

EFFECT OF MIXED COUNTERIONS ON THE AGGREGATION BEHAVIOR OF CETYLPYRIDINIUM CHLORIDE

T. Mukhim¹ and K. Ismail*²

¹Department of Chemistry, Lady Keane College, Shillong – 793001

²C/o Department of Chemistry, North Eastern Hill University, Shillong 793022

*For Correspondence. (kinehu@hotmail.com)

Abstract: Critical micelle concentrations (cmc) of cetylpyridinium chloride (CPC) in aqueous sodium bromide and tetrabutylammonium bromide (TBAB) solutions were determined at 30 °C from surface tension and conductance methods. Bromide decreases cmc of CPC more than chloride. A modified form of Corrin-Harkins equation has been used to describe the variation of cmc with added electrolyte concentration in the presence of mixed counter ions. From the slope of this equation the lower limit to the value of total counter ion binding constant (β) can be known and binding constants of the individual counter ions (β_1 and β_2) can be determined provided β is known. It is demonstrated that the mixed-electrolyte-model (MEM) of Shanks and Franses (*J. Phys. Chem.* 1992, 96, 1794) can be applied to analyze the conductance data of surfactant solution containing mixed counter ions. The value of β obtained from the MEM was then used to determine β_1 and β_2 . By this treatment we could show that (i) bromide preferentially binds to CPC micelle by replacing chloride counterion, (ii) bromide binding is more than chloride and (iii) aggregation number of CPC is higher in the presence of bromide. These observations are in accordance with the reported results of SANS and counter ion trapping studies.

1. Introduction:

Electrolytes and non-electrolytes on addition alter the micellization characteristics of surfactants and hence affect their performance. In almost all formulations containing surfactants different additives are used so that these formulations acquire the required properties. Therefore, it is of practical/industrial importance to study the effect of additives on the micellization parameters of surfactants.

Generally, the effect of added electrolyte on micellization parameters of ionic surfactants is entirely attributed to the counterions. However, scattered works indicate that co-ions can also affect the behavior and performance of ionic surfactants [1-3]. For example, Ikeda et al. [2] reported that the molecular weight of sodium dodecylsulfate (SDS) micelles in aqueous solutions of sodium salts changed in the order $\text{NaSCN} < \text{NaF} < \text{NaCl} < \text{NaBr} < \text{NaI}$, thus envisaging the effect of coions on the aggregation number of SDS. Influence of coions on the aggregation and adsorption behavior of sodium dioctylsulfosuccinate (AOT) [4,5] and SDS [6,7] has also been reported.

In this paper, the results of surface tension and conductance measurements made on aqueous solutions of cetylpyridinium chloride (CPC) at 30 °C in the presence of NaBr and tetrabutylammonium bromide (TBAB) are presented. These systems consisting of mixed counter ions and different coions were chosen in view of the following reasons: (1) Bromide counterion is reported to influence the micellization of cationic surfactants differently from chloride counterion [8-11]. The effect of mixed counter ions on the micellization behavior of ionic surfactants has been explored relatively less and in such systems the Corrin-Harkins (CH) equation [12] becomes inapplicable to determine the counter ion binding constant (β), thus requiring alternative treatment for the evaluation of β . (2) TBAB is a surface-active electrolyte [13] and its effect on SDS is reported to be different from other electrolytes [14-17]. Studying the chosen systems would therefore also enable us to understand the influence of non-aggregating surface-active (TBA^+) and non-surface-active (Na^+) coions on the aggregation of CPC.

2. Experimental Section:

CPC (Aldrich), NaBr (Merck) and TBAB (Aldrich) were used as received. Millipore water was used for preparing solutions throughout the experiment. Surface tension was measured by the Wilhelmy plate method using K11 Kruss Tensiometer. Conductance measurements were made at 1 kHz using B905 Wayne Kerr Automatic Precision Bridge. A dip-type conductivity cell having platinized platinum electrodes was used. The cell constant was determined using standard KCl solution. Temperature of the solutions was maintained at 30 °C by using Haake DC10 circulation bath.

3. Results and discussion:

Surface tension, conductance and critical micelle concentration. Surface tension (γ) and specific conductance (κ) values of CPC in aqueous NaBr and TBAB solutions at 303 K are shown in Figs. 1 and 2, respectively. The critical micelle concentration (cmc) values obtained from surface tension and conductance data are listed in Table 1. The variation of cmc of CPC with concentration of NaBr and TBAB is shown in Figure 3. For comparison we have also shown in Figure 3B the reported [11] cmc values of CPC as a function of NaCl. It is clear from Figure 3B that bromide counterion decreases cmc of CPC more than chloride counterion and the coions do not have any effect on the cmc. The trend in the variation of cmc indicates that the added bromide counterions replace the chloride at the micellar surface.

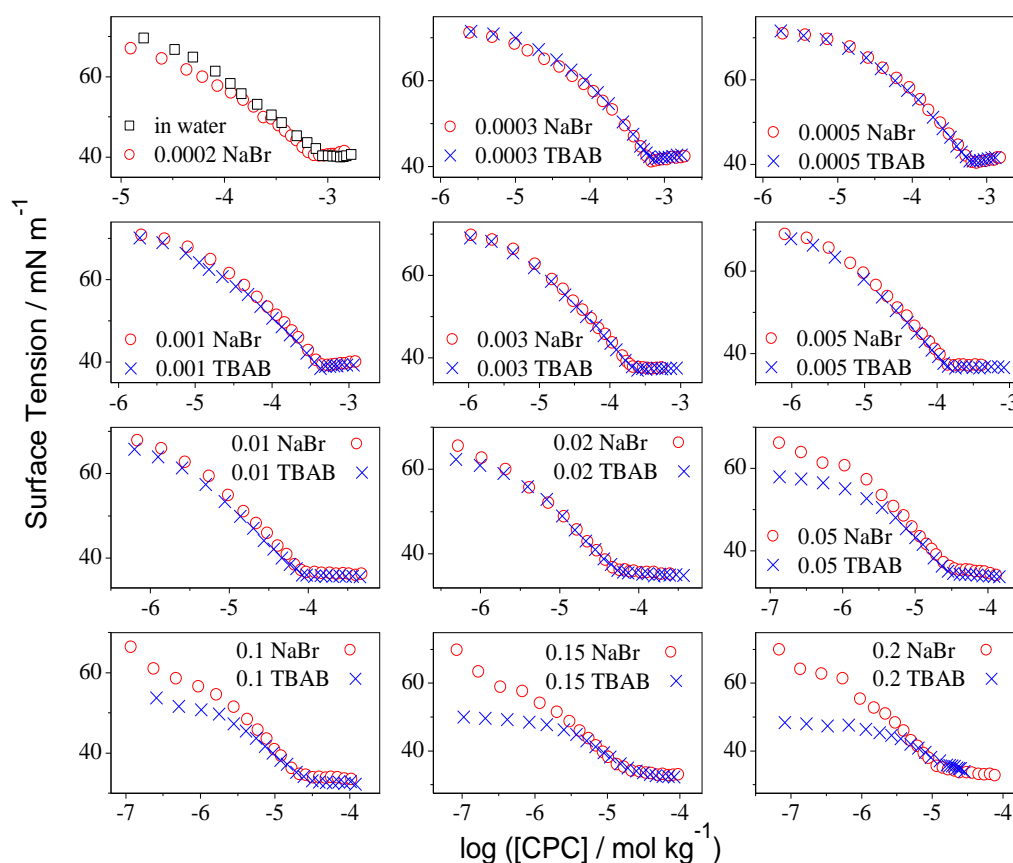


Figure 1: Surface tension isotherms of CPC in aqueous NaBr and TBAB solutions at 30 °C. Concentrations of NaBr and TBAB in mol kg⁻¹ are indicated in the layers.

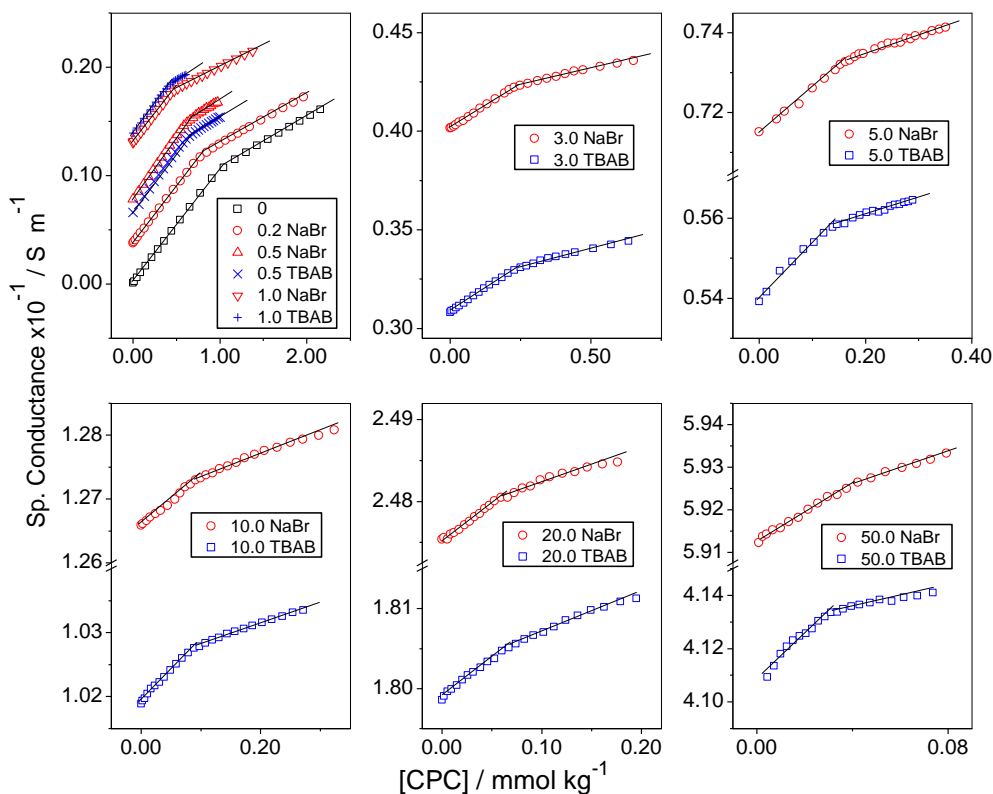


Figure 2: Specific conductivity isotherms for CPC in aqueous NaBr and TBAB solutions at 30 °C. Concentrations of NaBr (red symbols) and TBAB (blue symbols) in mmol kg^{-1} are indicated in the insets.

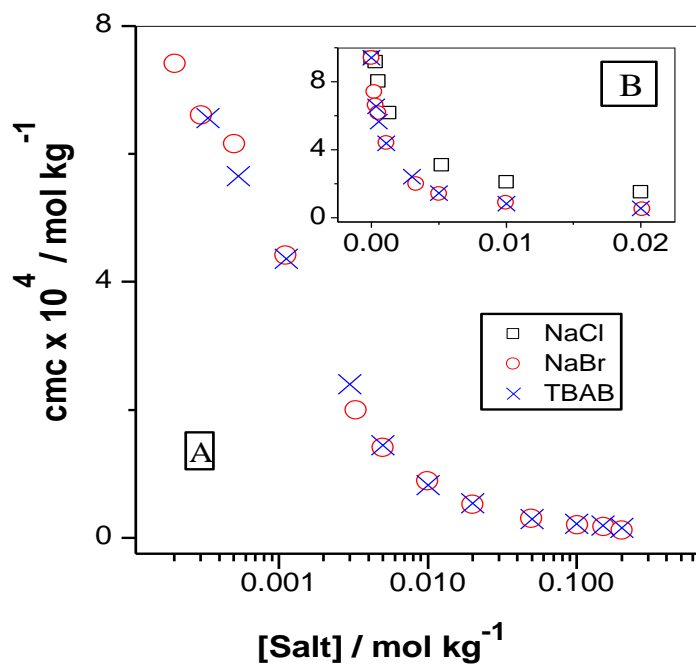


Figure 3: Variation of cmc of CPC with the concentration of added NaBr, TBAB and NaCl (data from ref. 4) at 30 °C.

Counterion binding constant. The counter ion binding constant, β , of an ionic surfactant is commonly determined by using the CH equation, $\ln c_0 = A - \beta \ln(c_e + c_0)$. c_0 and c_e represent cmc and concentration of added electrolyte. The CH equation is applicable when the system consists of single counter ion only. Since the systems under study have mixed counter ions, the CH relation needs to be modified. Modification to the CH equation to make it applicable to ionic surfactant solution containing mixed counterions was reported recently [18] and this modified CH equation is of the form

$$\ln c_0 = A - B \ln c_e \tag{1}$$

where $A = \Delta G_{0m}/[(1+\beta_1)RT]$ and $B = \beta_2/(1+\beta_1)$. ΔG_{0m} is the standard free energy of micellization per mole of surfactant monomer. β_1 and β_2 are the counterion binding constants for the chloride (counterion from the surfactant) and bromide (counterion from the added electrolyte) ions, respectively. The total counterion binding constant (β) of the surfactant is given by $\beta = \beta_1 + \beta_2$.

Equation (1) has been applied to CPC in aqueous NaBr and TBAB media by plotting $\ln c_0$ versus $\ln c_e$ (Figure 4). The values of B determined from Figure 4 were found to be 0.62 and 0.61 in the cases of NaBr and TBAB. Thus, the value of B is not influenced by the Na^+ or TBA^+ coions. Since $\beta_2 = B(1+\beta)/(1+B)$, the values of β_2 as well as β_1 can be determined if we know the value of β . Using the value of B from Figure 4, we get $\beta_2 = 0.38(1+\beta)$. Therefore, β must be more than 0.61, otherwise value of β_2 becomes unacceptable as it exceeds β value. The value of B thus provides a lower limit to the value of β .

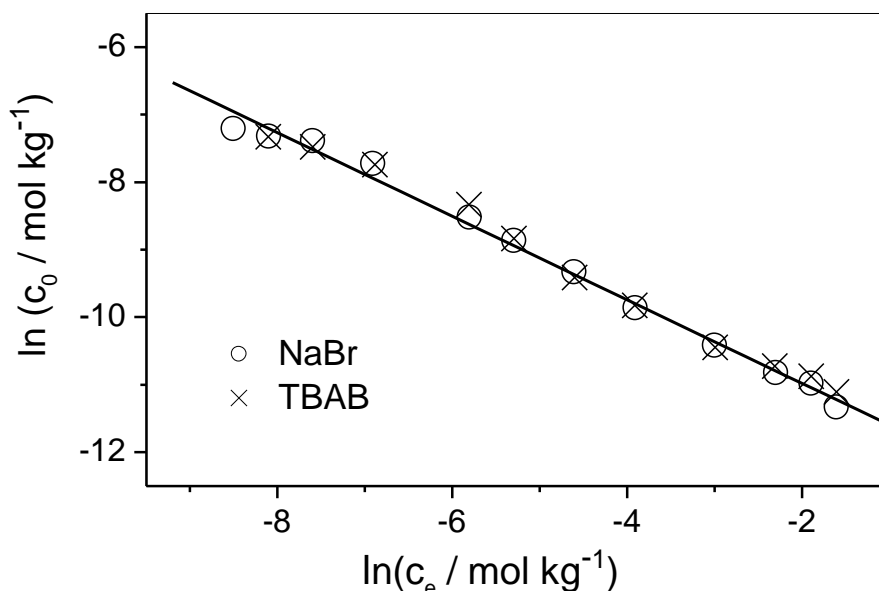


Figure 4: Plots of $\ln c_0$ versus $\ln c_e$ at 30 °C for CPC in aqueous NaBr and TBAB media.

In order to estimate β of CPC in the presence of chloride and bromide counter ions, we applied the mixed electrolyte model (MEM) [6,19-23] to the conductance data. This model is based on the Debye-Hückel-Onsager approach and the molar conductance, Λ , of the surfactant solution is given by the expression [6,19-23]

$$\Lambda = \{[\Lambda_1^0 - A_1 I^{1/2}/(1+B_0 a_1)](c_0/c)\} + \{[\Lambda_n^0 - A_n I^{1/2}/(1+B_0 a_n)][n(1-\beta)c_n/c]\} \tag{2}$$

In Eq. (2), a_i 's and Λ_i^0 's represent the effective ionic size and limiting equivalent conductance, respectively of monomer ($i = 1$) and micelle ($i = n$), c_n is the molar concentration of micelle and I is the ionic strength. B_0 and A_i are given by the relations

$$B_0 = [8\pi N_A e_0^2 / (1000 \epsilon k_B T)]^{1/2} I^{1/2} \tag{3}$$

$$A_i = \{(2.801 \times 10^6) |z_+ z_-| q \Lambda_i^0 / [(\epsilon T)^{3/2} (1+q^{1/2})]\} + \{41.25 (|z_+| + |z_-|) / [\eta (\epsilon T)^{1/2}]\} \tag{4}$$

where q is defined as

$$q = (\lambda_+^0 + \lambda_-^0) |z_+ z_-| / [(|z_+| + |z_-|)(|z_+| \lambda_-^0 + |z_-| \lambda_+^0)] \tag{5}$$

In Eqs. (3) to (5), k_B is the Boltzmann constant, ϵ is the dielectric constant of water, e_0 is the elementary charge, and η is the viscosity of water. λ_+^0 and λ_-^0 are the limiting ionic equivalent conductivities of cationic and anionic species of effective charges z_+ and z_- , respectively. The analysis of the conductance data using Eq. (2) was done by presuming spherical geometry for the CPC micelle. The data fitting was done using the method

described elsewhere [6,20-23]. According to this method, to compute the values of c_0 , n and β from Eq. (2), we first require the values of r_1 (radius of the CP ion), r_n (radius of the micelle), r_c (radius of the counter ion), a_1 , a_n , A_1 , A_n , Λ_1^0 , Λ_n^0 , λ_+^0 , λ_-^0 , and I .

Table 1: Best-fit Values of Cmc, β , Aggregation Number, Micellar Radius and Ionic Equivalent Conductance of Micelle for CPC in the Presence of NaBr, TBAB and NaCl at 30 °C Computed from MEM (σ denotes standard deviation in specific conductance).

[Salt] / mol kg ⁻¹	10 ⁴ cmc / mol kg ⁻¹	β	Agg. No.	Micelle radius, r_n / nm	10 ⁴ λ_{+mic}^0 / S m ² eq ⁻¹	σ / mS m ⁻¹
Medium = water						
0	9.8	0.66	31	1.42	76.16	0.08
Medium = Aqueous NaBr						
2 x 10 ⁻⁴	7.6	0.72	62	1.78	99.56	0.05
5 x 10 ⁻⁴	6.3	0.70	96	2.33	126.5	0.16
0.001	4.3	0.75	100	2.09	122.3	0.08
0.003	1.8	0.78	133	2.30	130.1	0.08
0.005	1.7	0.70	134	2.31	178.3	0.07
Medium = Aqueous TBAB						
5 x 10 ⁻⁴	6.0	0.70	100	2.36	130.0	0.08
0.001	4.3	0.71	96	2.07	138.0	0.09
0.003	2.1	0.78	129	2.28	127.5	0.06
0.005	1.6	0.70	131	2.29	175.6	0.13
Medium = Aqueous NaCl						
3 x 10 ⁻⁴	8.0	0.66	35	1.66	73.17	0.21
5 x 10 ⁻⁴	7.5	0.67	40	1.74	77.63	0.15
0.001	5.4	0.67	49	1.86	88.87	0.13
0.005	2.8	0.65	54	1.92	100.6	0.12

The value of r_1 was estimated approximately by using the Tanford relation [24]. According to this relation the volume of the cetyl chain, v , is given by $v = 27.4 + 26.9n_c$, where n_c refers to the number of carbon atoms in the cetyl chain. The volume of the CP ion (v_{CP}) was obtained by adding the volume of pyridinium ring (v_p) to the volume v . Based on the reported [25] length of the pyridinium ring, v_p was calculated to be approximately equal to 92 Å³. Thus, we obtained $v_{CP} \approx 549.8 \text{ \AA}^3$. Presuming this volume to be spherical, an effective radius of CP ion was calculated as

$$r_1 = [3v_{CP}/(4\pi)]^{1/3} \tag{6}$$

r_1 was found to be equal to 5.08 Å. r_n was calculated using the relation, $r_n = n^{1/3}r_1$. At 30 °C, the value of Λ_1^0 of CPC in water or electrolyte solution was estimated from the experimental κ data by extrapolation and was taken as equal to 108.2 x 10⁻⁴ S m² eq⁻¹. The value of λ_+^0 of CP ion at 30 °C was calculated by subtracting from Λ_1^0 the literature [26] value of λ_-^0 of Cl⁻ (85.4 x 10⁻⁴ S m² eq⁻¹). For dielectric constant (ϵ) and viscosity (η) at 30 °C we substituted the values 76.6 and 8.0 x 10⁻³ P, respectively. Presuming the micelle to be spherical, the value of λ_+^0 for the cationic micelle (λ_{+mic}^0) was computed using the Stokes–Einstein relation

$$\lambda_{+mic}^0 = z_n e_0 F / (6\pi\eta r_n) \tag{7}$$

where F is the Faraday constant. The charge on the micelle is $z_n = n(1-\beta)$, where n is the aggregation number. In the case of ionic surfactant solution containing single counter ion, the value of Λ_n^0 is calculated by adding the value of λ_-^0 of the counter ion to λ_{+mic}^0 . In the present system, the cationic micelle consists of mixed counter ions, chloride and bromide. Since the difference (1.8 x 10⁻⁴ S m² eq⁻¹) in the values of λ_-^0 of Cl⁻ and Br⁻ (87.2 x 10⁻⁴ S m² eq⁻¹) [26] is not much, we took the value of λ_-^0 approximately as equal to the average of the λ_-^0 values of Cl⁻ and Br⁻ (= 86.25 x 10⁻⁴ S m² eq⁻¹) and this average value was added to λ_{+mic}^0 to get the value of Λ_n^0 . Similarly, since the Stokes ionic radii of Cl⁻ (1.21 Å) and Br⁻ (1.18 Å) are very close [26], the values of a_1 and a_n were determined by adding an average Stokes ionic radius value (1.195 Å) to r_1 and r_n , respectively. Shanks and Franses [19] used four different models for the calculation of the ionic strength (I) and concluded that ionic micelles do not contribute to I . This conclusion made by Shanks and Franses [19] was found to be true in our earlier works [6,20-23]. Therefore, during data fitting I was calculated as $I = c$ (in the absence of electrolyte) and

$I = c + c_e$ (in the presence of electrolyte) when $c < c_0$ and $I = c_0$ (in the absence of electrolyte) and $I = c_0 + c_e$ (in the presence of electrolyte) when $c > c_0$.

The best-fit values of c_0 , β and n are given in Table 1. By this analysis we get β corresponding to each electrolyte concentration and, by taking an average (β_{av}) of such β values in each electrolyte media, we got $\beta_{av} = 0.73$ in NaBr and 0.74 in TBAB solutions. Using this average value of β , we obtained $\beta_2 = 0.66$ and $\beta_1 = 0.08$. Therefore, added bromide ion replaces chloride from CPC micelle and preferentially binds to the micelle. The evaluation of β , β_1 and β_2 thus confirms the replacement of bound chloride ions from the CPC micelle by bromide ions as inferred above to account for larger decrease in cmc on addition of bromide. Lower hydration of bromide compared to chloride is considered to be the reason for enhancement of micellization in the presence of bromide. Locations of chloride and bromide in the Hoffmeister series [27] also support stronger binding of bromide counterion than chloride on to micellar surface. For comparison sake, the values of c_0 , β and n of CPC in aqueous NaCl solution at 30 °C were also computed from the MEM using the reported κ data [28] (Table 1). The value of β_{av} for CPC in NaCl medium was found to be 0.66, which indicates that bromide binds more than chloride to the cetylpyridinium micelle. The values of n in the presence of NaBr and TBAB are comparable and are higher than the n values in the presence of NaCl.

It is interesting to note that the results obtained above regarding differential counter ion binding and aggregation number in the presence of chloride and bromide counter ions are similar to the observations reported from the SANS [8-11] and counter ion trapping studies [29,30] on CTAC, CTAB (cetyltrimethylammonium bromide) and CPC. This provides support to the above method of analyzing the data on surfactant systems containing mixed counter ions using the modified CH equation and the MEM.

4. Conclusions:

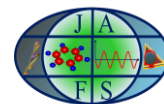
We make the following conclusions from this study: (1) The modified CH equation can be used to explain the variation of cmc with concentration of added electrolyte having a different counterion. From the modified CH equation β cannot be determined directly, but the lower limit to the value of β can be known. From the slope of this equation we can obtain values of binding constants of the individual counterions if β is known by other methods. (2) β of an ionic surfactant solution containing chloride and bromide counterions can be evaluated by applying the MEM.

Acknowledgment:

TM gratefully acknowledges the financial support received from the UGC.

References:

- [1] N. Muller and R. H. Birkhahn, *J. Phys. Chem.*, 72 (1968) 583.
- [2] S. Ikeda, S. Hayashi and T. Imae, *J. Phys. Chem.*, 85 (1981) 106.
- [3] R. Ranganathan, L. T. Okano, C. Yihwa, E. O. Alonso and F. H. Quina, *J. Phys. Chem. B*, 103 (1999) 1977.
- [4] I. M. Umlong and K. Ismail, *J. Colloid. Interface Sci.*, 291 (2005) 529.
- [5] U. Thapa, D. Ray, J. Dey, N. Sultana, V. K. Aswal and K. Ismail, *RSC. Adv.*, 5 (2015) 45956.
- [6] B. C. Paul, S. S. Islam and K. Ismail, *J. Phys. Chem. B*, 102 (1998) 7807.
- [7] I. M. Umlong and K. Ismail, *Colloids Surf A*, 299 (2007) 8.
- [8] V. K. Aswal and P. S. Goyal, *Phys. Rev. E*, 61 (2000) 2947.
- [9] V. K. Aswal and P. S. Goyal, *Phys. Rev. E*, 67 (2003) 051401.
- [10] V. K. Aswal, J. Kohlbrecher, P. S. Goyal, H. Amenitsch and S. J. Bernstorff, *Phys. Condens. Matter*, 18 (2006) 11399.
- [11] D. Varade, T. Joshi, V. K. Aswal, P. S. Goyal, P. A. Hassan and P. Bahadur, *Colloids Surf A*, 259 (2005) 95.
- [12] M.L. Corrin and W.D. Harkins, *J. Am. Chem. Soc.*, 69 (1947) 684.
- [13] K. Tamaki, *Bull. Chem. Soc. Jpn.*, 40 (1967) 38.
- [14] J. Mata, D. Varade, G. Ghosh and P. Bahadur, *Colloids Surf A*, 245 (2004) 69.
- [15] S. Kumar, D. Sharma and Kabir-ud-Din, *Langmuir*, 16 (2000) 6821.
- [16] S. Kumar, V. K. Aswal, A. Z. Naqvi, P. S. Goyal and Kabir-ud-Din, *Langmuir*, 17 (2001) 2549.
- [17] S. Kumar, D. Sharma, Z. A. Khan and Kabir-ud-Din, *Langmuir*, 17 (2001) 5813.
- [18] T. Mukhim, J. Dey, S. Das and K. Ismail, *J. Colloid. Interface Sci.*, 350 (2010) 511.



- [19] P. C. Shanks and E. I. Franses, *J. Phys. Chem.*, 96 (1992) 1794.
- [20] S. Dev, K. Gunaseelan and K. Ismail, *Langmuir*, 16 (2000) 6110.
- [21] K. Gunaseelan and K. Ismail, *J. Colloid Interface Sci.*, 258 (2003) 110.
- [22] K. Gunaseelan, I. M. Umlong, T. Mukhim and K. Ismail, *Langmuir*, 19 (2003) 7276.
- [23] J. Dey, U. Thapa and K. Ismail, *J. Colloid Interface Sci.*, 367 (2012) 305
- [24] C. Tanford, *The hydrophobic effect: formation of micelles and biological membranes*, Wiley-Interscience: New York, 1973.
- [25] D. F. Evans, A. Yamauchi, G. J. Wel and V. A. Bloomfield, *J. Phys. Chem.*, 87 (1983) 3537.
- [26] A. L. Horvath, *Handbook of aqueous electrolyte solutions*, Ellis Horwood: West Sussex, 1985.
- [27] W. Kunz, *Curr. Opin. Colloid Interface Sci.*, 15 (2010) 34.
- [28] T. Mukhim and K. Ismail, *J. Surf. Sci. Techno.*, 21 (2005) 113.
- [29] J. A. Loughlin and L. S. Romsted, *Colloids Surf*, 48 (1990) 123.
- [30] G. Mancini, and C. Schiavo, *Langmuir*, 12 (1996) 3567.