THE EFFECT OF Na-BASED SALTS ON CRITICAL AGGREGATION CONCENTRATION OF AQUEOUS PEG-SDS MIXTURES

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ABSTRACT

Critical aggregation concentration (CAC) is a well-known parameter used to study the interactions between constituents in an aqueous mixture containing surfactant molecules. In this study, we have studied the effect of Na-based salts on CAC of aqueous binary mixture of neutral polymer, polyethylene glycol (PEG) and anionic surfactant, sodium dodecyl sulfate (SDS) using viscometric method. To estimate CAC, we have applied Jiang model to the measured viscosity data. From the estimated results, we observe that the value of CAC decreases with the increase of salt molecules in the mixtures. This behavior confirms that the presence of salt molecules favors the binding of SDS molecule to the PEG chain.

1. INTRODUCTION

Aqueous solutions containing polymer and surfactant have been the subject of extensive researches in the past few decades [1]. The possibility to achieve polymer and surfactant aggregation at very low surfactant concentration occurs a delicate control over the properties of the mixture of soft materials [2]. This feature is being used in numerous applications, for example, pharmaceutical, biomedical, detergency, enhanced oil recovery, food, mineral processing etc. [3–7].

Polyethylene glycol (PEG) is a simple, synthetic and water soluble polymer [8]. The chemical structure of PEG contains two sites, one is known as hydrophobic (oxyethylene group) and the other is hydrophilic (hydrozen bonding) which is mainly responsible for the interaction with water molecule. PEG has attracted scientists' attention in terms of its hydration properties [9]. On the other hand, Sodium Dodecyl Sulfate (SDS) is a classic surfactant. Because of its anionic behavior, It has the ability to reduce the surface tension of aqueous solution and works as a surface active reagent [10, 11]. When both PEG and SDS are mixed together in pure water, the mixture provides some interesting features [5, 6, 12]. These interesting features can be studied by measuring the surface tension, viscosity and electrical conductivity of the mixtures.

Viscous behavior of aqueous PEG-SDS solutions has been studied for a long time to see the interactions between constituents. From the solutions, it is observed that at relatively low SDS con-centration, there are no intermolecular interactions between them and therefore the viscosity of the solution is observed almost constant with surfactant concentration [12]. After reaching a specific SDS concentration, known as the critical aggregation concentration (CAC) [12], the surfactant molecules start to bind to the polymer molecule and hence SDS-PEG aggregates/complexes are formed along the polymer chain. If the surfactant concentration in the

solution is increased further, the binding amount will also be increased and at a certain concentration free micelle will form and the concentration is referred to as critical micelle concentration (CMC) [5]. At CMC, the hydrophobic group of the surfactant is directed towards the interior of the cluster and the hydrophilic group is directed towards the solvent then a micelle formation is occurred. If we increase the surfactant concentration further from CMC in the solution, a saturation point called polymer saturation point (PSP) has been reached. At PSP, maximum possible number of miceller aggregates have been observed. After reaching the PSP, if SDS concentration increases in the solution, viscosity of PEG-SDS mixture decreases. In the meantime, to understand the physics behind this aggregation from both qualitatively and quantitatively Jiang et al. [6] developed a model using Cabane polymer-micelle model [13, 14] for binary PEG-SDS mixture and studied the viscous behavior of PEG-SDS mixture successfully. But to the best of our knowledge, the effect of Na-based salts on the mentioned parameters, especially on CAC, has not been studied yet.

In this research, therefore, we have studied the viscous behavior of PEG-SDS-salts mixtures using Ubbelohde viscometers and then applied the modified Jiang model to estimate CAC concentration.

This paper is organized in the following ways. The layout of the paper is as follows: In section 2 we have described the used samples and experimental method in brief. In section 3 we have presented our obtained results and then discuss them with arguments in the section. Finally, in section 4 we have concluded this study.

2. EXPERIMENTAL

2.1. Sample

Polyethylene glycol (PEG) of molecular weight 6000 g/mol, sodium dodecyl sulfate (SDS) of molecular weight of 288.37 g/mol, salts NaCl and NaI purchased from Sigma-Aldrich. All purchased samples have been used without further purification. To prepare aqueous solutions of PEG-SDS-salts, used nanopure water was collected from Centre for Advanced Research in Sciences (CARS), University of Dhaka. Ubbelodhe viscometers were used to measure the relative viscosities of PEG, PEG-SDS mixtures and PEG-SDS-salts mixtures in nanopure water. The weight of the samples was measured with SHIMADZU weighing balance AY220 which had the accuracy of measuring a sample within ±0.0001g. For measuring solutions of different μL ranges, we have used eppendorf research plus volumetric pipettes. For dissolving both SDS and PEG with and without salt molecules in nanopure water properly, a 78-1 Magnetic Hotplate Stirrer has been used. A temperature controlled water bath of J.P. Selecta was used to control the temperature of the solutions. This instrument can control the desired temperature within ±0.10C.

2.2. Preparation of solutions

At first, the base aqueous solutions of PEG, SDS and salts were prepared. Then, we have taken the appropriate amount of base solutions to make desired binary (PEG-SDS) and ternary (PEG-SDS-salts) mixtures for viscosity measurement. For example, 50 ml solution of 2.0 mM SDS 3.5 mM PEG and 0.01 M NaCl, we have used base solutions of 400 μL of 0.25 M SDS, 7000 μL of 0.025 M PEG, 5000 μL of 0.1M NaCl and 37600 μL nanopure water. All solutions used in this study were freshly prepared from the base solutions using a magnetic stirrer for 1-2 hours to form a consistent homogeneous solution at a low rotation per minute to avoid any mechanical degradation. Prior to all measurements, the solutions were carefully handled for not being exposed by dust. After preparing, all these solutions were kept at least 24 hours before taking data.

2.3. Calibration and measurement

Since we have used a new setup for the measurement of PEG-SDS-salts mixture, we need calibration of our instrument as well. Viscometer precision bath with Ubbelodhe viscometers (Model: VB-1423), purchased from a project of the Ministry of Science and Technology (MOST), has been used for measuring the relative viscosities of prepared solutions. The relative viscosities η_r of PEG, SDS, PEG-SDS mixtures and PEG-SDS-salt mixtures in nanopure water have been measured using Ubbelohde viscometers. The viscometers have been placed into a temperature controlled water bath. The accuracy of the temperature measurement was within ±0.10C. The prepared solutions were allowed to flow freely down. During the flow, the efflux time of lower meniscus of the solution from upper demarcation line to that of lower one was recorded using a stopwatch and this time was denoted as t and the time required for nanopure water to flow through the capillary tube was denoted as t_0. The relative viscosity of each PEG-SDS mixtures and PEG-SDS-salt mixtures in nanopure water were calculated from their ratio. Mathematically,

$$\eta_r = \frac{\eta}{\eta_0} = \frac{t\rho}{t_0\rho_0} \tag{1}$$

Where t and ρ_0 are the efflux time and density of the pure liquid. For very dilute solution, we can write $\rho = \rho_0$ and therefore Eq. (1) becomes

$$\eta_r = \frac{t}{t_0} \tag{2}$$

For instrumental calibration, we have measured the relative viscosities of PEG of molecular weight 6000 g/mol at temperature 25.15 °C. Then we have compared the measured data with another experimental data [7] from the available literature. A comparison of both data is listed in following Table 1.

Table 1: Relative viscosity of PEG of molecular weight 6,000 g/mol at 298.15 K.

C_p (gcm^3)	η_r	η (mPa.s)	η (mPa.s)[7]
0.0038	1.065	0.945	0.949
0.0106	1.192	1.058	1.061
0.0302	1.629	1.445	1.440

From the Table 1, we have seen that the measured data using our setup is almost consistent with literature data within experimental error. This consistency confirmed that our instrumental setup has been working properly. For each concentration of the solution, the flow time of both solution and solvent were taken at least three times to avoid parallax error. The error bar of the measured solution was ±0.01 mPas.

3. RESULTS AND DISCUSSION

In this section, at first, we have presented measured relative viscosity data of PEG and PEG-SDS mixtures with and without salts at temperature 303 K for molecular weight of PEG 6000 g/mol. Then, we have applied Jiang [6] model to the measured data to estimate CAC of the considered mixtures. Based on the obtained results, finally, we discuss the probable reason behind the interactions among the constituents in the mixture.

We have used Ubbelohde viscometers to measure viscosity. The relative viscosity (η_r) of the binary and ternary mixtures including the solvent viscosity (η_0) have been measured using the flow time ratio according to Eq. (2) [15]. The obtained data are presented in Table 2, Table 3 and Table 4.

Table 2: Relative viscosity data for PEG - SDS mixture with SDS concentrations at 303 K.

| C_s (mM)	PEG(6K)		
	1.0 mM	2.1 mM	3.5 mM
6.0	1.130	1.261	1.455
8.0	1.132	1.263	1.457
10.0	1.130	1.265	1.459
11.0	1.136	1.270	1.463
12.5	1.144	1.286	1.490
14.0	1.147	1.294	1.506
15.0	1.150	1.302	1.520
17.0	1.158	1.316	1.546
18.0	1.166	1.333	1.571
20.0	1.171	1.339	1.589
22.0	1.169	1.336	1.578
24.0	1.167	1.332	1.569

Table 3: Relative viscosity data for PEG-SDS-NaCl mixture of 6000g/mol with different NaCl concentrations.

C_s(mM)	NaCl(0.01M)			NaCl(0.05M)		
	1.0 mM	2.1 mM	3.5 mM	1.0mM	2.1mM	3.5 mM
3.0	-	-	-	1.097	1.191	1.329
4.5	-	-	-	1.097	1.193	1.331
6.0	1.117	1.201	1.391	1.099	1.195	1.334
7.0	1.117	1.203	1.395	1.101	1.198	1.337
8.5	1.118	1.205	1.399	1.117	1.232	1.400
9.0	1.119	1.237	1.403	-	-	-
10.0	1.134	1.264	1.457	1.128	1.256	1.442
11.0	-	-	-	1.131	1.263	1.453
11.5	1.138	1.278	1.473	-	-	-
12.0	-	-	-	1.133	1.268	1.462
13.0	1.143	1.286	1.489	-	-	-
13.5	-	-	-	1.138	1.277	1.475
15.0	1.147	1.294	1.505	1.143	1.279	1.479
16.5	1.145	1.290	1.499	1.141	1.275	1.476
18.0	1.143	1.287	1.491	1.138	1.272	1.470
19.0	1.141	1.284	1.487	-	-	-
20.0	1.139	1.281	1.483	-	-	-

Table 4: Relative viscosity data for PEG-SDS-NaI mixture of 6000g/mol at different PEG, SDS and NaI concentrations.

C_s(mM)	NaI(0.01M)			NaI(0.05M)		
	1.0 mM	2.1 mM	3.5 mM	1.0 mM	2.1 mM	3.5 mM
3.0	-	-	-	1.093	1.188	1.327
4.5	-	-	-	1.093	1.189	1.329
6.0	1.116	1.228	1.393	1.095	1.193	1.331
7.0	1.116	1.229	1.396	1.097	1.195	1.335
8.5	1.117	1.232	1.401	1.114	1.229	1.396
9.0	1.119	1.235	1.405	-	-	-
10.0	1.131	1.262	1.453	1.127	1.254	1.438
11.0	-	-	-	1.132	1.265	1.456
11.5	1.140	1.280	1.483	-	-	-
12.0	-	-	-	1.138	1.275	1.475
13.0	1.145	1.291	1.501	-	-	-
13.5	-	-	-	1.140	1.281	1.486
15.0	-	-	-	1.145	1.285	1.489
15.5	1.150	1.298	1.511	-	-	-
16.5	-	-	-	1.139	1.279	1.485
17.0	1.147	1.293	1.506	-	-	-
18.0	1.145	1.289	1.500	1.136	1.274	1.481
20.0	1.143	1.285	1.494	-	-	-

A representative data for PEG concentration Cp = 2.1 mM are also shown in Fig 1.
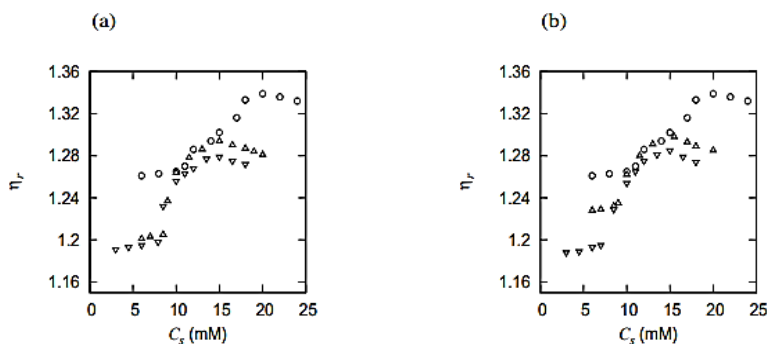
Fig. 1: Presents variation of measured relative viscosity data at 303 K for (a) NaCl (b) NaI salts at constant PEG concentration C_p = 2.1 mM. Symbols circle, uptriangle and downtriangle represent viscosity data salt free, 0.01M and 0.05M salt solutions, respectively.

Fig. 1 presents the variation of measured relative viscosity data at 303 K with different SDS and salt concentrations. From salt-free PEG-SDS mixture (circle symbols) of Fig 1, it has been observed that, the relative viscosity data changes its slope (takes an upward turn) at around Cs = 10 mM (which is defined as CAC) and then finally decreases from around Cs = 20 mM (which is defined as PSP). It has been also observed from the Fig. 1 that the addition of salt molecules to this mixture (up and down-triangles) decreases the viscosity as well as the CAC.

To quantify the CAC concentration from viscosity data, we have applied Jiang model [6]. We should note here that, in order to establish a new viscosity equation for PEG-SDS mixture, Jiang et al. modified Cabane polymer micelle model [14] by considering the partially stretched chain structure of the polymer-surfactant complex caused by the static-electrorepulsion of the resident charge. In their model, the viscosity of the solution is expressed by the following equation.

$$\frac{\eta_{SP}}{C_P} = \frac{A(1-\xi)^{0.5}}{C_P^{0.5}} + B\xi + D\xi^2 C_p \tag{3}$$

where $\eta_{sp}(= \eta_r -1)$ is the specific viscosity. The association coefficient, ξ, in Eq. (3), is defined as the ratio of the number of free segments to the number of complex segments and the parameter A is a function of l_B, Z and R_H. The symbol Z is related to the number of ionizable monovalent groups per polyion, R_H is the hydrodynamic radius of the polymer and l_B is Bjerrum length. The parameters, A and ξ in the above equation is used to explain the PEG-SDS interaction. From the model, we have also seen that it demands model parameters B and D as well which can be estimated from the following classic Huggins equation.

$$\frac{\eta_{SP}}{C_P} = B + DC_p \tag{4}$$

If we put $\xi = 1$, Eqn. (3) reduces to Huggins equation for pure polymer solution, and for $\xi = 0$, the equation reduces to the viscosity equation for pure polyelectrolyte solution [16]. To estimate parameters B and D, we have measured specific viscosity at 303 K for aqueous solution of 6000g/mol. From the fitting, the obtained values of B and D are 15.0 ml/g and 256.39 (ml/g)2, respectively. The fitting is shown in the Figure 2(a).
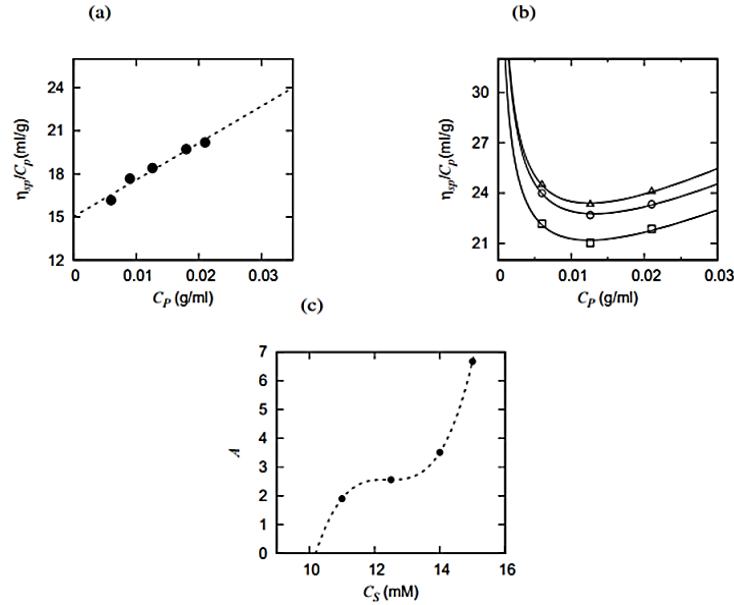
Fig. 2: Fittings of (a) Huggins equation, (b) Jiang model and (c) polynomial for CAC to the experimental data at $T= 303K$. In (b), symbol squares, circles and uptriangles represent variation of Cp at fixed $C_s = 10$ mM, $C_s = 12{:}5$ mM and $C_s = 14$ mM, respectively.

We should note here that, Jiang et al. obtained the values of B and D are 18.7 ml/g and 150.4 $(ml/g)^2$, respectively for molecular weight of PEG 6000 g/mol. If we compare their data to the current study, we have seen that the value of B is close to this study whereas the value of D is deviated much. We have tried to fit their data but failed to distinguish which data had been used in their study to estimate B and D. To understand the interaction between the PEG and SDS, the parameters A and ξ are estimated from non-linear fittings of the above equation [Eq. (3)] to the obtained data in Table 2. The detail data with fitting is shown in Fig 2(b). The obtained parameters A and ξ using the viscosity equation (3) are listed in Table 5.

Table 5: A representation of A and ξ data obtained from PEG-SDS mixture

C_s(mM)	M_w(6000g/mol)	
	A	ξ
10.0	1.79	0.890
11.0	1.90	0.894
12.5	2.56	0.931
14.0	3.51	0.964
15.0	6.67	0.989

From Table 5 we have seen that both the values of A and ξ increase with the surfactant concentration in the mixture. This increasing tendency is consistent with the model developed by Jiang et al. In Jiang model, the parameter A is given by

$$A = (4\pi)^{-1.5} R_H I_B^{0.5} Z^2 \tag{4}$$

From the above Eqn. (5) it is seen that the parameter A depends on R_H, l_B and Z where l_B is a function of temperature. With the increasing temperature, l_B decreases but it remains constant at constant temperature. They predicted that Z will increase with the rise of the SDS concentration in the solutions i.e. Z / C_s. The more charges there bare on the complex chains, the more expansive the macromolecule chain is, which results in an increase of R_H. R_H is not only related to the inherent softness of polymer but also a function of charges Z on the macromolecule chains. Thus, under low surfactant concentration, R_H is proportional to C_s. They concluded that, A has an increasing tendency with the increase of C_s as A is proportional to C_s^3. Thus, we have chosen a polynomial function up to third order like $A = a + bC_s + cC_s^2 + dC_s^3$ to fit the viscosity data to estimate CAC. The polynomial fitting for the plot of A vs C_s for 6000 g/mol at $T = 303$ K is shown in the Fig. 2(c). From the fitting, we have obtained the value of CAC 10.2 for PEG 6000 g/mol which is consistent with our measured relative viscosity data from which it takes an upward turn for binding of SDS molecules to PEG chain. This consistency confirms that the Jiang model is working on the measured data properly.

Next, to see the effect of Na-based salts on PEG-SDS mixtures, we have applied the similar method to the viscosity data in Table 3 and Table 4 to find out the parameters A and using Eqn. (3). The corresponding fitting values of the parameters A and ξ are listed in Table 6 for NaCl 0.01M and 0.05M and NaI 0.01M and 0.05M concentrations.

Table 6: Representation of A and ξ data obtained from fitting of Jiang model to PEG-SDS-Salt mixture data.

NaCl(0.01 M)			NaCl(0.05 M)			NaI(0.01 M)			NaI(0.05 M)		
C_s	A	ξ	C_s	A	ξ	C_s	A	ξ	C_s	A	ξ
9.0	1.18	0.804	7.0	0.79	0.690	8.5	1.14	0.806	7.0	0.674	0.711
10.0	1.77	0.884	8.5	1.11	0.804	9.0	1.17	0.808	8.5	1.02	0.810
11.5	2.14	0.917	10.0	1.53	0.875	10.0	1.69	0.891	10.0	1.48	0.868
13.0	2.58	0.936	12.0	1.86	0.909	11.5	2.38	0.933	11.0	1.55	0.839
15.0	3.39	0.961	13.5	2.17	0.922	13.0	3.24	0.960	12.0	2.14	0.919

The polynomial fittings for each salt concentration are presented in Fig. 3.
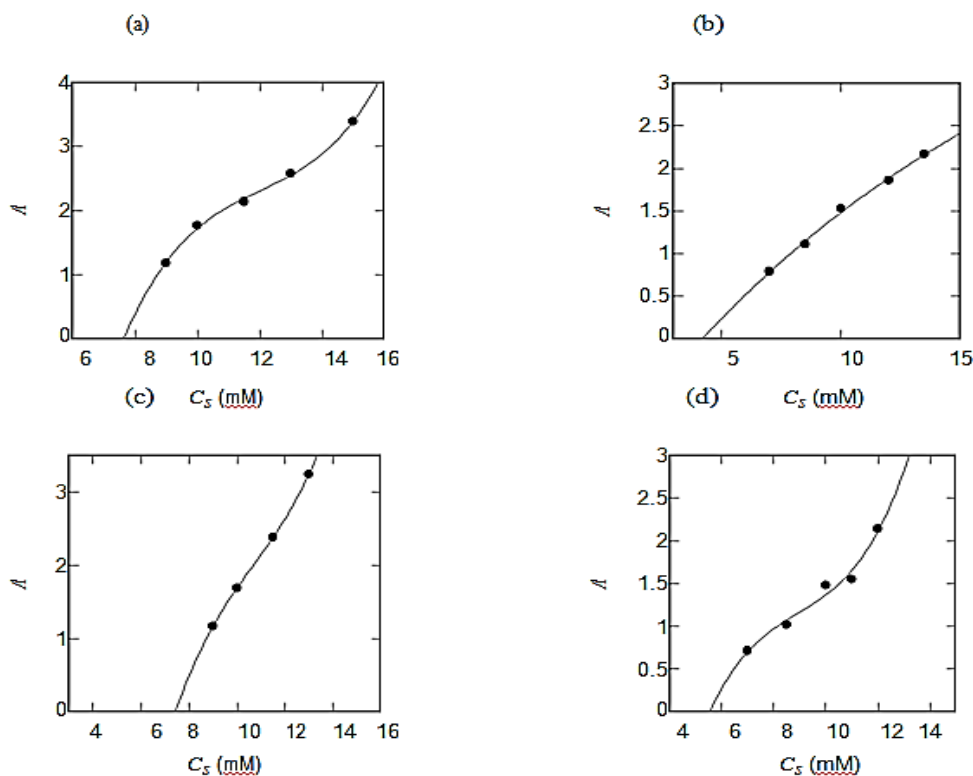
Fig. 3: The polynomial fitting of parameter A vs SDS at constant temperature 303 K for PEG 6000g/mol for NaCl (a)0.01M (b) 0.05M and for NaI (c) 0.01M and (d) 0.05M.

From the fitting, we have obtained the required values of CAC for PEG 6000 g/mol for different Na-based salt concentrations and are listed in Table 7. From the Table 7 it is seen that the CAC value varies with salt concentrations. From Table 5 and Table 7, it has been also observed that for a particular SDS concentration, the association coefficient, ξ, decreases with the increase of salt

molecules in the ternary mixture. In the Jiang model [Eq. (3)], ξC_p and $(1-\xi)C_p$ were defined as the number of free segment and the number of SDS-PEG complexes in the ternary mixture. The decrement of ξ means the increased number of PEG-SDS complexes in the mixture. This behavior supports the aggregation of SDS to the PEG chain via induced attractive interaction. Here, salt molecule plays an important role which induces attractive interaction between PEG and SDS molecules. Due to this attraction, SDS molecule has started to bind with PEG chain at low concentration of SDS than that of PEG-SDS mixture. In other word, the value of CAC is shifted towards lower concentration of SDS and hence the value of CAC decreases with the increase of salt molecules in the mixtures. For NaCl, it is seen that the degree of attraction is little bit more than that for NaI. The probable reason may be as follows. In the crystallization of protein molecules from aqueous mixture of PEG and NaCl, the reagent PEG is used to induce attractive interaction between protein molecules and salt NaCl is used to reduce electrostatic repulsion between protein molecules and thus acts as screening agent of electrostatic interaction [17]. From the quantitative data of ξ, in Table 7, with increased salt molecules indicates the more number of PEG-SDS complexes than that at low concentration of NaCl or NaI.

Table 7: Represents the values of CAC at temperature 303K and different salt concentration of NaCl and NaI.

NaCl (M)	CAC	NaI(M)	CAC
0.00	10.2	0.00	10.2
0.01	7.57	0.01	7.43
0.05	4.26	0.05	5.62

Since both SDS and PEG contain hydrophilic and hydrophobic parts, we can assume the similar phenomenon like the interaction in protein-PEG-salt mixture in this study. For effectiveness of salt molecules, there is a famous Hofmeister series where anions and cations have the rank of order [18]. In terms of the ion activity, it has been observed in the series that, Cl^- (chloride) ion is more effective than I^- (iodide) ion. Since the cation Na^+ is fixed in the studied ternary mixture, the behavior of salt molecules is consistent.

4. CONCLUSIONS

In this study, we have studied the effect of Na-based salt molecules on critical aggregation concentration (CAC) of PEG-SDS mixtures in nano-pure water. To investigate the interaction between PEG, SDS and Salt (NaCl, NaI) molecules, we have estimated the critical aggregation concentration (CAC) by applying modified Jiang model. From estimated CAC data, we observe that CAC values decrease almost linearly with increasing salt concentrations. Therefore, we can conclude that salt molecules favor the binding of surfactant molecules to the PEG chain.

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