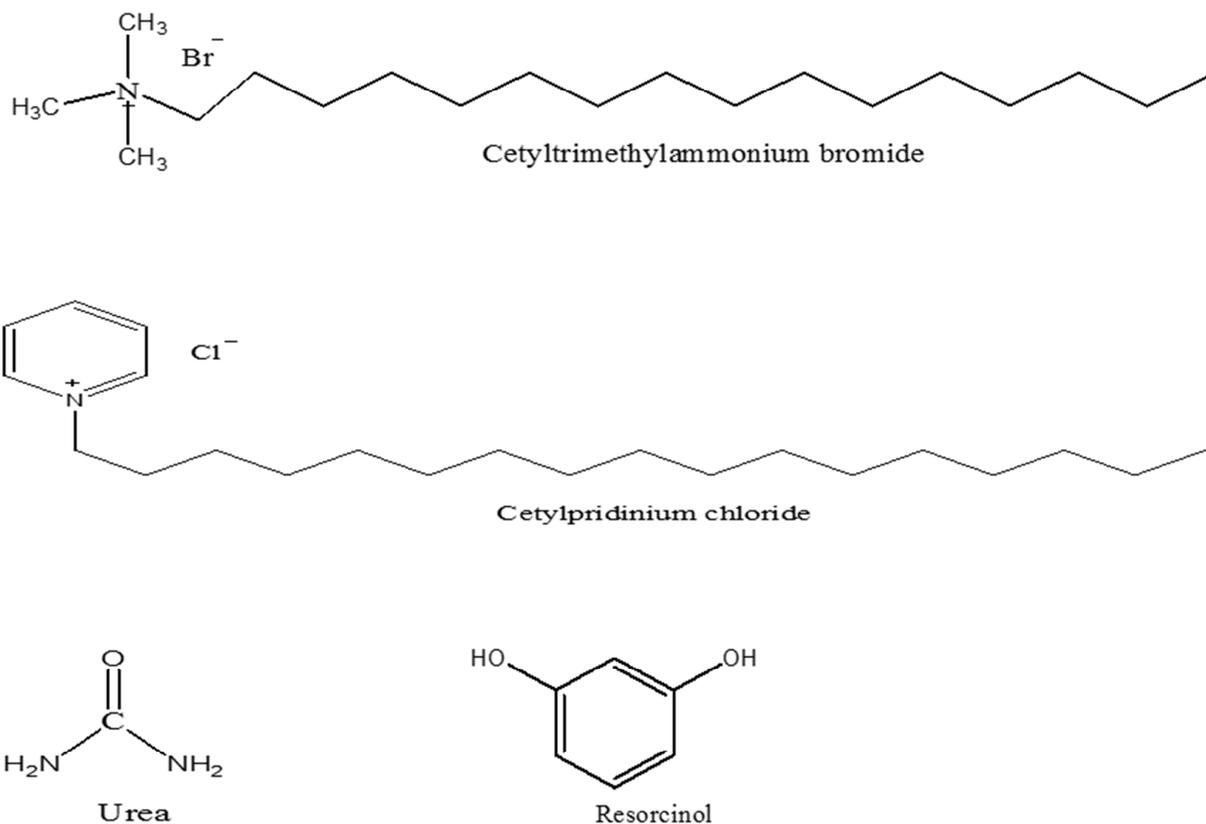


Figure 1. The structures of surfactants and the hydrotropes used in this work.

Table 1. Source and purity of the chemicals used in this work.

Chemical name	Provenance	Mass fraction purity
Urea	Rarkem	99.0%
Resorcinol	Merck (Germany)	99.0%
Cetylpridinium chloride	Sigma (USA)	99.0%
Cetyltrimethylammonium bromide	Sigma (USA)	99.0%

## 2.2. Method

### 2.2.1. Conductivity Measurements

The conductivity measurements were performed with a digital conductivity (model 4510 Jenway, UK). The cell constant was determined by calibration with several standard solutions of KCl of known specific conductivity. The conductivity ( $k$ ) measurements were made as a function of total surfactant concentration at different mole fraction of CpyCl to CTABr with and without hydrotropes (urea and resorcinol). The mixed solutions were prepared by diluting the concentrated stock solutions and were kept for at least 30 minutes for equilibration before measuring the conductivity. Electrodes were inserted in double walled glass cell containing the solution. The cell constant of the cell used was  $1\text{cm}^{-1}$ . Conductometry titration method involves the titration of a known volume of surfactants into a fixed volume of water (in case of no additive) or in the presence of assumed concentration of hydrotropes ( $8.0 \times 10^{-2}\text{M}$  urea and resorcinol) in a thermostatted beaker was employed. All measurements were made at  $25^\circ\text{C}$  in a thermostatted water bath (Haake D8), maintaining the temperature constant within  $\pm 0.1^\circ\text{C}$ . Originpro 8.0 software from OriginLab Corporation, USA were used to analyse the concentration-conductivity curves.

### 2.3. Theoretical Treatments

Based on pseudo phase separation model, for a non-ideal mixed micellization binary system, the CMC of the mixture is a function of (i) cmc of separate amphiphiles, (ii) activity coefficient ( $f_i$ ) and (iii) molar fraction ( $\alpha_i$ ) of the component  $i$  in the mixture of amphiphiles [23]. At that junction, the cmc of the binary mixed system could be shown as:

$$\frac{1}{\text{cmc}_{\text{mix}}} = \frac{\alpha_1}{f_1 \text{cmc}_1} + \frac{\alpha_2}{f_2 \text{cmc}_2} \quad (1)$$

$\alpha_1, \alpha_2$  denotes the mole fraction of CpyCl and CTABr respectively.  $\text{CMC}_1$  and  $\text{CMC}_2$  are the CMC of CpyCl and CTABr respectively. In agreement with equation (i.e., ideal mixed system) ( $f_1 = f_2 = 1$ ), equation 1 reduces to Clint equation [21]

$$\frac{1}{\text{cmc}_{\text{mix}}} = \frac{\alpha_1}{\text{cmc}_1} + \frac{(1-\alpha_1)}{\text{cmc}_2} \quad (2)$$

The nonideality in the mixing behaviour of the binary system (CpyCl/CTABr) could be quantitatively described by the proposition of Rubingh using the regular solution theory (RST) approximation [22]. The activity coefficients of the component in the mixed micelle is expressed as;

$$f_{\text{cpycl}} = \exp(\beta_{12}(1 - \chi_{\text{cpycl}}^{\text{Rub}})^2) \quad (3)$$

$$f_{\text{ctabr}} = \exp(\beta_{12}(\chi_{\text{cpycl}}^{\text{Rub}})^2) \quad (4)$$

Where  $\beta_{12}$  is a parameter which measures the extent of

interaction between the two surfactants in the mixed micelle and also dictate deviation from ideality. It can be evaluated from experimental CMC values thus;

$$\beta_{12} = \frac{\ln\left(\frac{\alpha_{\text{cpycl}} \cdot \text{cmc}_{\text{exp}}}{\chi_{\text{cpycl}}^{\text{Rub}} \cdot \text{cmc}_{\text{cpycl}}}\right)}{(1 - \chi_{\text{cpycl}}^{\text{Rub}})^2} \quad (5)$$

Where  $\chi_{\text{cpycl}}^{\text{Rub}}$  is the micellar mole fraction of component 1 (CpyCl) in the mixture. This requires solving for  $\chi_{\text{cpycl}}^{\text{Rub}}$  iteratively.

$$\frac{(\chi_{\text{cpycl}}^{\text{Rub}})^2 \ln\left(\frac{\alpha_{\text{cpycl}} \cdot \text{cmc}_{\text{exp}}}{\chi_{\text{cpycl}} \cdot \text{cmc}_{\text{cpycl}}}\right)}{(1 - \chi_{\text{cpycl}}^{\text{Rub}})^2 \ln\left(\frac{(1 - \alpha_{\text{cpycl}}) \cdot \text{cmc}_{\text{exp}}}{(1 - \chi_{\text{cpycl}}^{\text{Rub}}) \cdot \text{cmc}_{\text{ctabr}}}\right)} = 1 \quad (6)$$

The micelle mole fraction in the ideal mixing case for each of the mixtures was computed by assuming  $\beta_{12}$  value of zero in equation (5) and is given by

$$\chi_{\text{cpycl}}^{\text{id}} = \frac{\alpha_{\text{cpycl}} \cdot \text{cmc}_{\text{exp}}}{\text{cmc}_{\text{cpycl}}} \quad (7)$$

## 3. Results and Discussion

### 3.1. Determination of CMC of Mixed CpyCl/CTABr in the Absence/Presence of Hydrotropes

The conductivity ( $k$ ) versus [CpyCl/CTABr] at different mole fraction of CpyCl in the absence and presence of urea and resorcinol are showing in Fig 2a- c. As shown in these Figures, it is well known that the location of break-point appearing in the plot of specific conductivity versus concentration gives the CMC. However, as the concentration of CpyCl/CTABr increases in the absence and presence of urea and resorcinol, there appears a curvature around CMC making the precise determination of CMC difficult. This problem has been addressed using first differential conductivity approach which was best described by the Boltzmann-type sigmoid method [24] given by Eq. (8);

$$\frac{\delta k}{\delta c} = A_1 + \frac{A_1 - A_2}{1 + e^{(c - \text{cmc})/d}} \quad (8)$$

Where  $k$  is the specific conductivity,  $c$  is the total concentration of mixed CpyCl/CTABr,  $A_1$  and  $A_2$  are the upper and the lower limit of the sigmoid respectively. The CMC value is the centre of the sigmoid and  $d$  is the time constant, which is directly related to the independent variable range, where the sudden change of the dependent occurs. The typical plots of differential conductivity versus mixed surfactant concentration are shown in Fig 2d. The CMC value obtained for CpyCl/CTABr in the absence and presence of urea and resorcinol are presented in Table 2-4

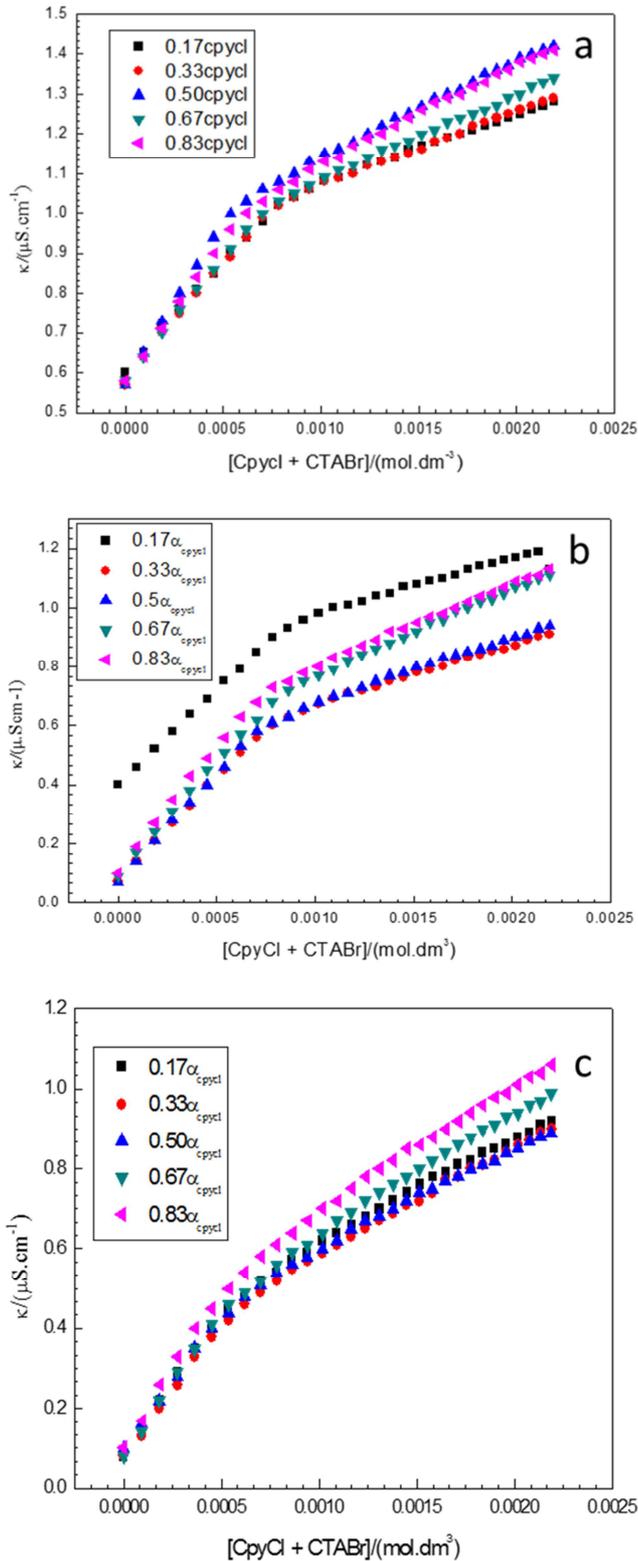


Figure 2. The plot of: a, b, c specific conductivity,  $K$ , versus concentration of mixed surfactant in water, urea, and resorcinol, d show the first derivative method.

### 3.1.2. Micellization of CpyCl/CTABr Mixed Micellar System in Aqueous Medium

In aqueous medium, CMC of mixed CpyCl/CTABr (observed) is less than  $\text{CMC}_{\text{mix}}$ (ideal CMC) and individual component values which decrease with increase in mole ratio of CpyCl to CTABr as shown in Table 2 and depicted in Fig 3a. This is an indication of non – ideal behaviour of the mixed system that shows that mixed micelle are formed at lower concentrations as compared to ideal mixing. The above action exemplifies favourable interaction occur between CpyCl/CTABr micelles. The observed decrease in CMC as the mole fraction of CpyCl increases in the mixture could be attributed to (i) increase in hydrophobic interaction between CpyCl and CTABr molecule (ii) decrease in electrostatic repulsion between their head group and finally (iii) decrease in surfactant charge density at higher concentration of surfactant. Akin behaviour was also found by Khan *et al.* and other researchers [25]. In general, decrease in CMC suggests charge micellization/screening. The values of  $\chi_{\text{cpycl}}^{\text{Rub}}$  and  $\chi_{\text{cpycl}}^{\text{id}}$  were recorded in Table 2 and plotted in Figure 3b for the different mole fraction of CpyCl in the mixed system. There is a clear indication from Figure 3b that  $\chi_{\text{cpycl}}^{\text{Rub}}$  deviate positively from ideal value ( $\chi_{\text{cpycl}}^{\text{id}}$ ) depends on the bulk mole fraction ( $\alpha_{\text{cpycl}}$ ) of the different component in the mixed micelles. Analysing  $\chi_{\text{cpycl}}^{\text{Rub}}$  data of CpyCl/CTABr binary system at different mole fraction (Table2) showed that  $\chi_{\text{cpycl}}^{\text{Rub}}$  are higher than  $\chi_{\text{cpycl}}^{\text{id}}$  at all mole fractions ( $\alpha_{\text{cpycl}}$ ). This is an indication that mixed micelle have high contribution of the CpyCl component than the CTABr and suggesting non ideal behaviour (synergism) at all mole fraction. Therefore, CpyCl molecules are rich in the mixed micelle over all range of mole fraction.

Table 2. The physicochemical parameters for CpyCl/CTABr mixed micelle in aqueous solution at 298.15K.

$\alpha_{c_{pycl}}$	$\chi_{c_{pycl}}^{Rub}$	CMC x $10^{-4}$	CMC <sub>mix</sub> x $10^{-4}$	$\beta_{12}$	$f_{c_{pycl}}$	$f_{ctabr}$	$G^E$	$\Delta H_M$	$\Delta S_M$	$\Delta G_M$	$\chi_{c_{pycl}}^{ideal}$
0.00	-	12.0	-	-	-	-	-	-	-	-	-
0.17	0.2263	7.9	9.4	-0.70	0.6583	0.9648	-302.94	-302.94	4.158	-1542.03	0.1415
0.33	0.3496	7.5	9.8	-1.11	0.6250	0.8730	-625.94	-625.94	4.351	-1922.56	0.2756
0.50	0.4578	7.3	10.3	-1.69	0.6083	0.7017	-1039.75	-1039.75	3.312	-2026.90	0.4089
0.67	0.5563	7.1	10.8	-2.67	0.5917	0.4384	-1630.23	-1630.23	0.983	-1923.1	0.5311
0.83	0.6362	6.1	11.4	-4.95	0.5083	0.1401	-2856.81	-2856.81	-3.194	-1905.1	0.6273
1.00	-	9.0	-	-	-	-	-	-	-	-	-

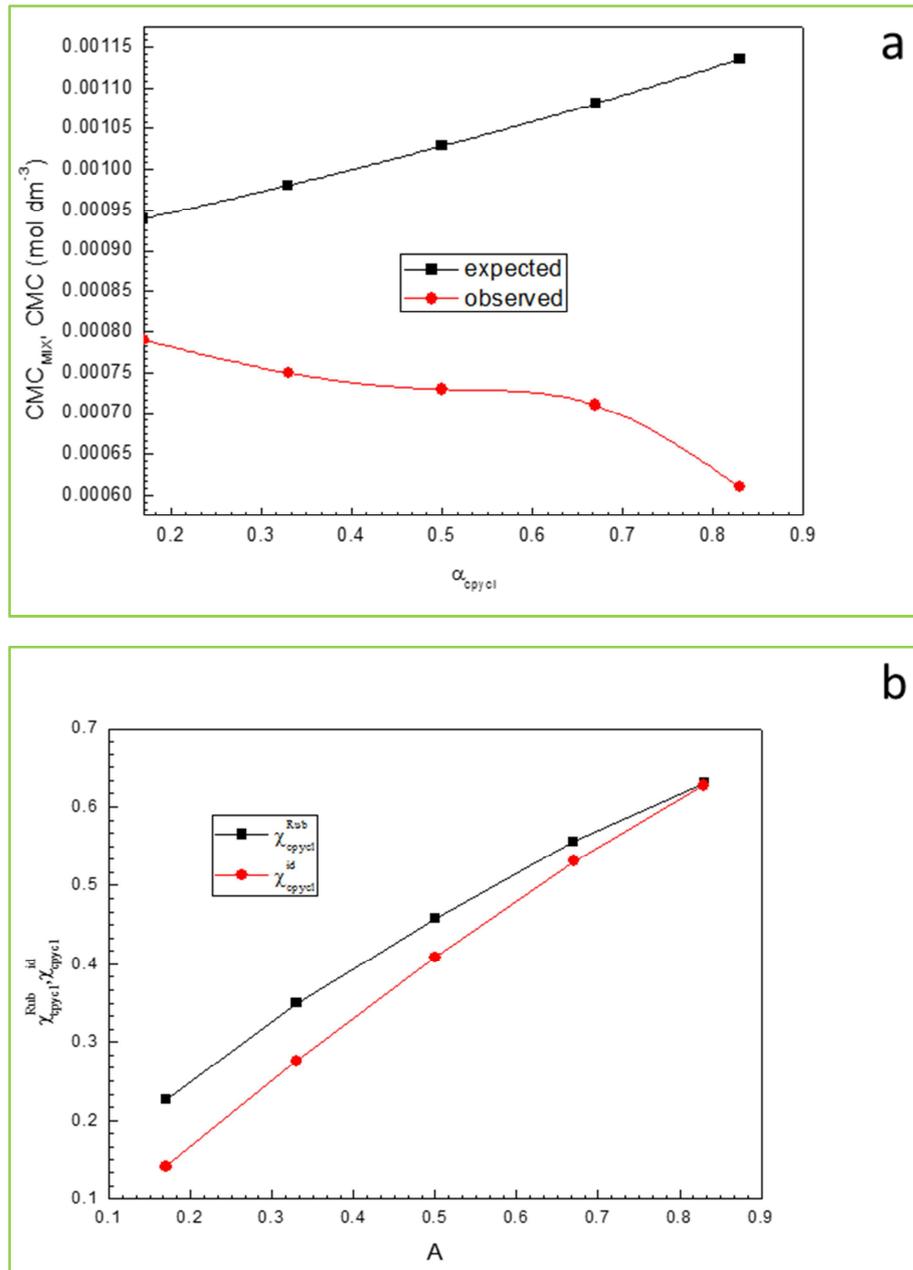


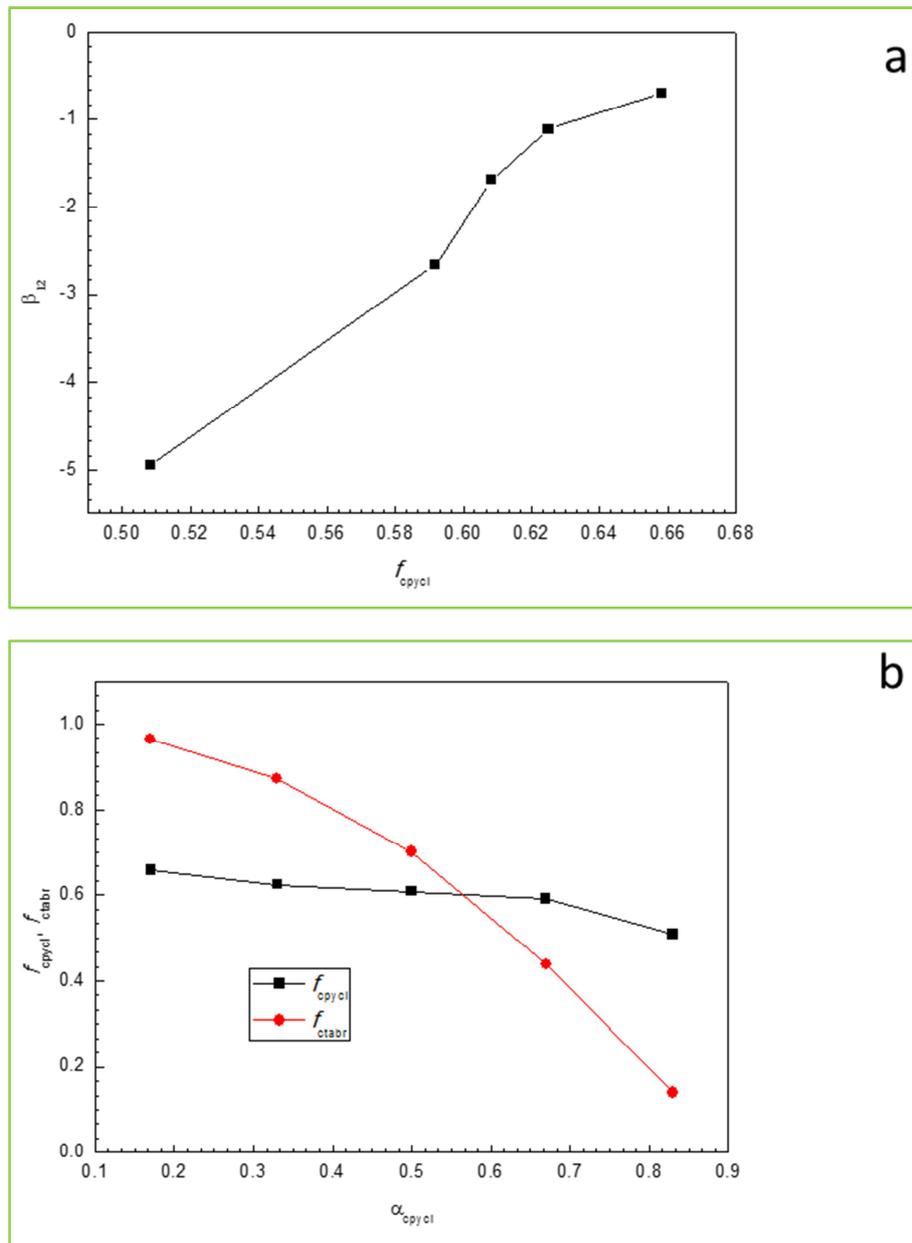
Figure 3. The plot of: a  $CMC_{MIX}/CMC$  versus mole fraction of CpyCl,  $\alpha_{C_{pyCl}}$ , b  $\chi_{C_{pyCl}}^{Rub} / \chi_{C_{pyCl}}^{id}$  versus mole fraction of cpycl,  $\alpha_{C_{pyCl}}$ .

Another very important variable is the interaction parameter. This is obtained according to Eq 5. The interaction parameter ( $\beta_{12}$ ) account for deviation of the mixed system

from ideality. The calculated value of  $\beta_{12}$  in aqueous solutions are listed in Table 2 which are observed to be negative over the whole mole fraction range studied. This could be interpreted in term of interaction between the two

components in the mixed micellar phase to be less repulsive than the interaction occurring between the individual components. Higher negative value of  $\beta_{12}$  shown in Table 2, is an indication of strong attraction between the different components in the mixed micelle [26-27] as well as suggesting strong synergism in the mixed micelle system. Plotting of  $\beta_{12}$  against the activity coefficient ( $f_{c_{pycl}}$ ) values (Figure 4a), further confirmed the above findings. This showed that  $\beta_{12}$  becomes increasingly negative with decrease in  $f_{c_{pycl}}$  which is an indication that, stability of the CpyCl/CTABr mixed micelle formed increases [28]. This is a desired condition sought for the practical application of this studied system.

Activity coefficient  $f_{c_{pycl}}$  and  $f_{c_{tabr}}$  are the most effective parameters which explain extent of deviation from ideality. Using regular solution theory by Rubingh [22],  $f_{c_{pycl}}$  and  $f_{c_{tabr}}$  can be evaluated from Eq. 3 and 4 respectively. Decreasing values of  $f_{c_{pycl}}$  and  $f_{c_{tabr}}$  with increasing value of  $\alpha_{c_{pycl}}$  indicates the increased interaction between the molecule of the two surfactant CpyCl and CTABr incorporated into the mixed micelle. The variation of  $f_{c_{pycl}}$  and  $f_{c_{tabr}}$  against  $\alpha_{c_{pycl}}$  are shown in Figure 4b which exhibits deviation from ideality.



**Figure 4.** The plot of: a  $\beta_{12}$  versus mole fraction of CpyCl,  $\alpha_{CpyCl}$ , b  $f_{CpyCl} / f_{CTABr}$  versus mole fraction of CpyCl,  $\alpha_{CpyCl}$  ( $\blacksquare = f_{c_{pycl}}$  and  $\bullet = f_{c_{tabr}}$ ).

### 3.1.3. Micellization of CpyCl/CTABr Mixed micellar System in $8.0 \times 10^{-2} \text{ Moldm}^{-3}$ Urea Solution

The analysed CMC data of CpyCl/CTABr binary system in the presence of different mole fraction ( $\alpha_{\text{cpycl}}$ ) of CpyCl at fixed concentration of urea ( $8.0 \times 10^{-2} \text{ moldm}^{-3}$ ) revealed that CMC values of CpyCl/CTABr were lower than the  $\text{CMC}_{\text{mix}}$  and it decreased in the poor regions of  $\alpha_{\text{cpycl}}$  ( $\alpha_{\text{cpycl}} = 0.17, 0.33, \text{ and } 0.5$ ) while in the rich regions of  $\alpha_{\text{cpycl}}$  ( $\alpha_{\text{cpycl}} = 0.67 \text{ and } 0.83$ ), CMC increased as indicated in Table 3 and showed in Figure 5. On the addition of urea to water, the following is observed; (i) increase in dielectric constant of the medium, (ii) water becomes more polar and urea-water mixture solvate both polar and ionic group of the surfactant mixture than water alone, (iii) the interfacial concentration of urea becomes equivalent as that in the bulk [29-30], and (iv) weakening of repulsive interaction between head groups. All these aforementioned stabilizing effects ascribed to urea

decreased CMC at the poor region of  $\alpha_{\text{cpycl}}$  as observed in Table 3. At the rich region of  $\alpha_{\text{cpycl}}$ , micellization of CpyCl/CTABr were hindered due to; (i) urea is absorbed at the interfacial micellar head group region of the mixed micelle and (ii) there is a better solvation of counterion and head group of the mixed CpyCl/CTABr. This action weakens the head group counterion interaction at the micelle – solution interface, hence destabilization effect is induced and the CMC increased as shown in Table 3. On a close inspection of Table 3, there is a clear indication that the values of  $\beta_{12}$  increased negatively from poor to rich region of CpyCl mole fraction ( $\alpha_{\text{cpycl}}$ ), indicating reduced micellar charge and increased attractive interaction (synergism). The activity coefficient  $f_{\text{cpycl}}$  and  $f_{\text{ctabr}}$  followed similar trend, in consonance with what was obtained in the aqueous medium.

Table 3. The physicochemical parameters for CpyCl/CTABr mixed micelle in Urea solution at 298.15K.

$\alpha_{\text{cpycl}}$	$\chi_{\text{cpycl}}^{\text{Rub}}$	$\text{CMC} \times 10^{-4}$	$\text{CMC}_{\text{mix}} \times 10^{-4}$	$\beta_{12}$	$f_{\text{cpycl}}$	$f_{\text{ctabr}}$	$G^E$	$\Delta H_M$	$\Delta S_M$	$\Delta G_M$	$\chi_{\text{cpycl}}^{\text{ideal}}$
0.00	-	12.0	-	-	-	-	-	-	-	-	-
0.17	0.1883	8.6	9.4	-0.51	0.7167	0.9822	-191.476	-191.476	3.875	-1346.49	0.1357
0.33	0.345	7.7	9.8	-1.03	0.6417	0.8842	-579.002	-579.002	4.419	-1896.01	0.2742
0.50	0.459	7.1	10.3	-1.80	0.5917	0.6854	-1103.18	-1103.18	3.166	-2046.74	0.4094
0.67	0.5671	8.2	10.8	-2.04	0.6833	0.5203	-1235.84	-1235.84	1.897	-1799.13	0.5372
0.83	0.6768	8.3	11.4	-3.53	0.6917	0.1986	-1912.63	-1912.63	-1.544	-1452.36	0.6583
1.00	-	9.0	-	-	-	-	-	-	-	-	-

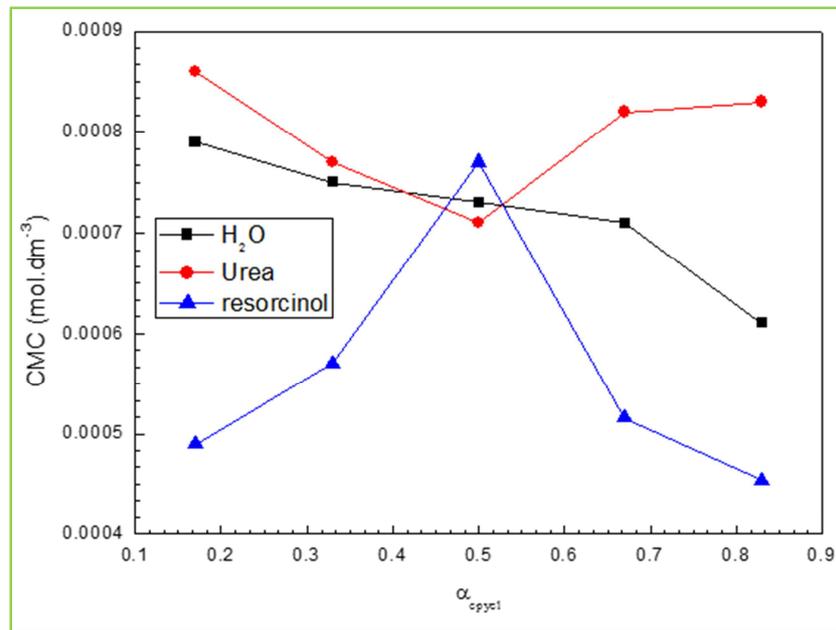


Figure 5. The plot of CMC versus mole fraction of  $\alpha_{\text{CpyCl}}$  (■ = water, ● = urea and ▲ = resorcinol).

### 3.1.4. Micellization of CpyCl/CTABr Mixed Micellar System in $8.0 \times 10^{-2} \text{ Moldm}^{-3}$ Resorcinol

Interaction of CpyCl and CTABr in solution of resorcinol endured number of physicochemical changes and often give up developed micellar properties. The CMC of pure and mixed CpyCl/CTABr as well as the  $\text{CMC}_{\text{mix}}$  were lower than that obtained in aqueous medium (Table 4). The CMC

increased over the poor region of CpyCl mole fraction ( $\alpha_{\text{cpycl}} = 0.17, 0.33, \text{ and } 0.50$ ), while in the rich region of CpyCl ( $\alpha_{\text{cpycl}} = 0.67 \text{ and } 0.83$ ) CMC decreases as shown in Figure 5. The increase in CMC observed up to 0.50 mole fraction of CpyCl is presumed to be as a result of: (i) decrease in dielectric constant plus less polarity of the

medium; (ii) exacting of salting-in effect causing increase in the water content at the head groups region of the micelle, thereby allowing the head group to move away from each other which eventually increases the CMC. As mole fraction of CpyCl increased further ( $\alpha_{\text{cpycl}} = 0.67$  and  $0.83$ ) resorcinol penetrate into the palisade layer of the micelles of CpyCl/CTABr thereby decreasing the efficient head group area of CpyCl/CTABr, thus favouring micellization as

observed in Figure 5. The  $\beta_{12}$  values in the presence of resorcinol were all negative as shown in Table 4, which is a clear indication of better interaction among the two surfactants (synergism). The  $\beta_{12}$ ,  $f_{\text{cpycl}}$  and  $f_{\text{ctabr}}$  values were at variance with what was obtained in aqueous and urea medium respectively. The values obtained for  $\chi_{\text{cpycl}}^{\text{Rub}}$  followed the same trend with what was obtained in aqueous medium.

**Table 4.** The physicochemical parameters for CpyCl/CTABr mixed micelle in Resorcinol solution at 298.15K.

$\alpha_{\text{cpycl}}$	$\chi_{\text{cpycl}}^{\text{Rub}}$	CMC x $10^{-4}$	CMC <sub>mix</sub> x $10^{-4}$	$\beta_{12}$	$f_{\text{cpycl}}$	$f_{\text{ctabr}}$	$G^E$	$\Delta H_M$	$\Delta S_M$	$\Delta G_M$	$\chi_{\text{cpycl}}^{\text{ideal}}$
0.00	-	12.0	-	-	-	-	-	-	-	-	-
0.17	0.33	4.9	9.4	-2.01	0.4083	0.8004	-1106.39	-1106.39	3.6052	-2180.72	0.1604
0.33	0.39	5.7	9.8	-1.99	0.4750	0.7403	-1172.29	-1172.29	3.3765	-2178.48	0.2882
0.50	0.46	7.7	10.3	-1.51	0.6417	0.7281	-929.65	-929.65	3.5537	-1988.65	0.4090
0.67	0.54	5.1	10.8	-4.02	0.4300	0.3069	-2473.50	-2473.50	-0.8249	-2227.68	0.5231
0.83	0.60	4.5	11.4	-6.21	0.3783	0.1036	-3677.65	-3677.65	-4.6111	-2303.55	0.6114
1.00	-	9.0	-	-	-	-	-	-	-	-	-

### 3.2. Thermodynamics Parameters of Micellization

Regular solution approach (RST) have been employed to compute the thermodynamics function of mixing which assumed that the excess entropy of mixing is equals to zero. The excess free energy, excess enthalpy and enthalpy of mixing are given by

$$G^E = H^E = \Delta H_M = RT(\chi_{\text{cpycl}}^{\text{Rub}} \ln f_{\text{cpycl}} + (1 - \chi_{\text{cpycl}}^{\text{Rub}}) \ln f_{\text{ctabr}}) \quad (9)$$

The excess free energy of micellization represents the deviation from the ideal behaviour. For an ideal mixing, the free energy of micellization is expressed as

$$\Delta G_{M,\text{ideal}} = RT(\chi_{\text{cpycl}}^{\text{Rub}} \ln \chi_{\text{cpycl}}^{\text{Rub}} + (1 - \chi_{\text{cpycl}}^{\text{Rub}}) \ln(1 - \chi_{\text{cpycl}}^{\text{Rub}})) \quad (10)$$

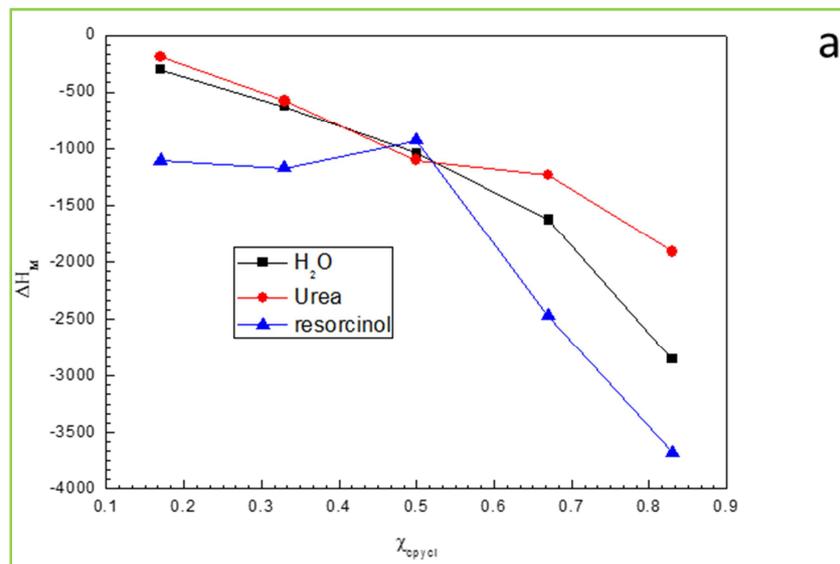
The non-ideal free energy of micellization is therefore given as

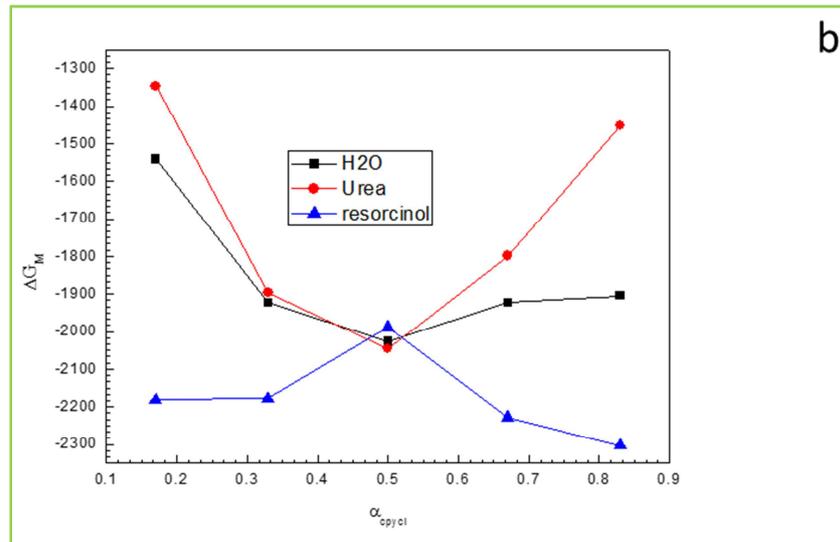
$$\Delta G_M = RT(\chi_{\text{cpycl}}^{\text{Rub}} \ln \chi_{\text{cpycl}}^{\text{Rub}} f_{\text{cpycl}} + (1 - \chi_{\text{cpycl}}^{\text{Rub}}) \ln(1 - \chi_{\text{cpycl}}^{\text{Rub}}) f_{\text{ctabr}}) \quad (11)$$

The entropy of micellization can be evaluated from

$$\Delta S_M = \frac{\Delta H_M - \Delta G_M}{T} \quad (12)$$

The thermodynamics parameters ( $\Delta G_M$  and  $\Delta H_M$ ) for the micellization of CpyCl/CTABr in aqueous, urea and resorcinol media are presented in Table 2, 3 and 4 and graphically shown in Figure 6a and 6b as a function of  $\alpha_{\text{cpycl}}$ . Both are negative as the mole fraction of CpyCl increased in the mixed micelle. This observation signified that the mixed micelle formed are more stable than the micelles of the individual surfactant. This further confirmed increase in the interaction between CpyCl and CTABr molecule and that the stability of the mixed micelle increased with increase in the concentration of CTABr in the mixture. Elucidating this observation, there is a clear signal that strong synergism could exist by increasing the concentration of CTABr in the mixed CpyCl/CTABr surfactant system.





**Figure 6.** a The plot of  $\Delta H_M$  versus mole fraction CpyCl,  $\alpha_{CpyCl}$  (■ = water, ● = urea and ▲ = resorcinol), b The plot of  $\Delta G_M$  versus mole fraction of CpyCl,  $\alpha_{CpyCl}$  (■ = water, ● = urea and ▲ = resorcinol.)

Majorly, the entropy change was positive while in most cases negative entropy is recorded as shown in Table 2-4. Positive values of entropy change in the mixed system signifying that micellization of amphiphiles is favoured entropically and it crystallizes the fact that iceberg-structure became liquefying at the hydrophobic portion of CpyCl/CTABr monomer [31]. In view of the fact that micellization is the process in which monomeric amphiphiles are transformed into micellar form, therefore, the entropy change is probably negative as shown in Table 2, 3 and 4 at the rich region of  $\alpha_{CpyCl}$

## 4. Conclusion

The present study demonstrated the influence of nonionic hydrotropes (urea and resorcinol) on the physicochemical properties of CpyCl/CTABr mixed micelle system and the result were as follows;

- (1) In an aqueous/ urea / resorcinol media, mixture of CpyCl/CTABr exhibit non ideal behaviour as the CMC's are less than the values calculated by using Clint equation
- (2) Negative values obtained for  $\beta_{12}$  in aqueous/ urea / resorcinol media indicate strong interaction between CpyCl and CTABr (synergism). The magnitude of the value of  $\beta_{12}$  increase in the order; resorcinol > aqueous > urea as  $\alpha_{CpyCl}$  increases.
- (3) The negative values of  $\Delta G_M$  and  $\Delta H_M$  signify that the mixed micelle formed are spontaneous and more stable.

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