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# Influence of iso-perthiocyanic acid and temperature on the aggregation properties of sodium dodecylsulphate in dimethylsulphoxide

S. Chauhan [a,*], Santosh Kumari [a], Kuldeep Kumar [a], Ahmad Umar [b,*], C.N. Sundaresan [c], R. Gupta [d]

[a] Department of Chemistry, Himachal Pradesh University, Summer Hill, Shimla 171005, India
[b] Department of Chemistry, Faculty of Science and Arts and Promising Centre for Sensors and Electronic Devices (PCSED) Najran University, P.O. Box 1988, Najran 11001, Saudi Arabia
[c] Department of Chemistry, Sri Sathya Sai Institute of Higher Learning, Brindavan Campus, Bangalore 560067, India
[d] Department of Bio-technology, Himachal Pradesh University, Summer Hill, Shimla 171005, India

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ABSTRACT

This paper investigates the effect of a heterocyclic compound, iso-perthiocyanic acid (IPA) (0.01, 0.05, and 0.10 mol·kg$^{-1}$) on the micellization behavior of sodium dodecylsulphate (SDS) (1–52 mmol·kg$^{-1}$) in dimethylsulphoxide (DMSO) by employing three conventional techniques viz. conductivity, density, and speed of sound measurements over a wide temperature range (293.15–313.15 K). From all the techniques, the critical micelle concentration (*CMC*) values have been determined, and the results have been discussed in terms of SDS-IPA solvophobic and hydrogen bonding interactions in DMSO. The temperature dependence of the *CMC* values has proved the dominance of disruption of structured DMSO molecules around the alkyl chain of SDS. Further, the $X_{CMC}$ values have been used to calculate the standard thermodynamic parameters of micellization like enthalpy ($\Delta H_m^o$), free energy ($\Delta G_m^o$), and entropy ($\Delta S_m^o$). The density and speed of sound data have been used to evaluate the volumetric and compressibility parameters like apparent molar volume ($\phi_v$), isentropic compressibility ($K_s$), and apparent molar isentropic compression ($\phi_\kappa$) to get more clear insight with regards to solute–solute / solute–solvent interactions existing in the present SDS–IPA–DMSO ternary system. In addition, an attempt has also been made to examine the antifungal activity of IPA in combination with SDS in aqueous medium.



## 1. Introduction

A large number of heterocyclic compounds such as derivatized form of azines, purines, pyrimidines, thiazoles, and oxazoles with various biological activities have witnessed great boom in the field of medicinal chemistry in the recent past [1–4]. Among these, thiazoles containing nitrogen as well as sulfur atom in the same ring are well known for their therapeutical, antibacterial, antifungal, and herbicidal activities [5,6]. Moreover, the dithiazoles have been considered to be the decisive compounds in peculiar arenas by virtue of their unusual physical properties, biological activities, and versatile chemistry [7]. The iso-perthiocyanic acid (3-amino-5-thione-1,2,4-dithiazole) or xanthane hydride belongs to class of 1,2,4-dithiazoles and exists as a pale yellow crystalline solid (Fig. 1). It has been first isolated by Wohler [8] in 1821 and believed to have pest controlling properties [9].

Surfactants, on the other hand, undergo the process of micellization and are therefore, used diversely in pharmaceutics, cosmetics, biology, food, and various life systems [10]. The additives have significantly influenced the micellar properties of surfactants [11], consequently, the investigations on the aggregation properties of surfactants by using different techniques in the absence and presence of the additives have fascinated the researchers in different fields [12–15]. In this context, probably sodium dodecylsulphate–additive systems have been investigated extensively specially in aqueous medium [16–18]. However, fewer studies have been reported in non-aqueous medium like dimethylsulphoxide [19,20]. Recently, Ali et al. [21] have performed experiments on SDS–lauric acid system in DMSO and concluded that solvophobic interactions have played a significant role in the micellization of SDS–lauric acid system.

Also, the physico-chemical properties of a given surfactant solution can be partially changed by varying the solvent properties which ultimately extend their use in the fields of poor water environments such as lubrication [21]. This can be done by using pure solvents of different polarity, mixed solvents containing either mixtures of water and non-aqueous solvent or mixtures of two non-aqueous solvents [22]. In addition, DMSO being a protophilic dipolar aprotic solvent (Fig. 1), is capable of dissolving both polar and non-polar solutes and has been used in broad range of pharmaceutics [23]. Further, both SDS and IPA contain polar and non-polar parts in their structure (Fig. 1) which

* Corresponding authors.
*E-mail addresses:* chauhansuvarcha@rediffmail.com (S. Chauhan), Ahmadumar786@gmail.com (A. Umar).

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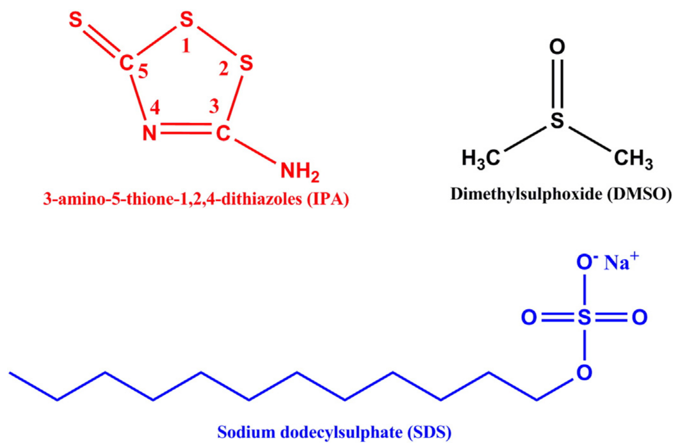


**Fig. 1.** Chemical structures of IPA, DMSO, and SDS.

makes them available for extensive industrial and pharmaceutical applications.

Therefore, the study of mixed surfactant aggregation processes in non-aqueous medium needs more attention which has led us to undertake the present study of SDS–IPA mixed micelles in non-aqueous medium (DMSO). The antifungal activities of IPA have also been demonstrated in aqueous medium in the presence of SDS.

## 2. Experimental details

### 2.1. Material

Dimethylsulphoxide of AR grade (99%) has been supplied by s.d. fine chem. Ltd (India) and used without further purification for all the experiments. Sodium dodecylsulphate of AR grade (99%) has been obtained from Himedia Pvt. Ltd. (India) and recrystallized from ethanol as cited in literature [16]. The heterocyclic compound iso-perthiocyanic acid (Mol. Wt. = 0.1502 kg·mol$^{-1}$) in its pure form (95%) has been provided by Dr. C.N. Sundaresan, Department of Chemistry, Sri Sathya Sai Institute of Higher Learning, Brindavan Campus, Bangalore (India) and has been used as such without further treatment.

### 2.2. Methods

Stock solutions of IPA (0.01, 0.05, and 0.10 mol·kg$^{-1}$) have been prepared in DMSO and used as solvent for the preparation of different SDS concentrations (1–52) mmol·kg$^{-1}$. All solutions have been prepared by using Shimadzu balance with a precision of ± 0.0001 g. Conductivity measurements have been carried out with digital Conductivity Meter Cyberscan CON-510, whose working principle and procedure has already been explained in our previous study [24]. The conductivity cell was calibrated with 0.01 mol.dm$^{-3}$ KCl sample solution supplied by Merck Chem. The temperature has been maintained constant at ± 0.1 K by circulating thermostated water through double walled conductivity vessel containing the solution. The reproducibility of conductivity measurements was estimated to be ± 15 μS·cm$^{-1}$.

The density and speed of sound values of SDS solutions in absence and presence of IPA have been measured simultaneously using Anton Paar DSA-5000 instrument. The working principle and calibration procedure of DSA-5000 instrument has already been reported elsewhere [25]. The uncertainty in density and speed of sound measurements is $\pm 2 \times 10^{-6}$ g·cm$^{-3}$ and ±0.2 m·s$^{-1}$, respectively.

For antifungal activities, IPA (10–90 mg/50 ml) has been added to different flasks containing 50 ml of nutrient Potato Dextrose Broth (PDB) in distilled water (conductivity 2–3 μ S·cm$^{-1}$ and pH 6.8–7.0 at T = 298.15 K). Each flask has been autoclaved before addition of fungus, Aspergillus Fumigatus and then incubation of the flasks has been carried out at 303.15 K with rotational speed of 150 RPM for 72 h in order to ensure the visible growth of the fungus. The minimum inhibitory concentration (MIC) has been decided by observing the growth of fungus in all the flasks containing different concentrations of IPA. The MIC of SDS (14.0–144 mg/50 ml) and IPA in presence of SDS (0.7 and 1.4 mg/50 ml) has been calculated by employing similar procedure as mentioned above.

## 3. Results and discussion

### 3.1. Conductivity measurements

The conductivity, $\kappa$, values for SDS in pure DMSO and DMSO containing IPA (0.01, 0.05, and 0.10 mol·kg$^{-1}$) at 293.15, 298.15, 303.15, 308.15, and 313.15 K have been summarized in Table SM I of supplementary material. Fig. 2 illustrates that the $\kappa$ values vary linearly with concentration of SDS in both pre- and post-micellar regions. The intersection point between the two straight lines gives the critical micelle concentration (*CMC*) values of SDS and are included in Table 1. The *CMC* values have also been determined from density and speed of sound values as shown in Fig. 2 and are found in good compliance with those determined from conductivity measurements (Table 1). However, the small difference in *CMC* values determined by three different methods may be attributed to the fact that process of micellization occurs in a stepwise manner, therefore, *CMC* extends across a narrow range of concentration [26,27]. The *CMC* values of SDS in DMSO at 308.15 and 313.15 K are in close agreement with the values reported in literature [19] (Table 1).

The temperature dependence of *CMC* values of SDS has been presented in Fig. 3, which clearly illustrates that the *CMC* values of SDS shows increase with rise in temperature at all studied concentrations of IPA. This type of behavior is a characteristic feature of most ionic and several non-ionic surfactants above ≈298.15 K as elicited in literature [28–30]. The increase or decrease in the *CMC* values with temperature can be explained on the basis of following two opposing outcomes:

i) The de-solvation of the ionic head groups of SDS/IPA by DMSO molecules at lower temperatures, which favors the micellization and decreases the *CMC* values.
ii) The disruption of the structured DMSO molecules surrounding the non-polar parts of SDS/IPA and the breaking up of the hydrogen bonds (>S=O·····H–N<) between DMSO and IPA at higher temperatures, which disfavors the micellization, and therefore, increases the *CMC* values.

Thus the observed increase in *CMC* values of SDS with temperature indicates that the outcome (ii) dominant over the outcome (i) for the present SDS–IPA–DMSO system. Further, it can be seen from Table 2 that the *CMC* values of SDS in DMSO + IPA are smaller than in pure DMSO and decrease with IPA concentration in DMSO. This decrease can be interpreted in terms of solvophobic and hydrogen bonding interactions of IPA with SDS and DMSO molecules. Actually, IPA seems to play a dual role, on one hand, it is reinforcing the structured DMSO molecules around the alkyl chains of SDS through hydrogen bonding (>S=O·····H–N<) with DMSO molecules, pointing the non-polar part towards the alkyl chains of SDS. On the other hand, the addition of IPA molecules decreases the electrostatic repulsive interactions between polar head groups of SDS molecules due to formation of hydrogen bonds between $H_2N$– groups of IPA and anions of SDS molecules [21, 34]. All this favors the micellization of SDS molecules and, therefore, a pronounced decrease in the *CMC* values has been observed in the presence of IPA than in its absence (Table 1). Another factor, which strongly favors the micellization of SDS in the presence of IPA and decreases the *CMC* values, are the solvophobic interactions between the alkyl chains of