Book Chapter

Effect of Anionic Micelles of Sodium Dodecyl Sulfate on Protonation Equilibria of Salicylic Acid Derivatives

Malla Ramanaiah[1]*, Sattaru Gouthamsri[1], Malla Balakrishna[2], Bendi Ramaraju[1] and Gollapalli Nageswara Rao[3]

[1]Department of Chemistry, Aditya Institute of Technology and Management, Tekkali, India
[2]Department of Chemistry, Lendi Institute of Engineering and Technology, Vizianagaram, India
[3]School of Chemistry, Andhra University, Visakhapatnam, India

***Corresponding Author:** Malla Ramanaiah, Department of Chemistry, Aditya Institute of Technology and Management, Tekkali 532201, India

Published **December 30, 2020**

This Book Chapter is a republication of an article published by Malla Ramanaiah, et al. at Cogent Chemistry in July 2016. (Malla Ramanaiah, Sattaru Gouthamsri, Malla Balakrishna, Bendi Ramaraju and Gollapalli Nageswara Rao (2016) Effect of anionic micelles of sodium dodecyl sulfate on protonation equilibria of salicylic acid derivatives, Cogent Chemistry, 2:1, 1217762, DOI: 10.1080/23312009.2016.1217762)

How to cite this book chapter: Malla Ramanaiah, Sattaru Gouthamsri, Malla Balakrishna, Bendi Ramaraju, Gollapalli Nageswara Rao. Effect of Anionic Micelles of Sodium Dodecyl Sulfate on Protonation Equilibria of Salicylic Acid Derivatives. In: VSR Rajasekhar Pullabhotla, editor. Prime Archives in Chemistry: 2nd Edition. Hyderabad, India: Vide Leaf. 2020.

Funding: The authors received no direct funding for this research.

Abstract

The impact of sodium dodecyl sulfate (SDS) on the protonation equilibria of 5-sulfosalicylic acid and 5-Hydroxysalicylic acid has been studied in various concentrations (0.0−2.5% w/v) of sodium dodecyl sulfate solution maintaining an ionic strength of 0.16 mol dm^{-3} Nacl at 303 K. The protonation constants have been calculated with the computer program MINIQUAD75 and the best fit models are arrived at based on statistical grounds employing crystallographic *R* factor, χ^2, skewness, and kurtosis. These protonation constants values have been found to shift in micellar media as compared to those in pure water. The differences in the values have been attributed to the solvent properties of the interfacial and bulk phases involving contribution from the micellar surface potential in the case of charged micelles. The trend of log values of stepwise protonation constants with mole fraction of the medium have been explained based on electrostatic and non-electrostatic forces operating on the protonation equilibria. Distributions of species, protonation equilibria, and effect of influential parameters on the protonation constants have also been presented.

Keywords

Protonation Equilibria; MINIQUAD75; Sodium Dodecyl Sulfate; 5-Sulfosalicylic Acid; 5-Hydroxysalicylic Acid

Introduction

Sodium dodecyl sulfate (SDS) or Sodium lauryl sulfate (SLS) is an anionic surfactant and profoundly influences the bulk properties of physiological systems. They can solubilize, concentrate, and compartmentalize ions and molecules [1].

Hence, the influence of anionic micellar media on the protonation equilibria of 5-sulfosalicylic acid and 5-Hydroxysalicylic acid are investigated in the presence of SDS. The use of aqueous micellar media is wide and varied such as in pharmaceutics, analytical chemistry, organic synthesis, and several industrial applications. Micelles are widely used in energy storage devices as well [2,3]. Amphiphilic molecules, containing both hydrophobic and hydrophilic moieties, associate in water above a certain concentration to form colloidal particles called micelles [4]. Micellar systems can shift acid–base equilibria. This shift in chemical equilibria can be explained in terms of differences between the properties of the bulk solvent and of the interfacial region and perturbation of the acid–base equilibria by the electrostatic field effect of the charged interface [5]. The dissociation equilibria of substituted benzoic acids in cationic and anionic micelles have been investigated potentiometrically [6]. It was shown that their p*Ka* values shift to about 0.5–3.0 in anionic micelles. The acid–base equilibria of a number of phenols, amines, and carboxylic acids in aqueous micellar solutions have been examined [7]. The present work is an attempt to study the effects of anionic micellar solution on the protanation equilibria of the two biologically or industrially useful acids, viz. 5-sulfosalicylic acid and 5-Hydroxysalicylic acid in the surfactant SDS.

Experimental

Chemicals and Standard Solutions

Solutions (0.05 mol dm^{-3}) of 5-sulfosalicylic acid (TCI, India) and 5-Hydroxysalicylic acid (TCI, India) were prepared in triple-distilled water by maintaining 0.05 mol dm^{-3} hydrochloric acid concentration to increase the solubility. Sodium dodecyl sulfate (Merck, India) was used as received. Hydrochloric acid (Merck, India) of 0.2 mol dm^{-3} was prepared. Sodium chloride (Merck, India) of 2 mol dm^{-3} was prepared to maintain the ionic strength in the titrand. Sodium hydroxide (Merck, India) of 0.4 mol dm^{-3} was prepared. All the solutions were standardized by standard methods. To assess errors in concentration determinations, the data were subjected to analysis of variance of

one way classification [8]. The strengths of alkali and mineral acid were determined using the Gran plot method [9,10].

Instrumentation and analytical procedures

Alkalimetric titrations were carried out in media containing varying compositions of SLS (0.0–2.5% w/v) maintaining an ionic strength of 0.16 mol dm^{-3} with sodium chloride at 303 ± 0.05 K. An Elico Li-120 pH meter was used. Potassium hydrogen phthalate (0.05 mol dm^{-3}) and Borax (0.01 mol dm^{-3}) solutions were used to calibrate the pH meter. In each titration, the titrand consisted of approximately 1 mmol of hydrochloric acid. The amounts of the ligands in the titrands ranged between 0.25 and 0.50 mmol. The glass electrode was equilibrated in a well-stirred sodium dodecyl sulfate-water mixture containing inert electrolyte for several days. At regular intervals, titration of strong acid against alkali used to check the complete equilibration of the glass electrode. The calomel electrode was refilled with SDS-water mixture of equivalent composition as that of the titrand. The initial concentrations of reactants are given in Table 1. The details of experimental procedure and titration assembly have been detailed elsewhere [11-14].

Table 1: Total initial concentrations of reactants (in mmol) in proton-ligand titrations.

% w/v SDS	No. of titration curves	TL0	
		5-Sulfosalicylic acid	**5-Hydroxysalicylic acid**
0.0	3	0.2482	0.2493
		0.3741	0.3727
		0.4977	0.4970
0.5	3	0.2488	0.2493
		0.3747	0.3740
		0.4996	0.4987
1.0	3	0.2478	0.2488
		0.3732	0.3747
		0.4968	0.4976
1.5	3	0.2515	0.2494
		0.3773	0.3723
		0.5031	0.4965
2.0	3	0.2483	0.2488
		0.3725	0.3739
		0.4967	0.4986
2.5	3	0.2464	0.2482
		0.3686	0.3723
		0.4898	0.4965

Modeling Strategy

The approximate protonation constants of 5-sulfosalicylic acid and 5-Hydroxysalicylic acid were calculated with the computer program SCPHD [13,15,16]. The best fit chemical model for each system investigated was arrived at using non-linear least-squares computer program, MINIQUAD75 [17], which exploit the advantage of constrained least-squares method in the initial refinement and reliable convergence of Marquardt algorithm. The variation of stepwise protonation constants (log *K*) with the mole fraction of the medium was analyzed on electrostatic grounds for the solute–solute and solute–solvent interactions.

Results and Discussion

Secondary Formation Functions

Secondary formation functions like average number of protons bound per mole of ligand ($\bar{n}_H$) and number of moles of alkali consumed per mole of ligand (**a**) are useful to detect the number of equilibria. Plots of $\bar{n}_H$ versus pH for different concentrations of the ligand should overlap if there is no formation of polymeric species. Overlapping formation curves for 5-sulfosalicylic acid and 5-Hydroxysalicylic acid (Figure 1) rule out the polymerization of the ligand molecules.

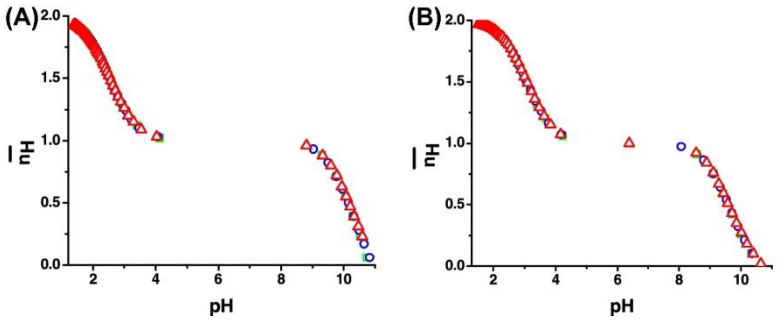

Figure 1: Plots of $\bar{n}_H$ versus pH in 1.0% w/v SDS-water mixture; (A) 5-sulfosalicylic acid (B) 5-Hydroxysalicylic acid, (Δ) 0.25, (○) 0.375, and (□) 0.50 mmol, respectively.

The pH values at half integral values of $\bar{n}_H$ correspond to the protonation constants of the ligands. Two half integrals (1.5 and 0.5) in the case of 5-sulfosalicylic acid (Figure 1(A)) and 5-Hydroxysalicylic acid (Figure 1(B)) emphasize the presence of two protonation–deprotonation equilibria in the pH range of present study. The number of plateaus in the formation curves corresponds to the number of these equilibria.

The plots of **a** vs. pH are given in Figure 2. The negative values of **a** correspond to the number of moles of free acid present in the titrand and the number of associable protons. The positive values of **a** indicate the number of dissociable protons in the ligand molecules. The maximum value of **a** in Figure 3 is +3,

which indicates that 5-sulfosalicylic acid and 5-Hydroxysalicylic acid has three dissociable protons.

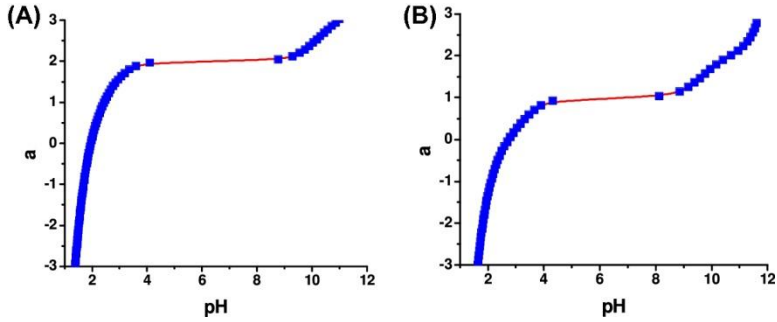

Figure 2: Variation of a with pH in 2.0% w/v SDS-water mixture; (A) 5-sulfosalicylic acid (B) 5-Hydroxysalicylic acid, respectively.

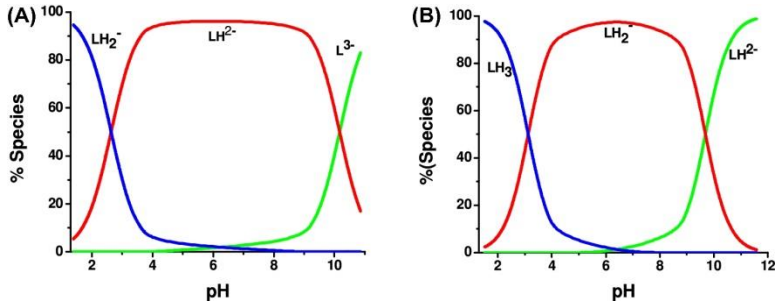

Figure 3: Species distribution diagrams of (A) 5-sulfosalicylic acid (B) 5-Hydroxysalicylic acid in 1.5% w/v SDS-water mixtures.

Distribution Diagrams

Typical distribution plots produced by DISPLOT [18-23] using protonation constants from the best-fit models are shown in Figure 3. A single representative plot is shown for each system at a particular SDS-water concentration. LH_2^- of 5-sulfosalicylic acid is present to an extent of 94% in the pH range 1.0–3.5. The distribution plot of 5-sulfosalicylic acid in Figure 3(A) shows the existence of LH_2^-, LH^{2-} and L^{3-} in the pH range 1.0–10.9. In the case of 5-Hydroxysalicylic acid, LH_2^- is present to an extent of 97.0% in the pH range 1.5–4.0. The distribution plot of 5-Hydroxysalicylic acid in Figure 3(B) shows the existence of

LH_3, LH_2^- and LH^{2-} in the pH range 1.5–11.5. The corresponding protonation–deprotonation equilibria of 5-sulfosalicylic acid and 5-Hydroxysalicylic acids are shown in Figure 4.

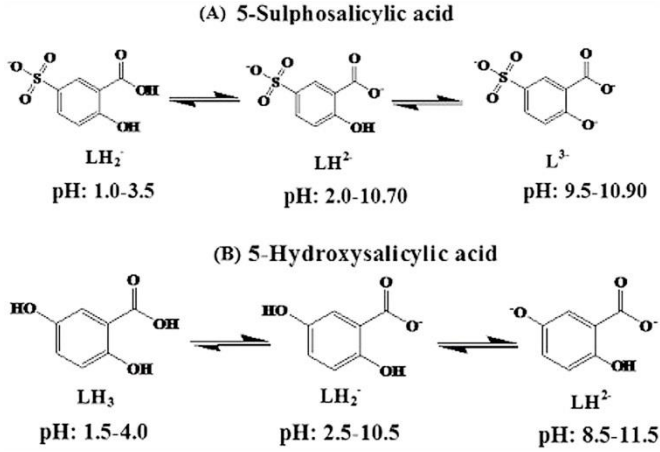

Figure 4: Protonation–deprotonation equilibria of (A) 5-sulfosalicylic acid (B) 5-Hydroxysalicylic acid.

Residual Analysis [14,20,24]

In data analysis with least squares methods, the residuals (the differences between the experimental data and the data simulated based on the model parameters) are assumed to follow Gaussian or normal distribution. When the data are fit into the models, the residuals should be ideally equal to zero. Further, a model is considered adequate only if the residuals do not show any trend. Respecting the hypothesis of the least squares analysis, the residuals are tested for normal distribution. Such tests are χ^2, skewness, kurtosis, and *R*-factor. These statistical parameters of the present data show that the best fit models portray the acido-basic equilibria of 5-sulfosalicylic acid 5-Hydroxysalicylic acid in SDS-water mixtures, as discussed below. Alkali metric titration data are simulated using the model parameters given in Table 2.

Table 2: Best fit chemical models of acido-basic equilibria of 5-sulfosalicylic acid and 5-Hydroxysalicylic acid in SLS-water mixtures. Temp = 303 K, Ionic strength = 0.16 mol dm^{-3}.

% w/v SDS	log β_1 (SD)	log β_2 (SD)	NP	U_{corr}	Skewness	Kurtosis	χ^2	*R*
5-Sulfosalicylic acid (pH range 1.60–10.90)								
0.0	11.17 (3)	13.84 (4)	125	17.56	1.07	4.73	25.90	0.0184
0.5	10.22 (2)	12.85 (4)	87	17.41	0. 63	50.26	15.52	0.0244
1.0	10.19 (3)	12.73 (4)	71	21.01	0.97	6.05	19.01	0.0316
1.5	10.17 (2)	12.80 (2)	61	27.11	−0.60	7.97	25.41	0.0133
2.0	10.16 (2)	12.78 (3)	73	11.16	1.45	1.25	25.51	0.0207
2.5	10.15 (2)	12.73 (2)	130	9.37	0.83	8.11	24.18	0.0124
5-Hydroxysalicylic acid (pH range 1.50–10.20)								
0.0	10.23 (1)	13.10 (3)	129	10.15	−0.06	3.38	5.38	0.0158
0.5	9.64 (2)	12.54 (3)	30	4.28	0.52	4.32	1.60	0.0192
1.0	9.59 (2)	12.68 (4)	72	2.57	1.33	9.67	37.44	0.0204
1.5	9.69 (3)	12.81 (5)	121	27.73	2.25	26.84	27.80	0.0235
2.0	9.66 (3)	12.88 (5)	47	7.11	−0.10	4.59	11.36	0.0096
2.5	9.70 (2)	13.03 (2)	59	6.66	0.30	6.71	18.00	0.0140

Notes: $U_{corr} = U/(NP - m) \times 10^8$; NP = number of points; m = number of protonation constants; SD = standard deviation.

χ^2 Test

χ^2 is a special case of gamma distribution whose probability density function is an asymmetrical function. This distribution measures the probability of residuals forming a part of standard normal distribution with zero mean and unit standard deviation. If the χ^2 calculated is less than the table value, the model is accepted.

Crystallographic R-Test

Hamilton's *R* factor ratio test is applied in complex equilibria to decide whether inclusion of more species in the model is necessary or not. In pH-metric method, the readability of pH meter is taken as the R_{limit}, which represents the upper boundary of *R* beyond which the model bears no significance. When these are different numbers of species, the models whose values are greater than *R*-table are rejected. The low crystallographic *R*-values given in Table 2 indicate the sufficiency of the model.

Skewness

It is a dimensionless quantity indicating the shape of the error distribution profile. A value of zero for skewness indicates that the underlying distribution is symmetrical. If the skewness is greater than zero, the peak of the error distribution curve is to the left of the mean and the peak is to the right of the mean if skewness is less than zero. The values of skewness recorded in Table 2 are between −0.60 and 2.25. These data evince that the residuals form a part of normal distribution; hence, least-squares method can be applied to the present data.

Kurtosis

It is a measure of the peakedness of the error distribution near a model value. For an ideal normal distribution, kurtosis value should be three (mesokurtic). If the calculated kurtosis is less than three, the peak of the error distribution curve is flat (platykurtic) and if the kurtosis is greater than three, the distribution shall have sharp peak (leptokurtic). The kurtosis

values in the present study indicate that the residuals form eptokurtic pattern in the case of 5-sulfosalicylic acid and 5-Hydroxysalicylic acid. Alkalimetric titration data are simulated using the model parameters given in Table 2.

Effect of Surfactant

These protonation constants have been considered in some detail to gain more information about the effect of solvent composition on the corresponding equilibria. For this purpose, log K_1 and log K_2 values have been plotted as a function of the mole fraction of SDS for 5-sulfosalicylic acid 5-Hydroxysalicylic acid. The logarithm of stepwise protanation constants of 5-sulfosalicylic acid and 5-Hydroxysalicylic acid determined in various SDS-water mixtures are listed in Table 3.

Table 3: Stoichiometric protonation constants of 5-sulfosalicylic acid and 5-Hydroxysalicylic acid in SDS-water mixtures. Temp = 303 K, Ionic strength = 0.16 mol dm^{-3}.

% w/v SLS	5-Sulfosalicylic acid		5-Hydroxysalicylic acid	
	log K_1	log K_2	log K_1	log K_2
0.0	2.66	11.17	2.86	10.23
0.5	2.63	10.22	2.9	9.64
1.0	2.54	10.19	3.08	9.6
1.5	2.62	10.17	3.12	9.69
2.0	2.62	10.16	3.22	9.66
2.5	2.58	10.15	3.33	9.70

The interface of anionic surfactant SDS is negatively charged and the anion from the acid molecule is repelled, thus leading to a decrease in acidity. Also, there is a possibility of electrostatic attraction of H^+ from acid molecule to the SDS micelles, which would cause an increase in the acidity. However, in the present study, the sum total of these factors cause lesser strain on the acid molecule leading to small variation of stepwise protanation constant values as compared to those in water.

The apparent variation in the magnitude of protonation constants in miceller media compared to aqueous solution (Figure 5) was attributed to the creation of concentration gradient of protons between the interface and the bulk solution [25]. Further, the

presence of micelles is known to alter the dielectric constant of the medium, which has direct influence on the protonation–deprotonation equilibria [26,27]. The linear variation of log values of stepwise protonation constants of 5-sulfosalicylic acid 5-Hydroxysalicylic acid with the mole fraction of SDS indicates the dominance of electrostatic forces in the protonation–deprotonation equilibria.

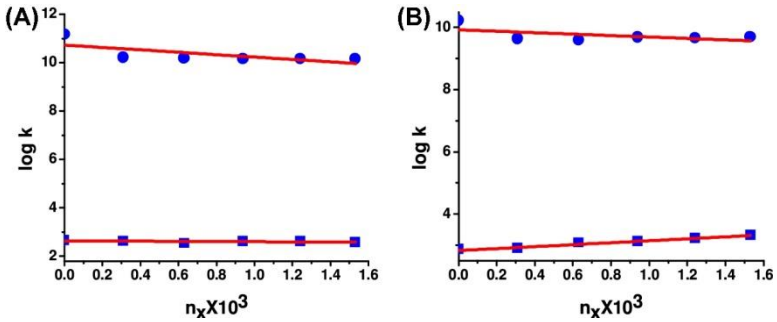

Figure 5: Variation of stepwise protonation constant (log *K*) with mole fraction of SLS in SLS-water mixtures. (A) 5-sulfosalicylic acid (B) 5-Hydroxysalicylic acid (■) log K_1 and (●) log K_2.

Effect of Systematic Errors in Best Fit Model

MINIQUAD75 does not have provision to study the effect of systematic errors in the influential parameters like the concentration of reactants and electrode calibration on the magnitude of protonation constant. In order to rely upon the best chemical model for critical evaluation and application under varied experimental conditions with different accuracies of data acquisition, an investigation was made by introducing pessimistic errors in the concentration of alkali, mineral acids and the ligands. The results of a typical system given in Table 4 emphasize that the errors in the concentrations of alkali and mineral acid affects the protonation constants more than that of the ligand.

Table 4: Effect of errors in influential parameters on the protonation constants of 5-sulfosalicylic acid and 5-Hydroxysalicylic acid in 2.5% (w/v) SDS-water mixture.

% Error	Ingredient	Log β_{mlh} (SD)			
		5-Sulfosalicylic acid		5-Hydroxysalicylic acid	
		LH	LH_2	LH	LH_2
	0	10.15 (2)	12.73 (2)	9.70 (2)	13.03 (2)
Acid	+4	10.21 (4)	12.88 (6)	9.75 (4)	13.13 (5)
	+2	10.18 (4)	12.80 (5)	9.73 (4)	13.08 (4)
	−2	10.13 (4)	12.67 (4)	9.68 (4)	13.01 (4)
	−4	10.11 (4)	12.61 (4)	9.67 (4)	12.99 (4)
Alkali	+4	10.09 (4)	12.60 (5)	9.65 (5)	12.98 (4)
	+2	10.12 (4)	12.66 (5)	9.67 (4)	13.00 (4)
	−2	10.20 (4)	12.82 (5)	9.72 (5)	13.05 (4)
	−4	10.24 (5)	12.92 (6)	9.75 (5)	13.09 (5)
Ligand	+4	10.19 (2)	12.78 (2)	9.75 (2)	13.07 (2)
	+2	10.17 (2)	12.76 (2)	9.72 (2)	13.05 (2)
	−2	10.11 (2)	12.70 (2)	9.68 (2)	13.01 (2)
	−4	10.09 (2)	12.68 (2)	9.66 (2)	12.99 (2)
Log F	+4	10.18 (2)	12.76 (2)	9.72 (2)	13.05 (2)
	+2	10.17 (2)	12.75 (2)	9.71 (2)	13.04 (2)
	−2	10.14 (2)	12.72 (2)	9.69 (2)	13.01 (2)
	−4	10.13 (2)	12.71 (2)	9.68 (2)	13.00 (2)
Volume	+4	10.16 (2)	12.74 (2)	9.71 (2)	13.04 (2)
	+2	10.15 (2)	12.73 (2)	9.70 (2)	13.03 (2)
	−2	10.15 (2)	12.73 (2)	9.70 (2)	13.03 (2)
	−4	10.14 (2)	12.72 (2)	9.69 (2)	13.02 (2)

Conclusions

- 5-sulfosalicylic acid (LH_3) has two ionizable hydrogen ions, which are the protons of the carboxyl group and hydroxyl group. K_1 and K_2 are the corresponding protonation constants of the carboxylate and phenolate groups, respectively. The deprotonation of the sulfonic acid group takes place at very low pH, which makes the use of a glass electrode unreliable in determining the corresponding protonation constant.
- 5-Hydroxysalicylic acid has three dissociable protons and can forms LH_3 at low pH and gets deprotonated with the formation of LH_2^- and LH^{2-} with increase in pH. The deprotonation of the second hydroxyl group takes place at

very high pH, which makes the use of a glass electrode unreliable in determining the corresponding protonation constant. K_1 and K_2 are the corresponding protonation constants of the carboxylate and phenolate groups, respectively.

- Secondary formation functions—number of moles of alkali consumes per mole of the ligand and average number of moles of protons bound per mole of the ligand—are useful in detecting the number of protonation equilibria and in guessing the approximate protonation constants.
- The linear variation of log values of protonation constants of 5-sulfosalicylic acid and 5-Hydroxysalicylic acid with increasing mole fraction of SDS in SDS-water mixtures indicates the dominance of electrostatic forces in the protonation–deprotonation equilibria.
- The effect of systematic errors in the influential parameters shows that the errors in the concentrations of alkali and mineral acids will affect the protonation constants more than that of the ligand.

References

1. Pelizzetti E, Pramauro E. Analytical applications of organized molecular assemblies. Analytica Chimica Acta. 1985; 169: 1–29.
2. Barmi MJ, Sundaram MM. Role of polymeric surfactant in the synthesis of cobalt molybdate nanospheres for hybrid capacitor applications. RSC Advances. 2016; 6: 36152–36162.
3. Ramkumar R, Sundaram MM. A biopolymer gel-decorated cobalt molybdate nanowafer: Effective graft polymer cross-linked with an organic acid for better energy storage. New Journal of Chemistry. 2016; 40: 2863–2877.
4. Szymula M, Radzki S. A study of molecular complex formation between propyl gallate and ascorbic acid in the microemulsion phase of sodiumdodecyl sulfate, pentanol and water system. Colloids and Surfaces B: Biointerfaces. 2004; 35: 249–257.
5. Jaiswal PV, Ijeri VS, Srivastava AK. Effect of surfactants on the dissociation constants of ascorbic and maleic

acids. Colloids and surfaces B: Biointerfaces. 2005; 46: 45–51.
6. Ezzio P, Edmondo P. Acid-base titrations of substituted benzoic acids in micellar systems. Analytica Chimica Acta. 1980; 117: 403–406.
7. Drummond CJ, Grieser F, Healy TW. Acid–base equilibria in aqueous micellar solutions. Part 1. 'Simple' weak acids and bases. Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases. 1989; 85: 521–535.
8. Rao RS, Rao GN. Computer applications in chemistry (p. 302). Mumbai: Himalaya Publishing House. 2005.
9. Gran G. Determination of the equivalence point in potentiometric titrations. Part II. The Analyst. 1958; 77: 661–671.
10. Gran G. Equivalence volumes in potentiometric titrations. Analytica Chimica Acta. 1988; 206: 111–123.
11. Ramanaiah M, GouthamSri S, Sailaja BBV. Effect of non ionic micelles on the chemical speciation of binary complexes of Pb(II), Cd(II) and Hg(II) with L-phenylalanine. Chemical Speciation and Bioavailability. 2013; 25: 285–290.
12. Ramanaiah M, Sailaja BBV. Protonation equilibria of L-phenylalanine and maleic acid in cationic micellar media. Chemical Speciation and Bioavailability. 2014; 26: 119–125.
13. Ramanaiah M, Gouthamsri S, Sailaja BBV. Formation of binary complexes of Pb(II), Cd(II) and Hg(II) with maleic acid in CTAB–water mixtures. Chemical Speciation and Bioavailability. 2014; 26: 231–239.
14. Rao CN, Ramanaiah M, Sailaja BBV. Speciation of binary complexes of Pb(II) and Cd(II) with L-asparagine in dimethyl sulfoxide-water mixtures. Bulletin of the Chemical Society of Ethiopia. 2016; 30: 71–78.
15. Ramanaiah M, Sailaja BBV. pH-metric investigation on binary complexes of Pb(II), Cd(II) and Hg(II) with maleic acid in SLS-water mixtures. Journal of the Indian Chemical Society. 2014; 91: 639–645.
16. Ramanaiah M, Seetharam P, Sailaja BBV. Chemical speciation of ternary complexes of Pb(II), Cd(II) and Hg(II)

with L-phenylalanine and maleic acid in TX100-water mixtures. Journal of the Indian Chemical Society. 2014; 91: 1011–1120.
17. Gans P, Sabatini A, Vacca A. An improved computer program for the computation of formation constants from potentiometric data. Inorganica Chimica Acta. 1976; 18: 237–239.
18. Balakrishna M, Rao GS, Ramanaiah M, Rao GN, Ramaraju B. Chemical speciation of binary complexes of Co(II), Ni(II) and Cu(II) with 5-sulfosalicylic acid in urea-water mixtures. Der Pharma Chemica. 2016; 8: 24–31.
19. Ramanaiah M, Gouthamsri S, Sailaja BBV. Stability of binary complexes of Pb(II), Cd(II) and Hg(II) with maleic acid in TX100-water mixtures. Bulletin of the Chemical Society of Ethiopia. 2014; 28: 383–391.
20. Ramanaiah M, Kumari VG, Sailaja BBV. Effect of anionic surfactant on the protonation equilibria of L-phenylalanine and maleic acid. Journal of the Indian Chemical Society. 2016; 93: 285–292.
21. Ramanaiah M, Rao CN, Sailaja BBV. Study of ternary complex stability constants of PbII, CdII, and HgII with L-phenylalanine and maleic acid in SDS-water mixtures. Proceedings of the National Academy of Sciences, India Section A: Physical Sciences. 2014; 84: 485–494.
22. Ramanaiah M, Sailaja BBV. Mixed ligand complex formation equilibria of some toxic metal ions with L-phenylalanine and maleic acid in CTAB-water mixtures. Journal of the Indian Chemical Society. 2014; 91: 1649–1660.
23. Rao CHN, Ramanaiah M, Sailaja BBV. Influence of dielectric constant on protonation equilibria of maleic acid and L-asparagine in acetonitrile water–mixtures. Chemical Speciation and Bioavailability. 2014; 26: 266–272.
24. Rao RS, Rao GN. Computer applications in chemistry (p. 277). Mumbai: Himalaya Publishing House. 2005.
25. Hartley GS, Roe JW. Ionic concentrations at interfaces. Transactions of the Faraday Society. 1940; 35: 101–109.