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Partitioning of thiophene derivatives between solvent and micellar media of cationic surfactant, cetyl trimethyl ammonium bromide

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ABSTRACT

This manuscript reports the interaction of thiophene derivatives i.e. 5-(2-(benzyloxy) phenyl) thiophene-2-sulfonamide (BPTS) and 5-bromothiophene-2-sulfonamide (BTS) with micellar media of cationic surfactant, cetyl trimethylammonium bromide (CTAB) using UV/visible spectroscopy. Quantitative measurement of the degree of solubilization and binding has been calculated in term of partition coefficient (K_x) and binding constant (K_b) respectively while the values of free energy of partition (ΔG_p), and free energy of binding (ΔG_b) give information about spontaneity of both processes.

1. Introduction

One of the most unique properties of surfactants is formation of micelles, due to non-covalent forces, above critical micelle concentration (cmc) and increase in solubility of insoluble materials in micellar solution. Hydrophilic surface and hydrophobic core impart heterogeneous structure to micelle and, thus, enabling them to act as biomembranes because they have ability to interact with both hydrophilic and lipophilic additives. The said property makes micellar media of surfactants valuable for a number of applications in laboratory and industry i.e. micellar catalysis, detergency, emulsion polymerization, enhanced oil recovery, dry cleaning and the most important of all drug delivery and removal of pollutants from aqueous media [1,2]. Thus the selection of the most suitable surfactant for the said purpose is of utmost importance. The calculation of parameters like binding constant, K_b, partition coefficient, K_x, free energies of binding and partition help to take decision in this regard. The values of aforementioned parameters not only enable us to understand interactions of additives with bio membranes but also to establish structure activity relationship [1].

Non-covalent forces may also induce self-aggregation in some non-amphiphilic organic compounds but this aggregation does not deserve to be called micellization rather called open association as there is no sharp change in their physical properties at cmc [3]. This open association may cause shift in λ_{max} of these compounds thus exhibiting red or blue shift. Red shift is produced by J-aggregates formed due to end to end stacking while H-aggregates cause blue shift being formed by plane to plane stacking. The value of tilt angle is less than 32° for J-aggregates and greater for H-aggregates [4].

Control release rate, less degradation of drug, increase in solubility and decrease in toxicity level of drugs make micelles excellent drug carriers [5]. Hydrophobic effects play major role to decide the locus of solubilizate within micelle, although, role of hydrophilic and electrostatic forces is not ignorable [6].

Thiophene is a five membered heterocyclic aromatic compound. Its chemical stability, easy synthesis and easy processing make its derivatives among one of the most studied organic compounds. Their applications in drug design, electronic devices, bio diagnostics and sensory devices have invited attention of many researchers. Many research groups have turned their attention toward oligomers and polymers of thiophenes due to their semiconductor, luminescence and sensory properties [7].

In our previous work we have reported solubilization of Chloroquine Diphosphate [8], Quinacrine 2HCl [9], Pefloxacin mesylate [10], benzothiazole [11], Benzalkonium Chloride [12] reactive blue 19 [13] and reactive red 223 and reactive orange 122 [14] in micellar solution of selected surfactants. In present work we want to explore the effect of structure on partitioning of two thiophene derivatives i.e. BPTS and

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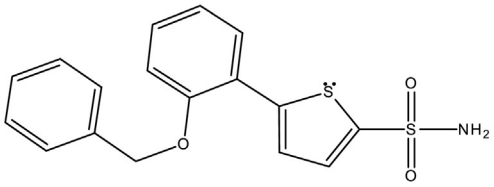
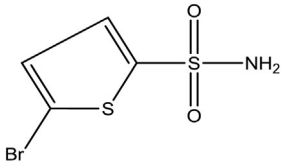
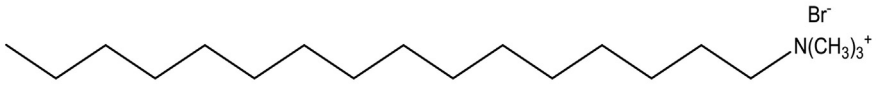


5-(2-(benzyloxy)phenyl)thiophene-2-sulfonamide (BPTS)



5-bromothiophene-2-sulfonamide (BTS)



Cetyl trimethyl ammonium bromide (CTAB)

Fig. 1. Structures of chemicals used.

BTS between solvent and micellar media of CTAB, a cationic surfactant. Fig. 1 shows structures of chemicals being used in study while resonance structures of both thiophene derivatives are given in Schemes 1 and 2.

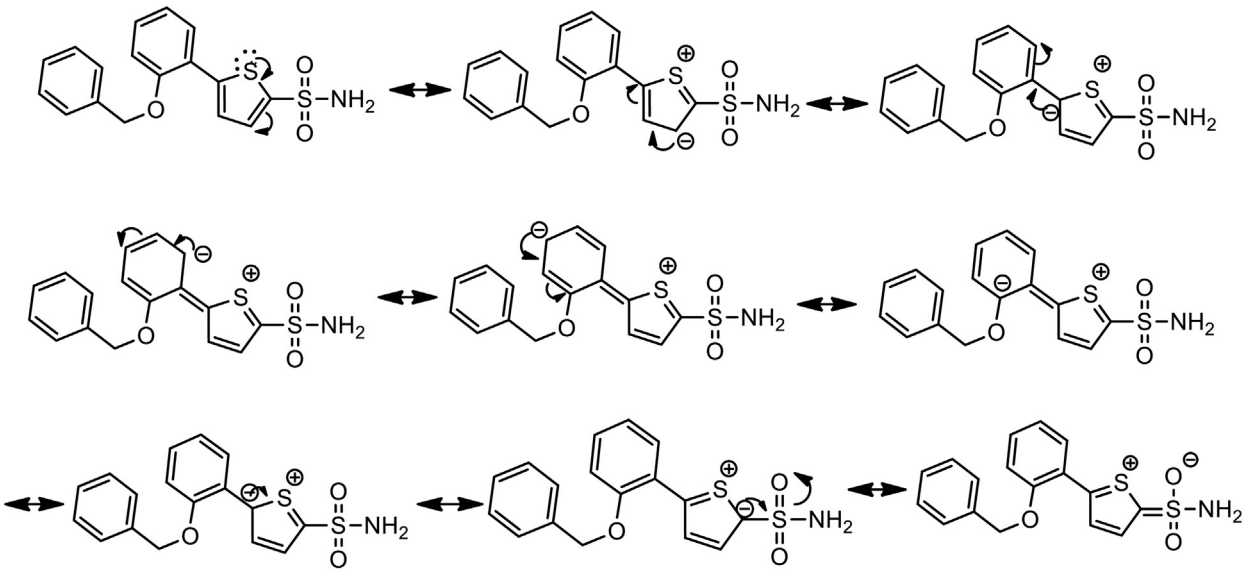
2. Parameters calculated

2.1. Partition and binding parameters

The molecules of Thiophene derivatives (i.e. BTS and BPTS) partition themselves between solvent and micellar media. Partition coefficient is the quantitative measure of degree of solubilization and we have employed differential absorbance method to calculate partition coefficient using Kawamura equation [15].

$$\frac{1}{\Delta A} = \frac{1}{K_c \Delta A_\infty \left(C_a + C_s^{mo}\right)} + \frac{1}{\Delta A_\infty} \tag{1}$$

In Eq.uation (1), C_a is concentration of additive (BPTS and BTS) in $mol \cdot dm^{-3}$ and C_s^{mo} denotes analytical concentration of surfactant (CTAB) after micellization calculated by subtracting cmc of CTAB from its experimental concentration [16]. ΔA and ΔA_∞ represent value of differential absorbance at experimental and infinite concentration of CTAB respectively. K_c is partition constant in unit of dm^3 per mol. K_c is



Scheme 1. Resonance structures of BPTS.