Research Article

Journal of Scientific Enquiry
Vol: 5, Pages: 54-62

Physicochemical studies of the effect of β-Cyclodextrin on aggregation behaviors of triphenyl tetradecyl phosphonium bromide (TTPB) in aqueous solution

Jayanta Kumar Midya*

Dept. of Chemistry, Jagannath Kishore College, P.O.- Ketika, Purulia, W.B.-723101
*Corresponding Author. E-mail address: jayanta.midya@gmail.com

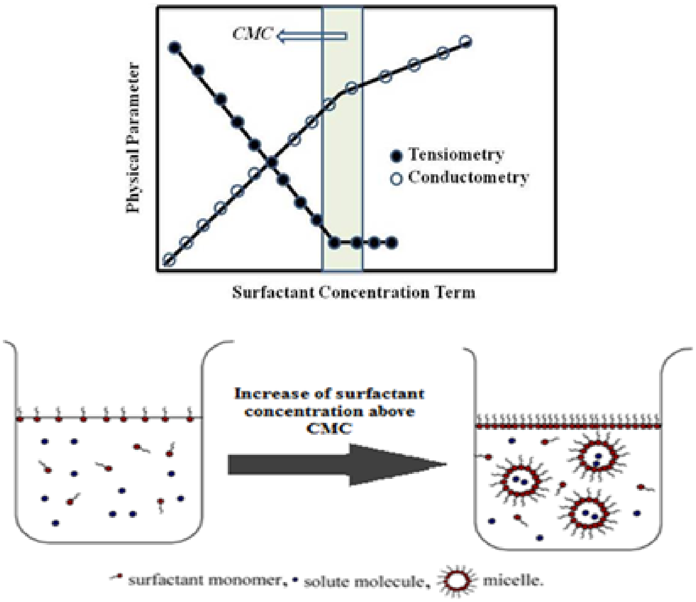
Received: 28.07.2025; Accepted: 27.10.2025; Published online: 31.12.2025
DOI: `https://doi.org/10.54280/jse.255103`

Abstract: The aggregation behaviour of cationic triphenyl tetradecyl phosphonium bromide (TTPB) in presence of β-cyclodextrin (β-CD) has been investigated by tensiometry and conductometry in aqueous media. The critical micelle concentration or CMC has been found to increase with increase in concentration of β-CD. From the data of surface tension and conductivity measurements, surface excess of TTPB (Γ_{max}), minimum area of the amphiphile head group at the surfactant saturated monolayer at air/solution interface (A_{min}), counter-ion binding (η), and Gibbs free energy for formation of micelle (ΔG_m^0) have been calculated by well known equations. Diffusion co-efficient (D_0) of Ferrocene probe is calculated from cyclic voltametry study which shows to increase with increase in [β-CD]. Hydrodynamic diameter and Packing parameter have also been calculated in this work.

Key words: TTPB; β-CD; Surface excess; Gibbs free energy; Diffusion co-efficient.

1 Introduction

Surfactants are amphiphilic molecules which tend to reduce the surface activity at air-liquid interface. Their extent of aggregation is different in various polar/nonpolar medium. They offer many important uses and applications in pharmaceutical, technological, biochemical, chemical and industrial fields by serving solubilisation, stabilities and detergency behaviour [1-4]. The cationic surfactants exhibit speciality when used as antifungal, antibacterial, and antiseptic agents. The self-assembly and interfacial behaviours of most cationic surfactants are based on long-chain quaternary ammonium groups, pyridinium or sulphonium as polar head-group [5-7]. But surface chemical studies on alkyl triphenyl phosphonium bromides (ATPBs) with polysaccharides are very limited [8-9]. The study is therefore, interesting to highlight the self-aggregation of TTPB (presence of three phenyl groups as head part) with polymer. Polymer-surfactant interactions exhibit fundamental importance in the understanding of their mutual behaviour in the mixed state to modify the rheological properties, and to enhance the stability of dispersions. β-Cyclodextrin (β-CD) is an cyclic oligosachharide polymer consisting of seven α 1-4 linked glucose units, and it belongs to a category of macrocyclic compounds which undergo completely hydrophobic interactions [10]. This compound is of great importance not only in chemistry but also in pharmaceutical technology, food industry, agro-chemistry, and other chemical industrial areas [11,12]. This is because cyclodextrin can form inclusion complexes with a wide variety of organic or inorganic compounds (guests) both in the solid phase and in solution [13]. Surfactants being amphiphilic can form complex with β-CD with their hydrocarbon chain and can enter into the hydrophobic cavity of β-CD. Thus, the micellization processes of the surfactants and some micellar parameters are affected accordingly to a certain extent. There have been reported some studies concerning the effect of β-CD on the micellization [14-16]. The critical micellar concentration (CMC) of a surfactant with all physical properties of a surfactant solution exhibits a sharp concentration dependent discontinuity in the region of self-aggregation (or micellization) which is schematically shown in the following scheme 1.



Scheme 1. Schematic presentation of determination of CMC by different methods (above) and micelle formation process (below).

Hydrophobic inner cavity of β-CD forms strong inclusion complexes with the hydrophobic tail of TTPB and thus impart significant influence on the micellar properties of this surfactant. The relevance of this study is due to the fact that these system can be employed to mimic the effect of CD on phospholipids, a major constituent of cell membrane. A lot of work has been done to study the inclusion complex formation between a variety of single ionic surfactants and the CD cavity [17]. Hence, The present work deals with to explore the nature of aggregation by cationic surfactant molecules in the presence of β-CD.

2 Experimental Section

2.1 Materials

Triphenyl tetradecyl phosphonium bromide (TTPB) ($\geq$ 98 %) was obtained from Caledon Laboratories, LTD, Canada. β-cyclodextrin (β-CD) ($\geq$ 97 %, Sigma Aldrich) was used as received. Double distilled water (κ 2-3 μS cm^{-1} at 25_{0}C) was used throughout the study. All the experiments were performed under a constant temperature either by placing the samples in water bath at a constant temperature through the solution-holding compartment of the instrument.

2.2 Tensiometry

Tensiometric measurements for air/solution interfacial tension were performed with a du Noüy tensiometer (Krüss, Germany) using a platinum ring detachment method. 6 mL of the water of β-CD solution was put in a double-wall jacketed container placed in a thermosetted water bath (accuracy, ± 0.1 K) at the requisite temperature container and surfactant solution of known concentration (10 to 15 times the CMC) was added into it progressively.

During such measurements, a time interval of 10 minute for equilibration was allowed after surfactant addition and thorough mixing in each case. The CMC values were determined from the break points in the surface tension vs. log [surfactant] plots. The determined surface tension (γ) values were reproducible within ± 0.1 mN m^{-1}.

2.3 Conductometry

The conductivity measurements were performed with Systronics Conductivity Cell (India) conductivity meter with a cell constant =1 cm^{-1}. The temperature of the solution was maintained with a temperature controlled circulator water bath of accuracy ±0.1 K. About 8 mL of solution was placed in a double-wall jacketed container and the temperature was controlled by a Hahntech DC-2006 circulating bath with an accuracy of ± 0.1 K. Surfactant solution of a known concentration was progressively added using a micro syringe. The specific conductance (κ) was measured after each addition followed by thorough mixing. The cmc values were computed from the plots of specific conductance (κ) vs. surfactant concentration.

2.4 Cyclic Voltametry

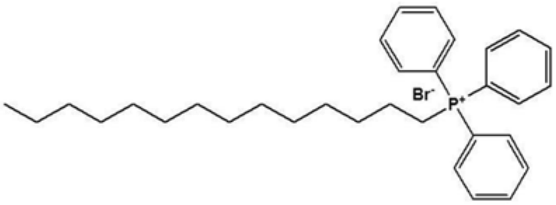
CV measurements were taken using an electrochemical analyzer (Digi-Ivy, DY 2300 series) consisting of a working Pt electrode (the interface at which the redox reaction of interest occurs), saturated Ag/AgCl as reference electrode and Pt wire as counter electrode. The electrode area was A =1.4 × 10^{-10} m^2. 1 mM ferrocene was used as the probe in the redox reaction. 100 mM KCl solution was used as the supporting electrolyte. The concentration of the electroactive probe does not affect the micellization of surfactants.

3 Results and discussion

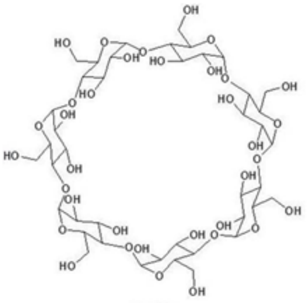
3.1 Surface Tension

The high value of surface tension of water originates from strong intra-molecular hydrogen bonding among the water molecules. This leads to enhanced cohesive force, which resists the separation of a water layers. TTPB surfactant molecules initially populate at the air/water interface in order to overcome the highly energetically unfavorable interaction of water with the hydrophobic tail of the surfactant. As a result, the surfactant head groups are coverted in the aqueous environment while the tail parts are projected in the air phase. This, in turn, hinders the intermolecular hydrogen bonding present on the surface of a pure aqueous phase, and surface tension starts decreasing. In presence of β-CD, tail group of TTPB is buried in the cavity of β-CD. The tail group of TTPB with β-CD complex gets stabilised in the bulk of aqueous solution. For a certain β-CD concentration, initially some TTPB will be required to complete the TTPB-β-CD complex. Beyond a certain [TTPB], there will be no β-CD to make the complex with TTPB. Then decrease in the γ value continues until the air/water interface is saturated with surfactant monomers. Beyond this saturation, the added surfactants assemble among themselves to form aggregates to ensure a hydrophilic periphery, hiding the hydrophobic tail within a cage to avoid water. Then, γ value does not change (beyond γ_{cmc}) after reaching a certain concentration of surfactant. This concentration of surfactant is called the critical micellar concentration (CMC) and is obtained from the break point in the γ vs log[surfactant] profile. The constant value of surface tension at the cmc is called cmc

https://doi.org/10.54280/jse.255103



Tetradecyl triphenyl phosphonium bromide (TTPB)



β-CD

and is a measure of the efficacy of the surfactant to populate at the air/water interface in the form of a monolayer prior to micellization. Hence, CMC will be higher in presence of [β-CD] as some surfactant molecules go for inclusion complex with β-CD.

3.2 Conductometry

The individual surfactant, being an electrolyte, dissociates in water. As a result, solution of gradually added surfactants shows increase in conductivity as the number of surfactant molecules increases. The rate of increase in conductivity decreases after a certain concentration of surfactants. That certain concentration is called critical micellization concentration (CMC). As the concentration of TTPB needed to reach the CMC increasing with increase of [β-CD], then breaking point (CMC) is observed at higher concentration of TTPB i.e., CMC values increase with enhancement of CD- surfactant complexation. CMC can be obtained from the breaking point of κ (conductivity) vs [surfactant] plot. From the ratio of pre- and post- micellar slopes degree of dissociation of surfactants (α) can be obtained. The change in counter ion binding (η) is discussed later.

3.3 Cyclic Voltametry and DLS study

The diffusion coefficients of the micelles in different concentrations of β-CD were determined from CV measurements. We use ferrocene as the electroactive probe. It does not perturb the micelles and their rate of entrance and exit into the aggregates with fast and reversible electron transfer is comparable to that of the surfactant monomer. Ferrocene is hydrophobic in nature and is expected that it is solubilised and diffused in the micellar phase. So the determined diffusion coefficient value can be assumed to be micellar diffusion coefficient. The oxidation of ferrocene was shown as

$$Fc \Leftrightarrow Fc^{+} + e^{-}$$

The self-diffusion coefficient was determined using the following equation

$$i_p = (2.69 \times 10^5) n^{\frac{(3)}{2}} A D_0^{\frac{1}{2}} v^{\frac{1}{2}} C_0$$

where n is the number of electrons involved in the redox reaction, A is the surface area of the Pt electrode, D_0 is the diffusion coefficient of the electroactive probe, C_0 is the concentration of the probe, i_p denotes the peak current and v is the scan rate. Hence, from the slope of i_p vs. plot, the D_0 values were obtained for micellar solution of TTPB in different concentrations of β-CD. DLS measurements are taken at 173^o angle in a Malvern Zetasizers Nano-zs apparatus with a He–Ne laser (k = 632 nm) at 30^oC. The sample cells are placed in a temperature-controlled, refractive index matched bath filled with cis-trans decahydronaphthalene (decalin). All experimented solutions are filtered 3–4 times through Millipore membrane filters (porosity 220 nm) to remove dust particles. The mean values of two repeat experiments are reported.

Determination of Critical Micellar Concentration

The CMC values of triphenyl tetradecyl phosphonium bromide (TTPB) have been determined in aqueous β-CD media from surface tension and conductance measurements. The concentration of β-CD varies from 0 to 9 mM. The CMC increases with increase in β-CD concentration in both techniques (Table 1). In case of conductometry, the value of CMC is slightly higher as compared to that obtained from surface tension measurement. But the pattern of change of CMC is similar for both methods. The increase in CMC may be due to the strong association of TTPB with β-CD compared to the formation of pure micelle [18]. The CMC values of each method and average values are reported in Table 1.

Table 1: CMC values of TTPB in aqueous β-CD medium at 298K.

[β-CD]	**CMC (mM)**		
(mM)	**Tensiometry**	**Conductometry**	**Ave**
0	0.41	0.63	0.52
1	1.01	1.10	1.05
3	2.14	2.40	2.25
5	3.16	3.64	3.45
7	4.08	4.92	4.50
9	5.02	6.20	5.91

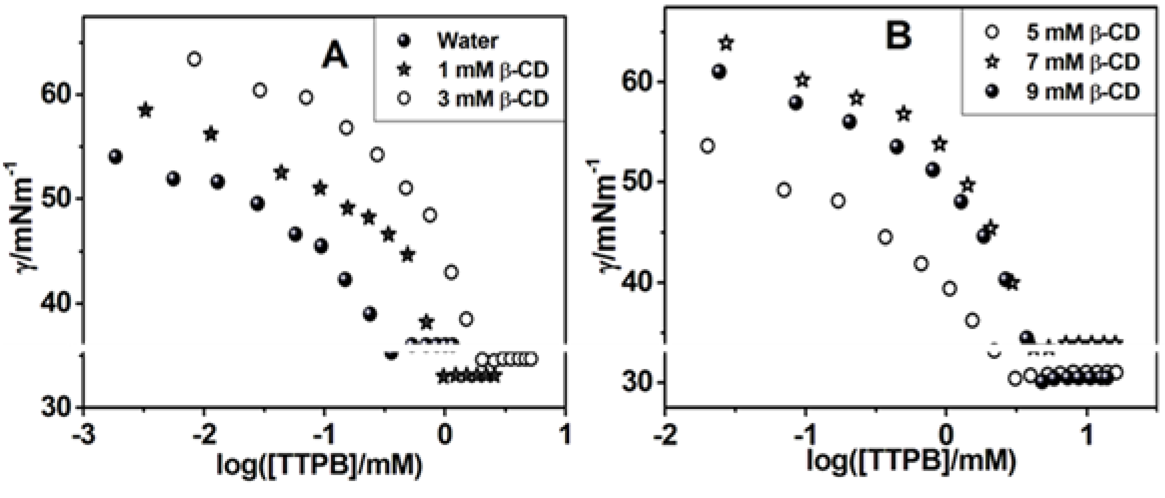


Figure 1: Tensiometric plot of γ vs log[TTPB] at different [β-CD], A: [β-CD] = 0, 1, and 3 mM and B: [β-CD] = 5, 7, and 9 mM.

The nonpolar alkyl part of TTPB interacts within the cavity of β-CD. The hydrophobic interaction plays the key role for this association. Due to strong association, TTPB-β-CD complex is stabilized in aqueous medium. This results more TTPB-β-

CD consumption to reach the CMC value which is higher at higher concentration of β-CD. This increase in CMC may diminish the thermodynamic activity of pure TTPB molecules with rise in β-CD concentration and for that micellization process is retarded [19].

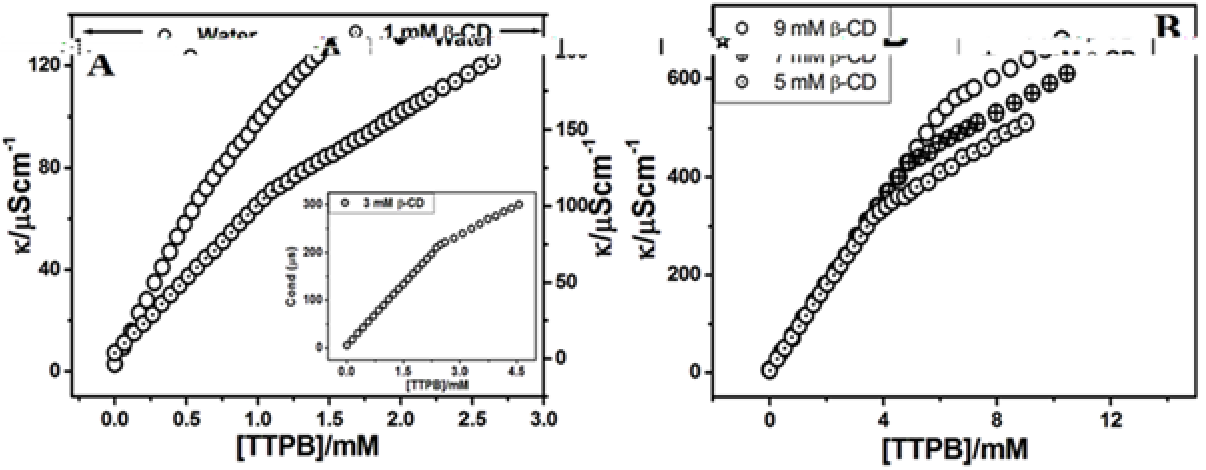


Figure 2: Conductometric plot of κ vs [TTPB] at different [β-CD], A: [β-CD] = 0, 1, and 3 mM (inset of A) and B: [β-CD] = 5, 7, and 9 mM.

Counter ion binding (η)

Degree of dissociation of the surfactant TTPB (α) is determined from the ratio of post- and pre- micellar slopes in κ vs [TTPB] in conductivity measurement (Figure 2). The counter ion binding (η) of the surfactant in micelle is related to the following equation-

$$\eta = 1 - S_2/S_1 \tag{1}$$

With increase in [β-CD], η tends to increase smoothly which follows a sigmoidal curve (Figure 3). The CMC vs [β-CD] profiles have yielded well-fitted linear curve, the equation obtained for tensiometric method,

$$CMC = 0.485 + 0.504[\beta - CD](R = 0.997)$$

and that for conductometric method,

$$CMC = 0.537 + 0.626[\beta - CD](R = 0.999)$$

The graph for the above equations is depicted in Figure 3. The values (η) are consistent with literature [20]. The interfacial adsorption property of the amphiphile is quantified by the Gibbs surface excess (Γ_{max}) and the minimum surface area per surfactant molecule (A_{min}) according to the Gibbs adsorption isotherm. The values of Γ_{max} and A_{min} can be calculated from the following equations [21,22].

Table 2: The variation of Γ_{max}, A_{min}, P, η, and Gibbs Free Energy of TTPB at different [β-CD].

[β-CD] (mM)	Γ_{max} ($\times 10^6$ molm^{-2})	A_{min}	P	η	$-\Delta G_m^0$ (kJmole^{-1}K^{-1})
0	2.10	0.83	0.257	0.40	40.34
1	2.60	0.62	0.328	0.46	38.64
3	4.42	0.39	0.567	0.54	38.39
5	3.29	0.52	0.424	0.58	37.94
7	7.51	0.25	0.951	0.62	37.45
9	7.78	0.21	0.998	0.64	36.98

https://doi.org/10.54280/jse.255103

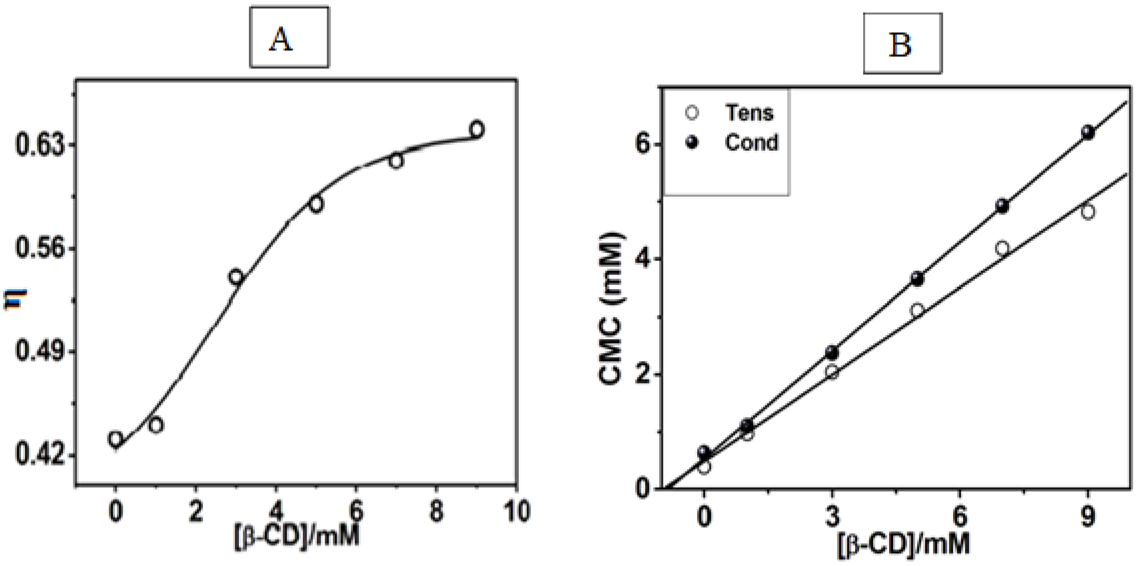


Figure 3: Graphs for pattern of change in η (A) and change of CMC (B).

$$\Gamma_{max} = -\frac{1}{2.303iRT} \lim_{C \to CMC} \frac{d\gamma}{d \log C} \quad (2)$$

where i is the number of ions dissociated per surfactant monomer, R is the universal gas constant, T is the absolute temperature and C is the concentration of surfactant.

$$A_{min} = -\frac{10^{18}}{N\Gamma_{max}} \quad (3)$$

N is Avogadro's constant. The values of Γ_{max} and A_{min} are reported in Table 2. It is pronounced that with increasing [β-CD] the value of Γ_{max} increases, as a consequence A_{min} decreases indicating lesser arrangement of TTPB molecules at the air/water interface. The nature of amphiphile packing in micelles and their structural geometry were estimated based on the proposition of Israelachvili [23], in terms of the packing parameter (P):

$$P = \frac{v}{Al_c} \quad (4)$$

where, l_c is the critical length of the hydrophobic chain of the monomer, A is the surface area of the head group and v is the critical volume of the hydrophobic chain. Both l_c and v for a saturated hydrocarbon chain with C_n number of carbon atoms can be obtained from the proposed formulas by Tanford [24]. Thus,

$$l_c = (0.154 + 0.1265C_n)nm$$
$$v = (0.0274 + 0.0269C_n)nm^3$$

Table 3: Diffusion Co-efficient (D_0) and Hydrodynamic Diameter

[β-CD] (mM)	**Diffusion Co-efficient (D_0X 10^{-14} m^2s^{-1})**	**Hydrodynamic Diameter (nm)**
0	1.53	0.89
1	2.43	1.12
3	2.72	1.15
5	3.00	1.41
7	3.44	1.58
9	3.66	1.81

Israelachvili's theory has suggested that for spherical assemblies P $\leq$ 0.333 [14]. In this study, P values are much lower than 0.333 upto [β-CD] = 1 mM, and concludes that spherical micelles were formed. At higher [β-CD], the shape of TTPB micelle tends to be non-spherical. This is consistent with ionic surfactants which reports to form spherical assemblies in aqueous medium close to their CMC values [25]. The standard free energy of micellization, ΔG_m^0 was calculated according to the pseudophase model by the relation,

$$\Delta G_m^0 = (1 + \eta) RT \ln X_{cmc}$$

where X_{cmc} is the mole fraction concentration of the surfactant at the micellar concentration. The negative value of ΔG_m^0 indicates that the micellization is spontaneous, and with increase in [β-CD] the value decreases slightly.

Determination of diffusion coefficient and hydrodynamic diameter

The diffusion coefficient value increases with increasing concentration of β- CD for higher interactions of β-CD and Ferrocene. The diameter of the micelle increases smoothly with increase in the concentration of β-CD as reported in Table 3.

4 Conclusion

In this work, the CMC values have measured tensiometrically and conductometrically. The change of CMC with (β-CD) follows a complete linear relationship whereas counter ion binding change also follows a sigmoidal relationship. Enhancement of CMC with increase in (β-CD) can be explained as barrier of hydrophobic part of surfactant into the cavity of β-CD from the surrounding medium and therefore hinders the formation of CMC. Gibbs free energy change for formation of micelle is spontaneous. The values of hydrodynamic diameter and diffusion co-efficient have been determined for all β-CD systems that supports a strong interaction of surfactant with cyclodextrin. As hydrophobic part of TTPB inserts into hydrophobic cavity of β-CD forming stable inclusion complex, this system can act as controlled release system such as drug delivery, formulation of cosmetics, pesticides etc. Solubilization of different substances and emulsion stabilization through the modulation of micellar structure can also be facilitated. This β-CD-surfactant complexes can trap organic pollutants (e.g., dyes, pesticides, oils) in the form of nano-aggregates and thus harness host-guest chemistry to improve solubility, stability, safety, and environmental concern.

Acknowledgements

The author would like to thank the Centre for Surface Science, Physical Chemistry Section, Department of Chemistry, Jadavpur University, Kolkata 700032, India for instrumentation facility.

References

[1] Tripathy, D. B., Mishra, A., Clark, J., & Farmer, T. (2018). Synthesis, chemistry, physicochemical properties and industrial applications of amino acid surfactants: A review. *Comptes Rendus Chimie, 21*(2), 112–130.

[2] Landry, J. M., Marangoni, D. G., Arden, D. A., MacLennan, I. J., & Kwak, J. C. T. (2009). Interaction of a cationic surfactant with an oppositely charged polymer. *Journal of Surfactants and Detergents, 12*, 155.

[3] Mandal, B., Moulik, S. P., & Ghosh, S. (2012). Physicochemistry of interaction of polyvinylpyrrolidone (PVP) with sodium dodecyl sulfate (SDS) in salt solution. *Journal of Surfaces and Interfaces of Materials, 1*, 77–86.

[4] Rodríguez, J. L., Ciolino, A. E., Pieroni, O. I., Vuano, B. M., & Schulz, P. C. (2007). A possible use of a polymeric amphiphile as petroleum pollution collector. *Journal of Surface Science and Technology, 23*, 111–130.

[5] Pillai, P., Maiti, M., & Mandal, A. (2022). Mini-review on recent advances in the application of surface active ionic liquids:

Petroleum industry perspective. *Energy & Fuels, 36*(15), 7925–7939.

[6] Yakea, A., Cordera, T., Moloyb, K., Coopec, T., Taylora, C., Hungb, M., & Penga, S. (2016). Fluorinated pyridinium and ammonium cationic surfactants. *Journal of Fluorine Chemistry, 187*, 46–55.

[7] Vekariya, R. L., & Kumar, N. S. (2023). Micellization behaviour of surface active N-alkyl pyridinium dodecylsulphate task- specific ionic liquids in aqueous solutions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 529*, 203–209.

[8] Prasad, M., Moulik, S. P., MacDonald, A., & Palepu, R. (2004). Self-aggregation of alkyl (C10-, C12-, C14-, and C16-) triphenyl phosphonium bromides and their 1:1 molar mixtures in aqueous medium: A thermodynamic study. *Journal of Physical Chemistry B, 108*(1), 355.

[9] Zhou, H., Yang, Z., Zhou, P., & Li, X. (2009). Effect of β-CD on the micellization of cetyltrimethylammonium in aqueous solution at high temperature. *Journal of Dispersion Science and Technology, 30*, 1390–1394.

[10] Uekama, K., Hirayama, F., & Irie, T. (1998). Cyclodextrin drug carrier systems. *Chemical Reviews, 98*, 2045.

[11] Chavanpatil, M. D., Khdair, A., Patil, Y., Handa, H., Mao, G., & Panyam, J. (2007). Polymer-surfactant nanoparticles for sustained release of water-soluble drugs. *Journal of Pharmaceutical Sciences, 96*, 3379–3389.

[12] Somasundaran, P., & Cleverdon, J. (1985). A study of polymer/surfactant interaction at the mineral/solution interface. *Colloids and Surfaces, 13*, 73–85.

[13] Martin, D. V. (2004). Cyclodextrins and their uses: A review. *Process Biochemistry, 39*, 1033–1046.

[14] Hao, L., Wang, H., Wang, Y., Meng, Y., & Nan, Y. (2023). Inclusion complexation of surfactant with β-cyclodextrin and its effect on the mixed micellization of cationic/anionic surfactants. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 668*, 131437.

[15] Shen, X., Belletête, M., & Durocher, G. (1997). Studies of the inclusion complexation between a 3H-indole and β-cyclodextrin in the presence of urea, sodium dodecyl sulfate, and 1-propanol. *Langmuir, 13*, 5830–5836.

[16] Abarca, R. L., Rodríguez, F. J., Guarda, A., Galotto, M. J., & Bruna, J. E. (2016). Characterization of β-cyclodextrin inclusion complexes containing an essential oil component. *Food Chemistry, 196*, 968–975.

[17] Vargas, C., Schönbeck, C., Heimann, I., & Kelle, S. (2018). Extracavity effect in cyclodextrin/surfactant complexation. *Langmuir, 34*(20), 5781–5787.

[18] Bakshi, M. S. (2000). Cationic mixed micelles in the presence of β-cyclodextrin: A host–guest study. *Journal of Colloid and Interface Science, 227*(1), 78–83.

[19] Tsianou, M., & Fajalia, A. I. (2014). Cyclodextrins and surfactants in aqueous solution above the critical micelle concentration: Where are the cyclodextrins located? *Langmuir, 30*(46), 13754.

[20] Dharmawardana, U. R., Christian, S. D., Tucker, E. E., Taylor, R. W., & Scamehorn, J. F. (1993). A surface tension method for determining binding constants for cyclodextrin inclusion complexes of ionic surfactants. *Langmuir, 9*(9), 2258–2263.

[21] Das, S., Ghosh, S., & Das, B. (2018). Formation of mixed micelle in an aqueous mixture of a surface active ionic liquid and a conventional surfactant: Experiment and modeling. *Journal of Chemical and Engineering Data, 63*, 3784–3800.

[22] Chattoraj, D. K., & Birdi, K. S. (1984). *Adsorption at liquid interfaces and the Gibbs equation.* Plenum.

[23] Israelachvili, J. N. (1991). *Intermolecular and surface forces* (2nd ed.). Academic Press.

[24] Tanford, C. (1980). *The hydrophobic effect* (2nd ed.). Wiley-Interscience.

[25] Jayaraman, A., & Mahanthappa, M. K. (2018). Counterion-dependent access to low-symmetry lyotropic sphere packings of ionic surfactant micelles. *Langmuir, 34*(6), 2290–2301.
