

## Estimation of micellization parameters of cetylpyridinium chloride in water using the mixed electrolyte model for conductance

K Gunaseelan, S Dev & K Ismail\*

Department of Chemistry, North-Eastern Hill University, NEHU  
Campus, Shillong 793 022, India

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The mixed-electrolyte model proposed recently by Shanks and Franses has been applied to estimate the critical micelle concentration, aggregation number, and counterion binding constant of cetylpyridinium chloride from its measured conductance data in water at 25°C. The surface potential of this cationic micelle has been computed by solving the non-linearized Poisson-Boltzmann equation. The electrostatic, hydrophobic, and the overall free energies of the ionic micelle formation have also been calculated. The present study also envisages that ionic micelles do not contribute to the ionic strength of the surfactant solution.

The conductance method is one of the widely used methods to determine the critical micelle concentration (cmc) of ionic surfactants. In this method, normally, cmc is estimated from the plot of specific conductance versus concentration without accounting for the ion-ion interactions. Although different methods of accounting for ion-ion interactions were reported<sup>1-4</sup>, the model proposed by Shanks and Franses<sup>4</sup> is better than the other approaches. Using the model of Shanks and Franses<sup>5</sup>, which may be called as the mixed electrolyte model, all the three micellization parameters, viz., cmc ( $c_0$ ), aggregation number ( $n$ ), and counterion binding constant ( $\beta$ ), can be directly estimated from conductance data. We have recently used this model to estimate the micellization parameters of sodium dodecyl sulphate (SDS) in water as well as in aqueous sodium acetate and sodium propionate solutions<sup>5</sup>.

In this note the mixed-electrolyte model of Shanks and Franses<sup>4</sup> has been employed to estimate the values of  $c_0$ ,  $n$ , and  $\beta$  of cetylpyridinium chloride (CPC) in water from the measured specific conductance data. Surface potential of CPC micelle in water and free energy terms of micellization were also estimated.

## Experimental

CPC (Aldrich) has been used without further purification. The electrical conductances of aqueous CPC solutions at 25°C were measured at 1 kHz using Wayne Kerr B905 automatic precision bridge as described elsewhere<sup>5</sup>.

## Results and discussion

The measured values of the specific conductance of aqueous CPC solutions at 25°C in the concentration range  $1.23 \times 10^{-4}$  to  $0.2463 \text{ mol kg}^{-1}$  are given in Table 1. Although conductance measurements of CPC at 25°C were made earlier by other workers<sup>6,7</sup>, those data were not listed in the literature and hence a direct comparison of the present conductance values with the previous data<sup>6,7</sup> could not be made. However, on comparing the cmc values, the literature values ( $= 0.0009^6$  and  $0.0010^7 \text{ mol dm}^{-3}$ ) are found to be lower than the present value ( $= 0.0011 \text{ mol kg}^{-1}$ ) determined from the plot of specific conductance versus concentration of CPC.

In the mixed electrolyte model for conductance of an ionic surfactant solution, the surfactant solution is considered to be a mixture of (i) an aqueous solution containing monomer ions ( $\text{CP}^+$ ) and  $\text{Cl}^-$  ions (monomer phase) and (ii) a micellar solution containing micelles and  $\text{Cl}^-$  ions (micellar phase). Both monomer and micellar phases are treated to be electrically neutral. In the micellar phase a neutral micelle of the form  $\text{CP}_n^{n(1-\beta)+} \text{Cl}_{n(1-\beta)}^-$  is considered to dissociate completely to give one mole of cetylpyridinium micelle,  $\text{CP}_n^{n(1-\beta)+}$  and  $n(1-\beta)$  moles of  $\text{Cl}^-$  counterions. The micelle is presumed to be spherical in shape and polydispersity of micelles has been ignored. As described earlier<sup>5</sup>, by applying the Debye-Hückel Onsager approach to account for the molar conductance,  $\Lambda$ , of the surfactant solution, we get

$$\Lambda = \frac{[\Lambda_1^0 - \Lambda_1^{1/2}/(1+B_0a_1)](c_0/c_1) + [\Lambda_n^0 - \Lambda_n^{1/2}/(1+B_0a_n)]}{[n(1-\beta)c_0/c_1]} \quad \dots (1)$$

In Eq.1,  $c_1$  is the total molar concentration of the surfactant and  $c_n$  is the molar concentration of micelle.  $a_1^*$ 's and  $\Lambda_i^0$ 's correspond to effective ionic sizes and limiting equivalent conductances, respectively of monomer ( $i=1$ ) and micelle ( $i=n$ ).  $I$  is the ionic strength and

Table I - Specific conductance ( $\kappa$ ) of CPC in water at 25°C

Conc. of CPC/ mol kg <sup>-1</sup>	$\kappa$ / S m <sup>-1</sup>	Conc. of CPC/ mol kg <sup>-1</sup>	$\kappa$ / S m <sup>-1</sup>	Conc. of CPC/ mol kg <sup>-1</sup>	$\kappa$ / S m <sup>-1</sup>	Conc. of CPC/ mol kg <sup>-1</sup>	$\kappa$ / S m <sup>-1</sup>
1.23×10 <sup>-4</sup>	0.0012	3.21×10 <sup>-4</sup>	0.0028	6.14×10 <sup>-4</sup>	0.0053	7.37×10 <sup>-4</sup>	0.0062
8.53×10 <sup>-4</sup>	0.0071	0.0011	0.0092	0.0013	0.0102	0.0016	0.0112
0.0018	0.0119	0.0021	0.0132	0.0023	0.0138	0.0026	0.0147
0.0029	0.0158	0.0031	0.0165	0.0035	0.0178	0.0038	0.0189
0.0041	0.0202	0.0044	0.0209	0.0047	0.0218	0.0049	0.0225
0.0053	0.0236	0.0056	0.0246	0.0058	0.0256	0.0061	0.0263
0.0066	0.0276	0.0069	0.0287	0.0073	0.0294	0.0077	0.0312
0.0082	0.0327	0.0088	0.0343	0.0095	0.0364	0.0099	0.0378
0.0105	0.0394	0.0109	0.0410	0.0116	0.0427	0.0120	0.0435
0.0126	0.0457	0.0132	0.0474	0.0137	0.0490	0.0143	0.0506
0.0147	0.0519	0.0155	0.0540	0.0160	0.0554	0.0165	0.0572
0.0170	0.0587	0.0176	0.0601	0.0183	0.0623	0.0190	0.0641
0.0198	0.0666	0.0205	0.0683	0.0209	0.0699	0.0217	0.0722
0.0226	0.0749	0.0232	0.0762	0.0239	0.0783	0.0248	0.0806
0.0255	0.0828	0.0261	0.0845	0.0269	0.0868	0.0278	0.0888
0.0286	0.0915	0.0293	0.0935	0.0299	0.0953	0.0307	0.0975
0.0315	0.0998	0.0323	0.1021	0.0330	0.1041	0.0336	0.1059
0.0341	0.1074	0.0350	0.1100	0.0356	0.1117	0.0363	0.1137
0.0370	0.1156	0.0382	0.1190	0.0393	0.1220	0.0410	0.1269
0.0421	0.1303	0.0426	0.1313	0.0435	0.1339	0.0445	0.1368
0.0462	0.1413	0.0474	0.1449	0.0483	0.1477	0.0498	0.1525
0.0514	0.1566	0.0524	0.1595	0.0536	0.1640	0.0548	0.1673
0.0561	0.1710	0.0578	0.1768	0.0590	0.1800	0.0609	0.1855
0.0620	0.1885	0.0637	0.1941	0.0657	0.1994	0.0668	0.2034
0.0683	0.2082	0.0707	0.2150	0.0722	0.2192	0.0737	0.2237
0.0755	0.2289	0.0772	0.2358	0.0781	0.2384	0.0790	0.2411
0.0798	0.2435	0.0807	0.2460	0.0815	0.2488	0.0824	0.2509
0.0836	0.2524	0.0846	0.2561	0.0861	0.2611	0.0881	0.2678
0.0893	0.2715	0.0911	0.2759	0.0929	0.2797	0.0952	0.2886
0.0966	0.2929	0.0978	0.2960	0.0994	0.3011	0.1007	0.3057
0.1023	0.3102	0.1033	0.3135	0.1052	0.3182	0.1066	0.3227
0.1085	0.3282	0.1101	0.3331	0.1112	0.3359	0.1130	0.3419
0.1151	0.3479	0.1166	0.3537	0.1186	0.3595	0.1208	0.3673
0.1235	0.3743	0.1252	0.3802	0.1269	0.3862	0.1281	0.3903
0.1295	0.3940	0.1308	0.3996	0.1328	0.4064	0.1344	0.4103
0.1358	0.4153	0.1371	0.4197	0.1392	0.4260	0.1408	0.4320
0.1429	0.4374	0.1443	0.4419	0.1462	0.4487	0.1477	0.4532
0.1494	0.4581	0.1510	0.4634	0.1529	0.4688	0.1548	0.4754
0.1572	0.4875	0.1594	0.4944	0.1613	0.4998	0.1624	0.5039
0.1642	0.5100	0.1660	0.5150	0.1677	0.5212	0.1693	0.5258
0.1709	0.5308	0.1721	0.5348	0.1736	0.5391	0.1757	0.5460
0.1781	0.5534	0.1801	0.5599	0.1827	0.5681	0.1845	0.5734
0.1869	0.5810	0.1879	0.5844	0.1897	0.5919	0.1918	0.5984
0.1936	0.6045	0.1950	0.6109	0.1971	0.6160	0.1992	0.6235
0.2013	0.6330	0.2029	0.6388	0.2047	0.6442	0.2061	0.6481
0.2076	0.6538	0.2096	0.6601	0.2111	0.6643	0.2129	0.6714
0.2159	0.6815	0.2178	0.6891	0.2198	0.6959	0.2220	0.7020
0.2237	0.7082	0.2254	0.7119	0.2270	0.7179	0.2286	0.7229
0.2310	0.7302	0.2331	0.7372	0.2348	0.7437	0.2372	0.7513
0.2384	0.7571	0.2407	0.7638	0.2427	0.7694	0.2444	0.7754
0.2463	0.7815						

Table 2 - Micellization parameters of CPC in water at 25°C

Parameters	Models for $I^0$			
	1	2 <sup>a</sup>	3 <sup>b</sup>	4 <sup>b</sup>
$10^4 c_0 / \text{mol kg}^{-1}$	$9.2 \pm 0.1$	9.0	9.0	9.0
$n$	$54 \pm 5$	25	80	5
$\beta$	$0.758 \pm 0.004$	0.680	0.750	0.600
Std. dev in $\kappa/\text{S m}^{-1}$	0.007	0.019	0.018	0.016
$r_1/\text{nm}$	1.807			
$10^4 \Lambda_1^0 / \text{Sm}^2 \text{eq}^{-1}$	86.60			
$10^4 \lambda_+^0 / \text{Sm}^2 \text{eq}^{-1}$	66.18			
$10^4 \Lambda_n^0 / \text{Sm}^2 \text{eq}^{-1}$	142.58			
$\psi/\text{mV}$	143			
$\Delta G_m^0 / \text{kJ mol}^{-1}$	-47.98			
$\Delta G_{cl}^0 / \text{kJ mol}^{-1}$	13.80			
$\Delta G_m^0 / \text{kJ mol}^{-1}$	-61.78			

a) Model 1 :  $I = c_1$  at  $c_1 < c_0$ ,  $I = c_0$  at  $c_1 > c_0$ ; Model 2 :  $I = c_1$  at  $c_1 < c_0$ ,  $I = c_0 + 0.5n(1-\beta)c_n$  at  $c_1 > c_0$ ; Model 3 :  $I = c_1$  at  $c_1 < c_0$ ,  $I = c_0 + 0.5n(1-\beta)^2c_n$  at  $c_1 > c_0$ ; Model 4 :  $I = c_1$  at  $c_1 < c_0$ ,  $I = c_0 + 0.5n(1-\beta)c_n [1+n(1-\beta)]$  at  $c_1 > c_0$ .

b) Since Model 1 for  $I$  gives best fit for conductance data, values of parameters other than  $c_0$ ,  $n$  and  $\beta$  are not listed for Models 2, 3 and 4 for  $I$ .

$$B_0 = [8\pi N_A e_0^2 / (10^3 \epsilon k_B T)]^{1/2} I^{1/2} \quad \dots (2)$$

$$A_1 = \{2.801 \times 10^6 |z_+ z_-| q \Lambda_1^0 / [(\epsilon T)^{3/2} (1+q^{1/2})] + [41.25 (|z_+| + |z_-|) / [\eta(\epsilon T)^{1/2}]]\} \quad \dots (3)$$

$$q = [|z_+ z_-| (\lambda_+^0 + \lambda_-^0)] / [(|z_+| + |z_-|) (|z_+| \lambda_-^0 + |z_-| \lambda_+^0)] \quad \dots (4)$$

In Eqs 2-4,  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature,  $\epsilon$  is the dielectric constant of water,  $e_0$  is the elementary charge,  $\eta$  is the viscosity of water and  $N_A$  is the Avogadro number.  $\lambda_+^0$  and  $\lambda_-^0$  are the limiting ionic equivalent conductivities of cationic and anionic species of effective charges  $z_+$  and  $z_-$ , respectively.

To compute the values of  $c_0$ ,  $n$ , and  $\beta$  using Eq 1, the values of  $r_1$  (radius of the surfactant monomer),  $r_n$  (radius of the micelle),  $r_c$  (radius of the counter ion),  $a_1$ ,  $a_n$ ,  $A_1$ ,  $A_n$ ,  $\Lambda_1^0$ ,  $\Lambda_n^0$ ,  $\lambda_+^0$ ,  $\lambda_-^0$ , and  $I$  are to be determined first. The value of  $r_1$  in Å was calculated from the relation

$$r_1 = [(3/4\pi)(27.4+26.9n_c)]^{1/3} \quad \dots (5)$$

where  $n_c$  is the number of carbon atoms per hydrocarbon chain of CPC<sup>7,8</sup>.  $r_n$  was taken as  $n^{1/3}r_1$ .  $\Lambda_1^0$  was determined from the experimental conductance data and its value is listed in Table 2. The value of  $\lambda_+^0$  for CP<sup>+</sup> ion was calculated by deducting from  $\Lambda_1^0$  the literature<sup>9</sup> value of  $\lambda_-^0$  for Cl<sup>-</sup>.  $\lambda_+^0$  for the micelle was computed using the Stokes-Einstein relation

$$\lambda_+^0(\text{micelle}) = z_n e_0 F / 6\pi\eta r_n \quad \dots (6)$$

where  $F$  is the Faraday constant and  $z_n = n(1-\beta)$  is the charge on the micellar ion. The value of  $\Lambda_n^0$  was obtained by adding to  $\lambda_+^0(\text{micelle})$  the value of  $\lambda_-^0$  for Cl<sup>-</sup>.  $a_1$  and  $a_n$  were determined by adding the Stokes ionic radius of Cl<sup>-</sup> to  $r_1$  and  $r_n$ , respectively. Substituting the values of  $z_+$  and  $\lambda_+^0$  for the micelle and the value of  $\Lambda_n^0$  for the micellar phase in Eqs 3 and 4, the value of  $A_n$  was determined. The method of data fitting is the same as given in our earlier paper<sup>5</sup>.

The value of  $I$  required for the data fitting was calculated in four different ways as suggested by Shanks and Franes<sup>1</sup> using the four models given in Table 2. The values of  $c_0$ ,  $n$ , and  $\beta$  obtained from the data fitting using the four models for  $I$  are given in Table 2. It is apparent from the data in Table 2 that model 1 for  $I$  fits the conductivity data (Table 1) to Eq.1 better than the other three models. Moreover, the values of  $c_0$ ,  $n$ , and  $\beta$  obtained for CPC from the data fitting using model 1 for  $I$  are comparable to their reported values<sup>7</sup>. From Table 2 it is also evident that model 4 for  $I$  provides unreasonable values for  $n$ . Similar observations were made when mixed electrolyte model was applied to estimate the micellization parameters of SDS in water<sup>4,5</sup>. The failure of model 4 for  $I$  in the present study also envisages that

micelles contribute to the conductivity but not to the effective ionic strength of the surfactant solution. This inference has been made by others<sup>4,5,10-12</sup> also and the exact reason for the highly charged micelles not contributing to the ionic strength is not known at present.

Using the values of  $c_0$ ,  $n$ , and  $\beta$  of CPC obtained from conductance data by applying mixed electrolyte model and model 1 for  $I$ , the surface potential,  $\psi$ , of CPC micelle in water was also computed as described earlier<sup>5</sup> by solving numerically the non-linearized Poisson-Boltzmann equation in spherical symmetry, which is of the form

$$d^2y/dx^2 = (e^y - e^{-y})/2x^4 \quad \dots (7)$$

where  $y = e_0\psi_r/k_B T$  and  $x = (Br)^{-1}$ .  $\psi_r$  is the electrostatic potential at a distance  $r$  from the center of the spherical micelle. The boundary conditions used are

$$y \rightarrow 0 \quad \text{as } x \rightarrow 0 \quad \dots (8)$$

$$dy/dx = 4\pi\rho_r e_0 / (\epsilon B k_B T x^2) \quad \text{at } r = r_n \quad \dots (9)$$

where  $B = [8\pi N_A e_0^2 c_0 / (10^3 \epsilon k_B T)]^{1/2}$ ,  $r_n$  is the radius of the micelle and  $\rho_r$  is the surface charge density at a distance  $r$  from the center of the reference micelle. The micellar surface charge density was calculated from the expression

$$\rho_r(r = r_n) = e_0 n(1-\beta)/(4\pi r_n^2) \quad \dots (10)$$

The value of  $\psi$  of CPC micelle obtained thus is listed in Table 2. The computed value of the radius of the spherical micelle,  $r_n$  is also given in Table 2. The free energy of ionic micelle formation per mole of monomer,  $\Delta G_m^0$ , was then calculated using the expression<sup>13</sup>

$$\Delta G_m^0 = RT(1+\beta)\ln x_{cmc} \quad \dots (11)$$

where  $R$  is the gas constant and  $x_{cmc}$  is the  $c_0$  value in mole fraction unit. The electrostatic free energy of

micellization,  $\Delta G_{el}^0$  was computed as  $F\psi$ , where  $F$  is the Faraday constant. The hydrophobic free energy of micellization,  $\Delta G_{hy}^0$  was then computed from the expression,  $\Delta G_{hy}^0 = \Delta G_m^0 - \Delta G_{el}^0$ . The values of  $\Delta G_m^0$ ,  $\Delta G_{el}^0$ , and  $\Delta G_{hy}^0$  obtained thus are given in Table 2.

The mixed electrolyte model suggested by Shanks and Franses is successfully applied to estimate directly the values of cmc, aggregation number and counterion binding constant of CPC in water from the conductance data. Once these micellization parameters are estimated, it has been possible to compute the other micellization parameters of the ionic micelle like surface potential and free energy terms of micellization. The present study also envisages that ionic micelles do not contribute to the ionic strength of the surfactant solution.

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