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Paper Authors
Y. Triveni, B.B.V. Sailaja, S. Pratima kumari, V. Nagalakshmi

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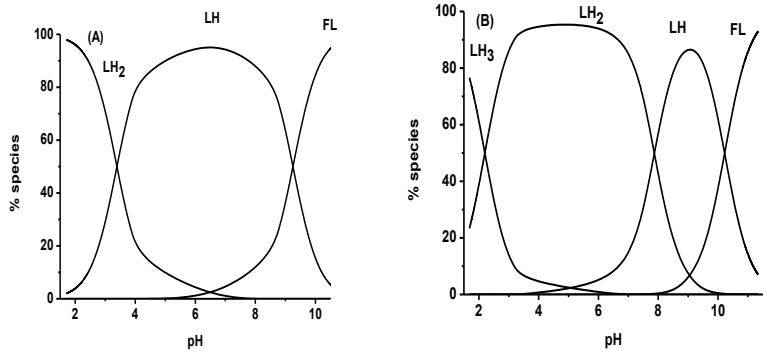
Effect of anionic micelles of sodium dodecyl sulphate on protonation equilibria of L-Methionine and L-Cysteine

Y. Triveni[1], B.B.V. Sailaja[2*]S. Pratima kumari[3], V. Nagalakshmi[4]
[1,2]School of Chemistry, Andhra University, Visakhapatnam-530003, **INDIA**
[3,4]Ch.S.D.St.Theresa's College, Eluru, W.G.Dt, A.P

Abstract:

Solute–solvent interactions of L-methionine and L-cysteine are studied in sodium dodecyl sulfate–water mixtures (0.5–2.5% w/v) at 303.0 ± 0.1 K at an ionic strength of 0.16 M using a pH-metric technique. The protonation constants were estimated with the computer program MINIQUAD75. Selection of the best fit chemical model of the protonation equilibria is based on the standard deviation in protonation constants and residual analysis using a sum of squares of residuals in all mass-balance equations. The effect of solvent on protonation constants is discussed based on electrostatic and non-electrostatic forces operating on the protonation equilibria. The distribution of species, protonation equilibria and effects of influential parameters on the protonation constants are also presented.



Species distribution diagrams of (A) Met and (B) Cys in 1.5% w/v SLS- water mixture

Keywords: sodium dodecylsulfate, protonation constant, MINIQUAD75, L-methionine, L-cysteine

AIMS AND BACKGROUND

The protonation equilibria of various bio-ligands in surfactant medium are popular in recent years [1–4]. Protonation constants of L-Methionine and L-Cysteine and were determined in other micellar media [5] recently. The present study is an attempt to examine the effect of anionic micelle on the protonation constants of L-Methionine and L-Cysteine. Surfactant is widely used in our life and work. Its basic and application studies in surface chemistry and organic chemistry are always very active, for example, in the interaction with dyes [6, 7, 8–10]. Understanding the interaction of surfactants with organic and inorganic compounds is helpful to investigate the synergistic mechanism of surfactants, like in separation, trace analysis and washing.

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1.Introduction

Sodium dodecyl sulphate: Sodium dodecyl sulfate (SDS), synonymously sodium lauryl sulfate (SLS), or sodium lauril sulfate, is a synthetic organic compound which is an anionic surfactant. It is the family of organosulfate compounds and has the formula, $CH_3(CH_2)_{11}SO_4Na$. It consists of a 12-carbon tail attached to a sulfate group, it is the sodium salt of a 12-carbon alcohol that has been esterified to sulphuric acid. It is an alkyl group with a pendant terminal sulfate group attached. As a result of its hydrocarbon tail and its anionic head group, it has amphiphilic properties that allow it to form micelles and so act as a detergent. It is used as an emulsifying agent and whipping aid. It is commonly used as a component for lysing cells during RNA extraction and/or DNA extraction and for denaturing proteins in preparation for electrophoresis in the SDS-PAGE technique. It is synthesized by reacting lauryl alcohol from a petroleum or plant source with sulphur trioxide to produce hydrogen lauryl sulfate, which is then neutralized with sodium carbonate to produce SLS. It is potentially effective topical microbicide, for intravaginal use, to inhibit and possibly prevent infection by various enveloped and non-enveloped viruses such as the herpes simplex viruses, HIV, and the Semliki Forest virus [11]. The toxicity of SLS depends largely on the marine species, water hardness, and water temperature [12, 13, 14].

Methionine (Met) is an essential amino acid which cannot be produced by the body, must be provided by the diet which is found in meat, fish, and dairy products, and plays an important role in many cell functions. It supplies sulphur and other compounds required by the body for normal metabolism and growth. It is the initiating amino acid in the synthesis of eukaryotic proteins; *N*-formyl methionine serves the same function in prokaryotes. It is used to prevent liver damage in acetaminophen (Tylenol) poisoning. It is also used for increasing the acidity of urine, treating liver disorders, and improving wound healing. Cerebrospinal fluid levels of Met, homocysteine and cystathionine were studied in patients with psychotic disorders [15]. Met is synthesized from cysteine and *o*-phosphohomoserine involving three enzymes, cystathionine synthase, cystathionine*β*-lyaseand methionine synthase [16].

Cysteine (Cys) is a sulphur-containing amino acid in humans, which is important for protein synthesis, detoxification, and diverse metabolic functions. It is widely applied in many fields, like food additives, pharmaceutical industry, feed stuff and cosmetic additives. Currently, four manufacturing methods have been developed to produce L-cysteine. These are acid or alkali hydrolysis of hair, chemical synthesis, microbe fermentation [17] and bioconversion of 2-amino-thiazoline-4-carboxylic acid (DL-ATC)[18]. Bioconversion of DL-ATC by whole-cell biocatalyst, a competent method with advantages of low energy requirement and high molar yield, has being substituted for acid or alkali hydrolysis of hair as a main method for the production of L-cysteine on industrial scale[19]. It is often involved in electron-transfer reactions, and helps the enzyme catalyze its reaction. The sulfhydryl group has a high affinity for heavy metals, so that proteins containing cysteine, such as metallothionein, will bind metals such as mercury, lead and cadmium tightly [20]. Due to this it has the ability to undergo redox reactions, hence cysteine has antioxidant properties

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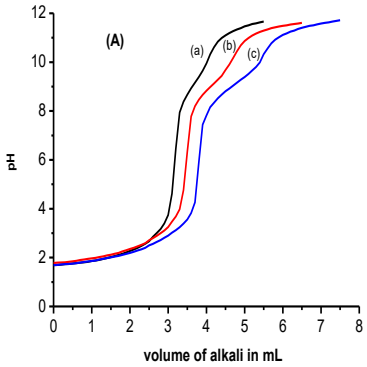
2. CHEMICALS AND PROCEDURE

2.1 Reagents: 0.05 mol L^{-1} solutions of L-Methionine (Met) and L-Cysteine (Cys) (Himedia, India) was prepared in triple distilled water by maintaining 0.05 mol L^{-1} acid (HCl) concentration to increase the solubility. SDS (Himedia, India) was used as received. To maintain the ionic strength in the titrant, Sodium chloride (Merck) of 2 mol L^{-1} was prepared. Solutions of 0.4 mol L^{-1} Sodium hydroxide and 0.2 mol L^{-1} HCl were also prepared and were standardized by standard methods.

The titrimetric data were obtained by using calibrated ELICO (Model LI-120) pH-meter (readability 0.01). The glass electrode was equilibrated in a well stirred solvent solution containing inert electrolyte. The effects of variations in asymmetry, liquid junction potential, activity coefficient, sodium ion error and dissolved carbon dioxide on the response of glass electrode were accounted for in the form of correction factor [**21**]. For the determination of protonation constants of L-Methionine and L-Cysteine, initially titrations of strong acid with alkali were carried out at regular intervals to check whether complete equilibration was achieved. Then the calomel electrode was refilled with solvent solution of equivalent composition as that of the titrand. The titrations were carried out in media containing varying amounts of surfactants maintaining an ionic strength of 0.16 mol dm^{-3} with NaCl at 303K. In these titrations, the titrand consisted of mineral acid and ligand, in the presence and absence of metal ion, in a total volume of 50 cm^3. Titrations were performed by adding each time 0.1cm^3 portions of sodium hydroxide (0.4 mol dm^{-3}) to the titrand. The pH meter reading was recorded only after a constant value was displayed. Typical duplicate titrations showed that equilibration is fast and titration data do not differ by more than 0.02 units.

2.2Alkalimetric titration assembly: The titrations with alkali were performed in media having different compositions of SDS-water (0.5–2.5% w/v) keeping an ionic strength of 0.16 mol L^{-1} with sodium chloride at 303.00 ± 0.05 K using an Elico LI-120 pH meter. The pH meter is calibrated with Potassium hydrogen phthalate (0.05 mol L^{-1}) and borax (0.01 mol L^{-1}) solutions. The glass electrode was equilibrated in a SDS-water mixture containing inert electrolyte for several days. At regular intervals, an acid–base titration was carried out to check for complete equilibration. In each titration, the titrant consists of 1 mmol of hydrochloric acid and 0.25 to 0.50 mmols of the ligand and it is titrated by adding 0.1cm^3 of sodium hydroxide each time to the titrant. The curves for the alkalimetric titrations are given in Figure 1.



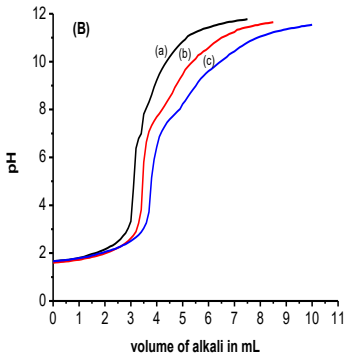


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Figure1. Alkalimetric titration curves in 2.0 w/v SDS-water mixtures: **(A)** Met (B) Cys
(a) 0.25, (b) 0.375 and (c) 0.50 mmol, respectively.

2.3 Modeling strategy: The computer program SCPHD was used to apply the correction factor to the pH meter reading. The protonation constants of L-Methionine and
L-Cysteine in different concentrations of SDS- water mixture were calculated using MINIQUAD75. The variation of stepwise protonation constants was examined on the basis of interactions between solute-solute and solute-solvent. The primary alkalimetric data were simulated [22] models.

3. Results and Discussion

The best fit chemical model for each system investigated was arrived at using non-linear least–squares method in the initial refinement and reliable convergence of Marquardt algorithm [**23**]. The variation of stepwise constants was analyzed mainly on electrostatic grounds on the basis of solute-solute and solute-solvent interactions. The results of best fit models that contain the type of species and overall protonation constants of L-Methionine and L-Cysteine in SDS-water mixtures along with some important statistical parameters are given in Table-1. The values of low standard deviation (SD) in log β and Ucorr (sum of the squares of deviations in concentrations of ligand and hydrogen ion at all experimental data points corrected for degree of freedom) show that the experimental data can be depicted by the model. The values of kurtosis in table 1 signify that the residuals form leptokurtic patterns [24]. The skewness values (-0.83 and 0.42) explain that the residuals form a part of normal distribution and therefore, least squares method is applicable to the present data. The acceptability of the model is more apparent from the low crystallographic R-values.

Table 1: Best fit chemical models of protonation equilibria of Met and Cys in SDS-water mixtures Temp= 303 K, Ionic strength=0.16 mol dm^{-3}.

% w/v SDS	$\log\beta_1$(SD)	$\log\beta_2$(SD)	$\log\beta_3$(SD)	NP	$U_{corr}x10^8$	Skewness	Kurtosis	χ^2	R-factor
	METHIONINE (pH range 1.80-10.80)								
0	8.93(07)	11.17(09)	---	54	26.23	0.42	5.45	5.93	0.0410
0.5	9.01(06)	11.64(09)	---	79	43.53	-4.73	31.12	67.11	0.0408
1.0	9.06(10)	11.48(13)	---	83	93.22	-2.07	9.32	30.53	0.0540
1.5	9.25(03)	12.64(07)	---	39	15.34	-1.11	6.74	19.64	0.0384
2.0	9.06(02)	12.62(04)	---	46	6.02	0.08	4.86	10.61	0.0218
2.5	8.99(03)	12.08(07)	---	38	14.37	-1.75	8.12	25.89	0.0386
	CYSTEINE (pH range 1.6-11.40)								
0	10.53(02)	18.67(01)	20.53(09)	60	14.13	-0.83	6.41	22.67	0.0241
0.5	10.55(03)	18.04(02)	19.85(09)	87	86.31	-0.19	3.57	24.53	0.0565
1.0	10.54(06)	18.66(06)	21.09(15)	67	91.06	-0.33	4.25	27.67	0.0619
1.5	10.22(03)	18.09(04)	20.29(12)	95	61.82	-2.89	17.18	69.45	0.0547
2.0	10.66(05)	18.46(07)	21.34(11)	87	76.54	-0.34	6.78	35.65	0.0345
2.5	10.49(03)	18.39(03)	20.65(08)	96	72.56	-1.56	8.29	50.42	0.0573

U_{corr}=U/(NP-m), where m=number of species; NP=Number of experimental points; SD=standard deviation

3.1 Secondary formation functions

Secondary formation functions like number of moles of alkali consumed per mole of ligand (a) and average number of protons bound per mole of ligand (n_H) are useful to detect the number of equilibria. Plots of a with pH (Figure 3) have two and three plateaus, respectively, for Met and Cys indicating the existence of two and three equilibria. Plots of n_H verses p^H (Figure -2) of different concentrations of the ligand should overlap if there is no formation of polymeric species.

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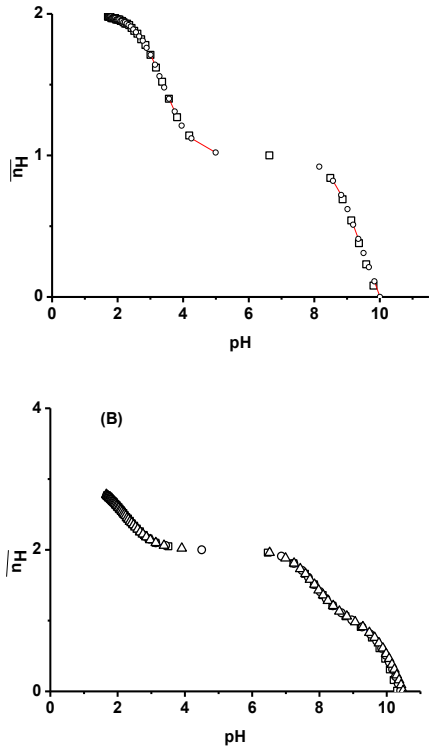

Fig 2: Plots of $\bar{n}_H$ versus pH of (A) Met and (B) Cys: ( ) 0.25, (○) 0.375, and (Δ) 0.50 mmol, respectively. in 1.5% w/v SDS- water mixture

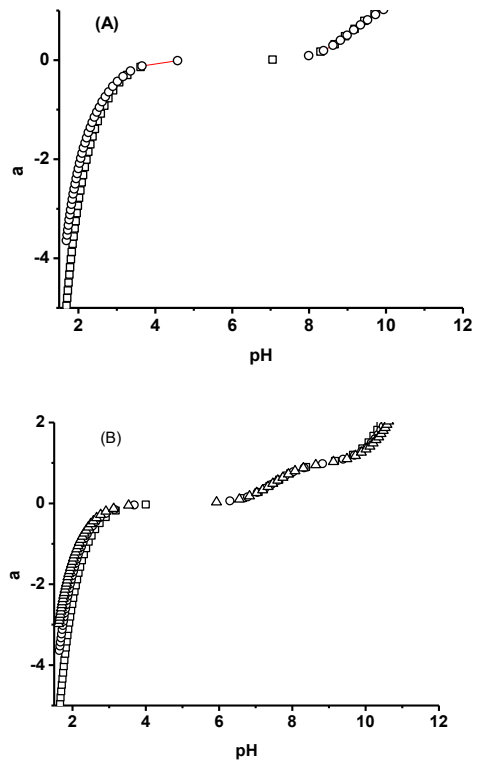

Fig 3: Variation of a with pH in 0.5 % w/v SDS–water mixture; of (A) Met and (B) Cys ( ) 0.25, (○) 0.375, and (Δ) 0.50 mmol, respectively.

3.2 Distribution diagrams

L-Methionine has two functional groups (amino and carboxyl) and both of them participate in the protonation equilibria and possess two protonation constants. On the other hand, L-Cysteine has three functional groups (amino, carboxyl, thioether) and they participate in the protonation equilibria and posses three protonation constants. The species distribution diagrams (Figure 4) occurred from the protonation constants show the existence of LH_2, LH, FL in the case of Met and LH_3, LH_2, LH, FL in the case of Cys in different pH ranges. The most predominant species in Met is LH form and for Cys it is LH_2 and the corresponding pH range is 1.5-10.5 and 1.5-10.0.

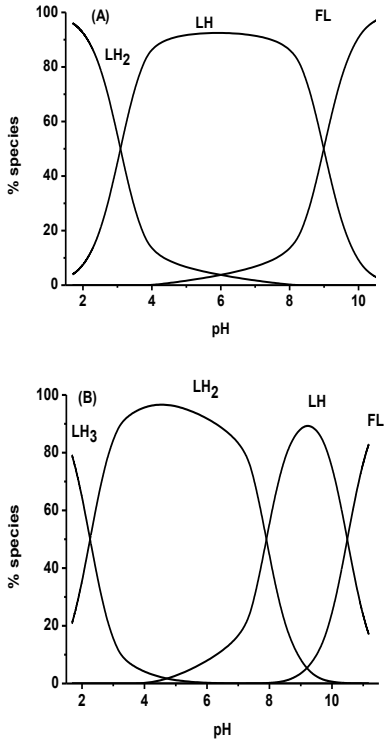

Fig4: Species distribution diagrams of (A) Met and (B) Cys in 2.5% w/v SDS-water mixture

3.3 Effect of Solvent

The variation of protonation constant or change in free energy with co-solvent

content depends upon two factors, viz., electrostatic and non-electrostatic. Born's classical treatment holds good in accounting for the electrostatic contribution to the free energy change [25].According to this treatment, the energy of electrostatic interaction or the logarithm of step-wise protonation constant (log K) should vary linearly with the mole fraction of the medium.

The log K values in the present study are linearly increasing (Figure 5) with increasing molefraction of the medium in both the amino acids. Many workers were of the opinion that both electrostatic and non-electrostatic effects should be considered even in the case of simple acido-basic equilibria; one dominates the other, depending upon the nature of solute and solvent [26-28].

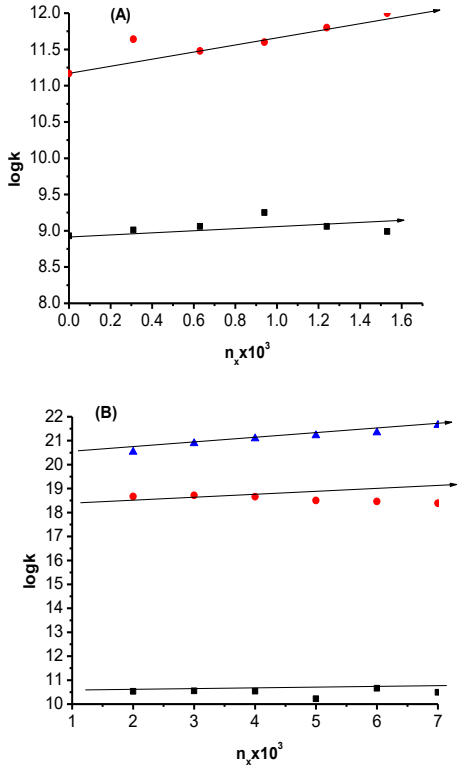

Figure 5: Variation of stepwise protonation constant (log K) with mole fraction of SDS -water mixture
(A) L- Met (□) $logK_1$, (Δ) $logK_2$, (B) L-Cys (□) $logK_1$, (○) $logK_2$, (Δ) log K_3

3.4Effect of systematic errors on best fit model

In order to rely upon the best fit chemical models for critical evaluation and application, the effect of systematic errors in the concentration of ingredients like mineral acid, alkali and ligand on the magnitude of protonation constants was investigated and the order of ingredients due to incorporation of errors is alkali>ligand>acid. The results of the above investigations are given in Table 2.

Table 2: Effect of systematic errors in influential parameters on the protonation constants ofMet and Cys in 0.5% w/v CTAB-water mixture

Ingredient	%	log β_{mlh} (SD)

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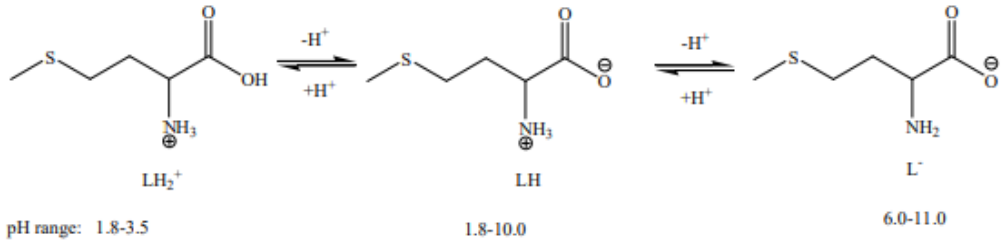
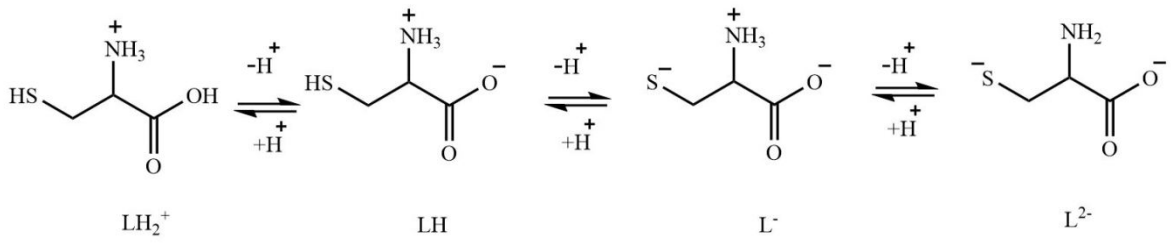
	Error	Met		Cys		
		11	12	11	12	13
	0	9.06(2)	12.62(04)	10.66(05)	18.46(07)	21.34(11)
Alkali	-5	9.56(3)	12.69(02)	10.88(07)	Rejected	21.76(04)
	-2	Rejected	12.98(06)	11.43(03)	19.05(02)	22.06(06)
	+2	9.34(23)	12.35(11)	11.54(32)	19.45(23)	Rejected
	+5	9.89(12)	12.88(34)	11.22(16)	rejected	21.98(19)
Acid	-5	9.35(14)	Rejected	11.95(23)	19.66(14)	21.45(09)
	-2	9.77(06)	12.88(14)	Rejected	18.76(15)	21.89(32)
	+2	9.45(12)	12.12(16)	11.63(17)	19.32(27)	21.98(34)
	+5	9.96(18)	12.67(28)	11.56(36)	19.67(18)	22.23(17)
Ligand	-5	8.95(23)	12.54(15)	10.32(18)	18.19(38)	20.96(16)
	-2	9.34(12)	12.60(15)	11.26(11)	18.96(16)	21.89(25)
	+2	9.22(16)	12.21(23)	11.45(33)	19.32(16)	21.96(18)
	+5	9.66(19)	12.76(28)	11.09(17)	19.25(23)	21.54(16)



Protonation-deprotonation equilibria of L-methionine



Protonation-deprotonation equilibria of L-cysteine

4. Conclusions:

- The protonation constants and number of equilibria could be determined from the secondary formation functions like average number of protons bound per mole of ligand n_H and number of moles of alkali consumed per mole of ligand

- The study of the effect of systematic errors in the ingredients indicated that the order of influence of the ingredient concentration on protonation constants is alkali>ligand>acid.
- The log K values of protonation constants increase linearly with increasing molefraction of SDS-water mixtures. This trend indicates the dominance of electrostatic forces over than non-electrostatic forces in the protonation-deprotonation equilibria.

References

[1]. G. N. Rao, K. G. Sudarsan: "Effect of Micelles on Speciation of Ternary Complexes of Nickel(II) with L-arginine and L-histidine". Chem. Spec. Bioavailab., 18, 71 (2006).

[2]. V. U. S. Sagar, G. HimaBindu, K. G. Sudarsan, G. N. Rao: "Speciation Studies of Binary Complexes of Nickel(II) with L-arginine and L-histidine in Micellar Medium". J. Indian Chem. Soc., 82,598 (2005).

[3]. K. V. Lavanya, G. N. Rao, M. Rajesh, M. S. Babu:"Micellar Effect on Protonation Equilibria of L-arginine and L-histidine". J. Indian Chem. Soc., 81, 384 (2004).

[4]. B. B. V. Sailaja, T. Kebede, G. N. Rao, M. S. P. Rao:" Effect of Surfactants on Protonation equilibria of Oxalic and Malonic Acids". J. Indian Chem. Soc., 79,155 (2002).

[5].Y.Triveni, B. B. V. Sailaja:"Protonation Equilibria of L-Methionine and L-Cysteine In Cationic Micellar Media".IJSRR 2019, 8(1), 2734-2744.

[6]. B.Simon, J.Span: A Study of Dye – Surfactant Interactions. Part 1." Effect of Chemical Structure of Acid Dyes and Surfactants on the Complex Formation". Dyes and Pigments, 36,1(1998).

[7]. J. C. Russell, U. P. Wild, D. G. Whitten: "The Heptanol Swollen Micelle: Fluorescence and Absorbance Probe Studies of Size and Solubilization Properties". J. Phys. Chem., 90, 1319 (1986).

[8]. D. Danino, Y. Talmon, H. Levy et al:" Branched Thread-like Micelles in an Aqueous Solution of a Trimeric Surfactant". Science, 269, 1420 (1995).

[9]. D. Danino, Y. Talmon, R. Zana:" Alkanediyl-alpha,omega-bis(dimethylalkylammonium bromide) Surfactants (Dimeric Surfactants). 5. Aggregation and Microstructure in Aqueous Solutions".Langmuir, 11, 1448 (1995).

[10]. R. Zana, Y. Talmon:"Dependence of Aggregate Morphology on Structure of Dimeric SurfactantsNature".362, 228 (1993).

[11].PiretJ,Lamontagne J,Bestman-Smith, J,Roy, S, Gourde, P,Desormeaux, A, Omar, R.F,Juhasz, J. & Bergeron, M.G. (2000)."In vitro and in vivo evaluations of sodium laurylsulfate and dextran sulfate as microbicides against herpes simplex and human immunodeficiency viruses". J. Clin. Microbiol.**38** (1): 110–19.

[12]. Lewis MA. "The effects of mixtures and other environmental modifying factors on the toxicities of surfactants to freshwater and marine life". Water Res. 1992;26(8):1013–23.

[13]. Warne MS, Schifko AD. "Toxicity of laundry detergent components to a freshwater
cladoceran and their contribution to detergent toxicity". Ecotoxicol Environ Saf.
1999;44:196–206.
[14]. Zheng YJ, Chen L, Chen YP, Huang R."Acute toxicity of sodium dodecyl sulfate
(SDS) on selected aquatic organisms.Nong Ye Huan Jing KeXueXueBao".
2006;25:496–8.
[15]. B. Regland, L. Abrahamsson, K.Blennow, B. Grenfeldt, C.G. Gotlfries, *J. Neural*
*Transm.***2004**, *111*, 631-640.
[16]. M. Noji, K. Saito, *Sulphur in plants*, A review **2003**,135–144.
[17] Maier T, Winterhalter C., "Microorganism with deregulated Cysteine metabolism,
useful for high level production of cysteine and its derivatives has increased activity of thecysb transcription Regulator". Germany, WO200127307-A **(2001)**
[18]. Sano K, Mrrsugi K. "Ezymatic production of L-cysteine from DL- 2-amino-thiazoline-
4-carboxylic acid by Pseudomonas.Thiazolinophilum: optimal conditions for enzyme
formation and enzymatic reaction". *Agric. Biol. Chem*. **42**, 2315 **(1978) .**
[19].Hee RO, Yeong J.J., Soo CS., " Continuous L-cysteine production using immobilized
cell reactors and product extractors". *Process Biochem*.32, 201 **(1997).**
[20]. Baker DH, Czarnecki-Maulden GL (June 1987). "Pharmacologic role of cysteine in
ameliorating or exacerbating mineral toxicities". J. Nutr. **117** (6): 1003–10.
[21]. K. V. Santhee Devi, B. Rama Raju, G. N. Rao, " Effect of dielectric constant on
protonationequlibria of L-dopa and 1, 10 - phenanthroline in dioxan-water mixtures", *ActaChim.Slov.*,**2010**, 57, 398.
[22]. R. S. Rao, A. Satyanarayana, P. V. K. Rao., "SOPHD: Simulation of pH Metric Data".
In: Proc. Summer Simulation Conference, 1984, p. 563.
[23]. Gans P., Sabatini A., Vacca A., Inorg. Chim.Acta 1976, 18, p237
[24]. M. P. Latha, V. M. Rao, T. S. Rao, G. N. Rao., " Determination of Protonation Constants of L-glutamic Acid and L-methionine in 1,2-propanediol-water Mixtures".
ActaChim.Slov., 54, 160 (2007)
[25].G. Gran, Anal. Chim.Acga. 1988, 206, 111-123.
[26] N. Padmaja, M. S. Babu, G. N. Rao, R. S. Rao, K. V. Ramana, Polyhedron,1990, 9,
2497 – 2506.
[27] G. N. Rao"Complex equilibria of some biologically important metal ions in aqua-
organic media", Ph. D. thesis, Andhra University, Visakhapatnam, India 1989.
[28] P. Gans, A. Sabatini, A. Vacca, Inorg. Chim.Acta 1976, 18, 237 – 239.