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Partitioning of structurally related thiophene derivatives between solvent and micellar media of anionic surfactant sodium dodecyl sulphate

Rizwan Saeed[a], Muhammad Usman[a,*], Asim Mansha[a], Nasir Rasool[a], Syed Ali Raza Naqvi[a], Ameer Fawad Zahoor[a], Hafiz Muhammad Abdur Rahman[b], Usman Ali Rana[c], Eman Al-Zahrani[d]

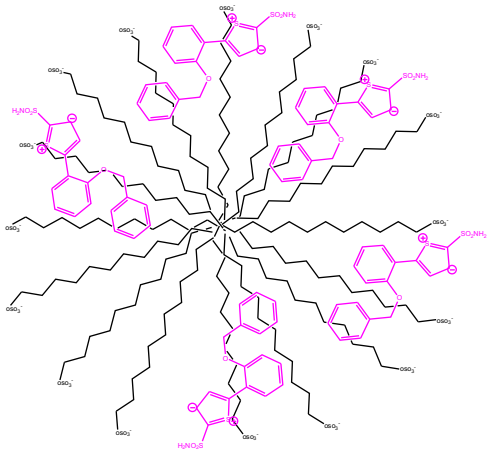
[a] Department of Chemistry, Government College University, Faisalabad 38000, Pakistan
[b] Department of Chemistry, Forman Christian College, Lahore 54600, Pakistan
[c] Sustainable Energy Technologies Center, College of Engineering, PO-Box 800, King Saud University, Riyadh 11421, Saudi Arabia
[d] Chemistry Department, Faculty of Science, Taif University, 888 Taif, Saudi Arabia

HIGHLIGHTS

- SDS causes shift in spectra of BPTS and BTS.
- BTS has greater degree of binging and partition with SDS than BPTS.
- Electrostatic and hydrophobic forces favour partitioning.

GRAPHICAL ABSTRACT

The study reveals that the bulky substituents and extensive delocalization from conjugated aromatic groups can have negative influence on the solubilization of thiophene derivatives by micellar solution of anionic surfactant, Sodium dodecyl sulphate (SDS).



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ABSTRACT

The present study describes the detailed investigations of the solubilization of thiophene derivatives i.e. 5-(2-(benzyloxy) phenyl) thiophene-2-sulfonamide (BPTS) and 5-bromothiophene-2-sulfonamide (BTS) by micellar solution of anionic surfactant, Sodium dodecyl sulphate (SDS). The interaction of SDS in the solution containing aforementioned compounds was investigated by electrical conductivity and UV–vis spectroscopy. The data of electrical conductivity was used to calculate thermodynamic parameters like free energy (ΔG_m), enthalpy (ΔH_m) and entropy (ΔS_m) of micellization of SDS in the presence of thiophenes, whereas UV–vis spectroscopy was used to calculate the extent of solubilization in term of partition coefficient (K_x), free energy of partition (ΔG_p), binding constant (K_b) and free energy of binding

* Corresponding author.
E-mail addresses: usm_ca@yahoo.com, usmche@gmail.com (M. Usman).

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Partitioning
Spectroscopy
Micelle
Partition coefficient

(ΔG_b). The experimental results from thermodynamic parameters reveal that the solubilization of said thiophene derivatives was spontaneous, in addition to enthalpy and entropy driven. The large molecular size, aromatic nature with extensive delocalization and less charge density of BPTS was found to have a negative impact on solubilization of this compound, which was observed from poor binding capacity and inadequate partitioning displayed by this compound.

1. Introduction

Unique structure of amphiphilic compounds enables their molecules to adsorb at air-solution interface and to form self-aggregates, called micelles, above critical micelle concentration (CMC). The heterogeneous structure of micelles containing hydrophilic surface and hydrophobic core enable them to mimic biomembranes [1,2]. The micelles can, thus, interact with both hydrophilic and hydrophobic compounds, making them useful materials for both lab-scale and industrial applications. It has been reported that the physicochemical properties of organic compounds change due to interactions with surfactants and these changes can be quantified by measuring the binding constant "K_b", partition coefficient "K_x" and thermodynamic parameters. Calculations of aforementioned parameters are important not only to understand the interactions of drugs with bio membranes but also to establish structure activity relationship [3].

Self-aggregation is not limited to surfactants but some non-amphiphilic organic compounds also undergo this process due to non-covalent forces between their molecules which causes shift in their absorption maxima (λ_{max}). Aggregates exhibiting red and blue shifts are called "J" and "H" aggregates, respectively. "J" type aggregates are formed due to end-to-end stacking, while the formation of "H" type aggregates occur due to plane-to-plane stacking. For "J" type aggregates, tilt angle, "α" (angle between line of centers in aggregates and long angle of individual molecules is less than 32°, while tilt angle is greater than this value and, sometimes, approaches to 90° in case of "H" type aggregates [4].

Micelles are very important drug carriers as they not only enhance solubility of less soluble compounds but also control release rate, minimize degradation of drug and reduce its toxicity level [5]. Ion-dipole interactions between polar solutes and micellar surface, having high charge density, cause electrostatic interactions between the two species while hydrophobic core of micelle attracts nonpolar moeties of solutes. Locus of solute within micelle, although, mainly depends on hydrophobic effects but hydrophilic and electrostatic effects are not too insignificant to be ignored [6]. Surface tension, fluorescence, electrical conductivity and UV–vis spectroscopy are very important techniques to study micelle formation as they are useful for determination of CMC [7].

Thiophene is a heterocyclic aromatic compound consisting of 5-membered ring. It is among the most studied heterocyclic compounds due to chemically stability, easy synthesis and easy processing. Thiophene based compounds have received a huge interest from research community due to their importance for drug design, electronic devices, biodiagnostics and sensory devices. Oligomers and polymers of thiophenes are under investigation because they have semiconductor, luminescence and sensory properties [8].

In past, we have reported the solubilization of Chloroquine Diphosphate [9], Quinacrine 2HCl [10], Pefloxacin mesylate [11] and benzothiozole [12] in micellar media. In the present study, we intend to study the influence of molecular structure of two thiophenes i.e. BPTS and BTS, on their solubilization in micellar solution of anionic surfactant, SDS. Fig. 1 shows the structures of chemical compounds used in the present study, while the Schemes 1 and 2 indicate resonance structures of BPTS and BTS, respectively.

2. Parameters calculated

2.1. Thermodynamic parameters

Following expression helps to calculate free energy of micellization (ΔG_m) for SDS in the presence of thiophenes;

$$\Delta G_m = (2-\beta)RT\ln X_{CMC} \quad (1)$$

In Eq. (1), "β" is the degree of dissociation that can be calculated from the ratio of the slopes of conductivity versus concentration plot in post and pre-micellar regions. "R" is the general gas constant, "T" is the absolute temperature; X_{CMC} is critical micelle concentration in terms of mole fraction.

$$\beta = \frac{S_2}{S_1} \quad (2)$$

In Eq. (2), S_1 and S_2 represent the slopes of the straight lines in the pre micellar and post micellar region, respectively.

Eqs. (3) and (4) were employed to calculate the enthalpy (ΔH_m) and entropy (ΔS_m) of micellization for SDS-thiophene system, respectively [8–13].

$$\Delta H_m = -2.3(2-\beta)RT^2\left[\frac{\partial(\log X_{cmc})}{\partial T}\right]_P \quad (3)$$

$$\Delta S_m = \frac{\Delta H_m - \Delta G_m}{T} \quad (4)$$

2.2. Calculation of partition and binding parameters

The molecules of additives *viz.* BTS and BPTS partitioned themselves between solvent and micellar media. The differential absorbance method was used to explore the degree of solubilization in term of partition coefficient, as reported by Kawamura et al. [14].

$$\frac{1}{\Delta A} = \frac{1}{K_c \Delta A_\infty (C_a + C_s^{mo})} + \frac{1}{\Delta A_\infty} \quad (5)$$

In Eq. (5), C_a is the concentration of additive (BPTS or BTS) in mol.dm^{-3} and $C_s{}^{mo}$ is analytical concentration of SDS after it underwent micellization, calculated as $C_s - CMC_o$. Here, CMC_o is the CMC of SDS in absence of additives and C_s is the total surfactant concentration in mol dm^{-3} [12]. ΔA is differential absorbance and ΔA_∞ represents its value at infinite concentration of SDS. K_c is partition constant having value in dm^{3}mol^{-1}. The dimensionless quantity partition coefficient, K_x is obtained as $K_x = K_c n_w$, where n_w accounts for the number of moles of water per dm^3.

The value of free energy change for the transfer of additive from solvent to micellar phase was calculated using the following relation;

$$\Delta G_p = -RT\ln K_x \quad (6)$$