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Refractive index, conductometric, and fluorescence probe study on interaction of valine with aqueous solution of anionic surfactant, sodium dodecyl surfactant (SDS), at 298.15, 303.15, 308.15 and 313.15 K

Alok Gupta <sup>1,\*</sup> and Anju Singh <sup>2</sup>

<sup>1</sup> Department of Chemistry (IET), Bundelkhand University Campus, Jhansi, India. <sup>2</sup> Department of Chemistry, Institute of Basic Science, Bundelkhand University, Jhansi, India.

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# Abstract

Interactions between amino acid (valine) and surfactant (sodium dodecyl sulphate) was investigated using refractive index and conductance data. These data were used to calculate molar refraction (RD), and limiting molar conductance

 $(\Lambda_m^0)$  and these parameter further utilized to find out solute-solvent interactions between amino acid and surfactant at 298.15, 303.15, 308.15 and 313.15 K temperatures. Also fluorescence measurements using pyrene as a photophysical probe have also been carried out for the present amino acid-surfactant systems.

Keywords: Amino acids; Surfactants; Refractive index; Conductometric; Fluorescence and solute-solvent interaction

# 1. Introduction

The studies of interactions of proteins with amphiphilic molecules are of vast importance, not only in vivo but also in technical applications [1, 2]. However, due to the complex conformational and configurational three-dimensional structures of proteins, direct investigations of solute/solvent effect on these biological macromolecules are quite difficult [3]. It is, therefore, more convenient to study the physicochemical properties of the building blocks of proteins, i. e., amino acids, in aqueous medium [4, 5]. Studies on the interaction of amino acids with surfactants can contribute towards an understanding of the surfactants as tools to isolate, solubilize, and manipulate membrane proteins for subsequent biochemical and physical characterization [6-8]. Surfactant are the substance which decrease the surface tension of liquids [9-13] and they are used in many biological, agricultural and chemical processes [14-18]. It has been reported that SDS acts as a more potent protein denaturant than urea and guanidine hydrochloride [19]. It is worth to mention that refractive index, conductometric and fluorescence studies can be used to find out solute-solvent interaction between amino acid (valine) and surfactant (SDS), which will be useful for biotechnological and chemical industry. Moreover, refractive index studies of amino acids in aqueous surfactants can provide valuable clues for understanding the protein unfolding [20] and about the hydrophobic interactions of non-polar side chains [3]. Fluorescence measurements using pyrene as a photophysical probe have also been carried out for the present amino acid-surfactant systems. The ratio of the first over the third vibrational peak  $(I_1/I_3)$  of pyrene fluorescence has been measured which is very sensitive to the polarity of the probe microenvironment [21]. Taking these in consideration in the present paper we have reported the refractive index, conductometric and fluorescence studies of (0.015, 0.035, 0.055 and 0.075 m) in 0.02 m aqueous SDS at 298.15, 303.15, 308.15 and 313.15 K.

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<sup>\*</sup> Corresponding author: Alok Gupta

## 2. Material and method

The amino acid valine (Loba Chemie, Purity > 99%) and sodium dodecyl sulphate (Central Drug House, CDH, Pvt limited, Purity 99%) were dried over  $P_2O_5$  in vacuum desiccator before use. First stock solution of 0.02 m SDS was prepared in double distilled water and was used as a solvent to prepare (0.015, 0.035, 0.055 and 0.075 m) solutions of the amino acid. The weightings were done on an electronic balance (Precisa XB-220A, Swiss make) with a precision of ±0.1m g. The refractive indices of the solutions were measured by using a thermostated Abbe refractometer. The refractometer was calibrated by measuring the refractive indices of double distilled water and toluene at the desired temperatures. The values of refractive index were obtained for sodium D light. The reproducibility of refractive index measurements was within ±0.0001. Conductance were measured with a (Control Dynamics, India) conductivity bridge having a cell constant 1.02. Pyrene fluorescence measurements were carried out using a Fluorolog-3 modular spectrofluorometer (model FL 3-11) with single Czerny–Turner grating excitation and emission monochromators having 450 W Xe arc lamp as the excitation source and PMT as the detector (Horiba Jobin Yvon). The pyrene concentration was fixed at  $1.0 \times 10^{-6}$ M, and the fluorophore was excited at a wavelength of 337 nm. The excitation slit width was 2.0 nm, while the emission slit was maintained at a width of 1.0 nm. The emission spectrum was scanned over the range 360–460 nm. The temperature of the test solution during the measurements was maintained to an accuracy of ±0.02 K in an electronically controlled thermostated water bath (JULABO, Model-MD, Germany).

### 3. Results and discussion

#### 3.1. Refractive index study

A number of workers [22-30] have measured refractive index of liquids and liquids solutions using Abbe Refractometer. When a ray of light passes from one medium to another, it suffers refraction, that is, change of direction. The experimental values of refractive indices presented in Table 1 show an increasing trend with increasing concentration of valine in the mixtures. This indicates that the refractive index is directly related to the interactions present in the solutions. Similar view has also been proposed by Soto et al. [31]. For mixtures of interacting components, the molar refractivity of each component is given by the equation:

$$R_D = 4\pi\alpha N_A$$

where  $\alpha$  is the molecular polarizability. The refractive index data was used to calculate the molar refraction  $R_{D}$ , by using the Lorentz-Lorenz equation

$$R_{D} = \left[\frac{\left(n_{D}^{2}-1\right)}{\left(n_{D}^{2}+2\right)}\right] \left(\sum_{i=1}^{3} \frac{x_{i}M_{i}}{\rho}\right)$$

where  $x_i$  is the mole fraction and  $M_i$  is the molar mass of the i<sup>th</sup> component of the solution. The values of  $R_D$  vs valine concentration at different temperatures for the studied system is given in table 2. It is evident from table 2 that  $R_D$ increases linearly with increasing amount of valine in the given system. As  $R_D$  is directly proportional to the molecular polarizability, table 2 reveals that overall polarizability of the system under study increases with increasing amount of valine in the solutions. No significant effect of temperature has been observed on the  $R_D$  values of the studied systems.

#### 3.2. Conductometric study

The values of specific conductivities,  $\kappa$ , of valine at temperature 298.15, 303.15, 308.15, and 313.15 K is given in table 1. The limiting molar conductance,  $\Lambda_m^0$ , m for valine in aqueous surfactant solution was obtained by extrapolating the linear plots of molar conductance,  $\Lambda m$  vs m1/2 to zero concentration. The  $\Lambda_m^0$  values for valine in aqueous surfactant solution at different temperatures is recorded in Table 2. The  $\Lambda_m^0$  has been regarded as a measure of valine – surfactant/water interactions [32-36]; the greater the magnitude of  $\Lambda_m^0$ , the greater is the interaction. The large and

positive values of limiting molar conductance of valine in aqueous SDS solution and an increasing trend of  $\Lambda_m^0$  with increase in temperature, show that valine –surfactant/water interactions are stronger and increase with rise in temperature which supports results from refractive index values.

# 3.3. Fluorescence study

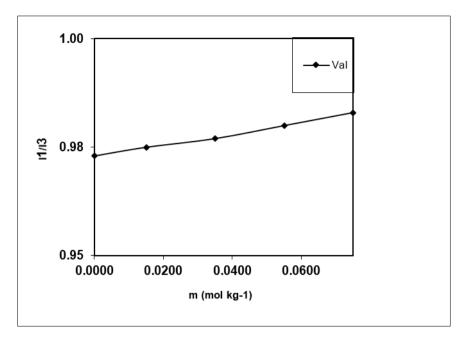
The ratio between the intensities of the first and the third of the major vibrational peaks in pyrene's fluorescence spectrum is quite sensitive to the probe microenvironment. As pyrene is hydrophobic in nature, the onset of micelle formation has been shown by a sudden decrease in the  $I_1/I_3$  ratio, if a surfactant is added to aqueous solutions containing pyrene, due to the strong distribution of pyrene into micelles [37]. As the solution in our study is micellar, the  $I_1/I_3$  ratio is already much lower than in water (Fig. 1). It can be seen that the  $I_1/I_3$  ratio is not affected much by increasing the concentration of valine in aqueous surfactant solution. This behavior can be supported by the results reported earlier [38] that the addition of valine does not affect considerably the micellization of ionic surfactants. Furthermore, this behavior can be attributed to the contribution of solvophobic interactions.

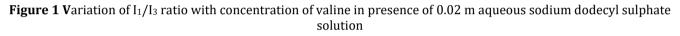
**Table 1** Values of refractive index,  $n_D$ , and specific conductivity, $\kappa$ , of valine in aqueous surfactant solutions at T=298.15, 303.15, 308.15, and 313.15 K

m/(mol.kg <sup>-1</sup> )	298.15 K	303.15 K	308.15 K	313.15 K		
nD						
0.000	1.3320	1.3318	1.3310	1.3307		
0.015	1.3322	1.3319	1.3312	1.3308		
0.035	1.3327	1.3322	1.3316	1.3311		
0.055	1.3331	1.3325	1.3320	1.3316		
0.075	1.3334	1.3328	1.3325	1.3319		
ĸ						
0.000	0.363	0.407	0.454	0.505		
0.015	0.296	0.326	0.356	0.376		
0.035	0.377	0.407	0.453	0.505		
0.055	0.364	0.428	0.488	0.558		
0.075	0.329	0.399	0.459	0.509		

**Table 2** The values of molar refraction (RD), and limiting molar conductance  $(\Lambda_m^0)$  for value in aqueous surfactant solutions at T=298.15, 303.15, 308.15, and 313.15 K

m/(mol.kg <sup>-1</sup> )	298.15 K	303.15 K	308.15 K	313.15 K		
10 <sup>6</sup> . R <sub>D</sub> / (m <sup>3</sup> .mol <sup>-1</sup> )						
0.000	3.9213	3.9040	3.8913	3.8829		
0.015	4.2394	3.5240	3.6728	3.5466		
0.035	4.2551	3.6343	3.7378	3.6538		
0.055	4.2762	3.8532	3.8010	3.6761		
0.075	4.3579	3.9961	3.9188	3.7099		
$\Lambda_{\rm m}^0$ /(Scm <sup>2</sup> mol <sup>-1</sup> )						
	24.45	26.20	28.28	29.92		





# 4. Conclusion

In the system of amino and surfactants the refractive index values increases linearly with increasing amount of amino acids, it means that molecular polarizability is also increasing with increase in amount of amino acids. The highly positive values of limiting molar conductance of valine in aqueous surfactant solution increases with rise in temperature showing strong valine –surfactant/water interactions and this value increases with rise in temperature.

## **Compliance with ethical standards**

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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