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Effect of Non-Ionic Micelles on Protonation Equilibria of L-Dopa And Catechol

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ABSTRACT

The effect of Triton X-100 (TX100) on the protonation equilibria of L-Dopa and Catechol has been studied in various concentrations (0.0-2.5% v/v) of TX100 solution maintaining an ionic strength of 0.16 mol L^{-1} at 303 K. The best fit chemical models have been selected based on statistical grounds employing crystallographic R factor, χ^2, skewness, kurtosis and the protonation constants have been calculated with the computer program MINIQUAD75. Dopa has three dissociable protons and one amino group which associate with proton. It exists as LH^{4+} at low pH and gets deprotonated with the formation of LH_3, LH^{-}_2 and LH^{2-} successively with increase in pH. Catechol has two dissociable protons. It exists as LH_2 at low pH and gets deprotonated with the formation of LH^- and L^{-2} with increasing pH. The trend of log values of step-wise protonation constants with mole fraction of the medium has been explained based on electrostatic and non-electrostatic forces operating on the protonation equilibria.

Keywords: Protonation equilibria, MINIQUAD75, Triton X-100, L-Dopa, Catechol.

INTRODUCTION

L-Dopa (L-3,4-dihydroxiphenylalanine) is a naturally occurring dietary supplement. It is a popular drug in the treatment of manganese poisoning and Parkinson's disease (PD) [1] which are accompanied by neurologically similar sequels [2]. Dopa is richest natural source is from plant kingdom like the seeds of Mucuna Pruriens [3]. Dopa increases dopamine concentration, since it is capable of crossing the blood brain barrier, where dopamine itself cannot. Once dopa enters the central nervous system (CNS) it is converted in to dopamine by the enzyme aromatic L-amino acid decarboxylase, also known as dopa decarboxylase. However, conversion to dopamine also occurs in the peripheral tissues, causing adverse effects and decreasing the available dopamine to the CNS. So it is the standard practice to co-administer a peripheral dopa decarboxylase inhibitor. Compounds containing dopa were found to cross linked proteins [4].

Catechol (1,2-dihydroxybenzene) occurs naturally in fruits and vegetables such as onions, apples and crude beet sugar, and in trees such as pine, oak and willow. It is used as a reagent for photography,

dyestuffs, rubber, plastic production, organic synthesis and pharmaceutical industry [5]. Catechols are intermediary products in the degradation of aromatic compounds and lignin by microorganism [6]. In humans and mammals, catechol can occur as metabolites in the degradation of benzene or estrogens or as endogenous compounds, such as neurotransmitter and their precursors [7]. It is present in cigarette smoke at 100-360 μg per cigarette [8].

Triton X-100 (poly ethylene glycol P- (1, 1, 3,3-tetramethyl butyl) –phenyl ether (or) octyl phenol ethoxylate (or) polyoxy ethylene octylphenyl ether) is a non-ionic surfactant which has a hydrophobic polyethylene oxide group and a hydrophobic group. The hydrocarbon group is a 4-(1,1,3,3-tetramethylbutyl) – phenyl group. It can be used to permeabilize eukaryotic cell membranes. It is also used in conjunction with zwitterionic detergents to solubilize membrane proteins in their native state. They can solubilise, concentrate and compartmentalize ions and molecules [9-11]. Protonation constants of L-dopa and catechol were determined in various media [12-15]. The effect of surfactants on protonation equilibria of various α-amino acids studied earlier in our laboratory [16-19]. Therefore, the effect of non-ionic micelles on protonation equilibria of L-Dopa and Catechol in TX100-water mixtures has been investigated. An insight into the protonation equilibria is also helpful in understanding the metal-ligand equilibria associated with these ligands.

MATERIALS AND METHODS

Materials: Solutions (0.05 mol L^{-1}) of L-dopa (Loba, India) and catechol (Finar, India) were prepared in triple-distilled water by maintaining 0.05 mol dm^{-3} acid (HCl) concentration to increase the solubility. TX100 (MW = 647, d = 1.07; Merck) were also prepared in triple-distilled water. Sodium chloride (Qualigens, India) of 2 mol L^{-1} was prepared to maintain the ionic strength in the titrant. 0.4 mol L^{-1} Sodium hydroxide (Qualigens, India) was prepared. Acid and alkali solutions were standardized by standard methods. To assess the errors that might have crept into the determination of the concentrations, the data were subjected to analysis of variance of one way classification (ANOVA) [20]. The strengths of alkali and mineral acid were determined using the Gran plot method [21].

Alkalimetric titrations: Alkalimetric titrations were carried out in media containing varying compositions of TX100-water (0.5–2.5% v/v) maintaining an ionic strength of 0.16 mol L^{-1} with sodium chloride at 303 ± 0.05 K. An Elico LI-120 pH meter was used. Potassium hydrogen phthalate (0.05 mol L^{-1}) and borax (0.01 mol L^{-1}) 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 mmols. The glass electrode was equilibrated in a well stirred TX100-water mixture containing inert electrolyte for several days. At regular intervals strong acid was titrated against alkali to check the complete equilibration of the glass electrode. The calomel electrode was refilled with TX100-water mixture of equivalent composition as that of the titrand. The details of experimental procedure and titration assembly have been detailed elsewhere [22]. Typical alkalimetric titrations are given in figure 1.

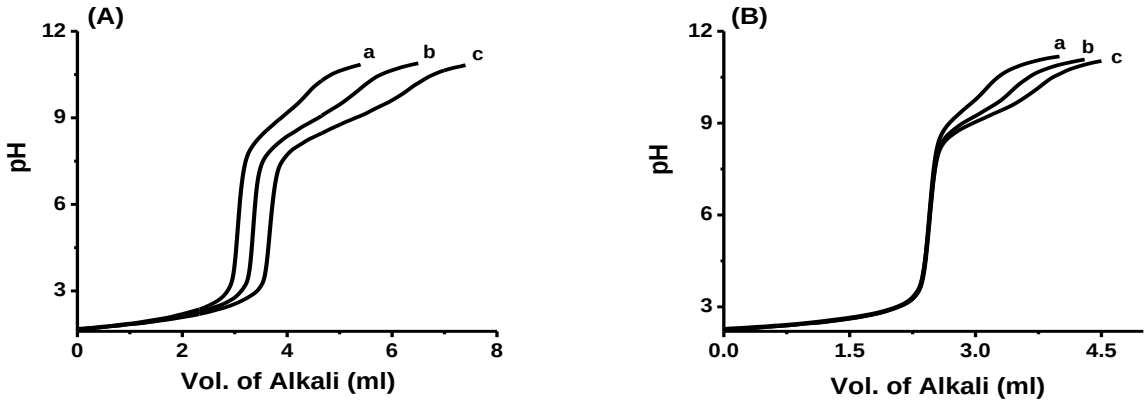

Figure 1. Alkalimetric titration curves in 1.0% v/v TX-100-water mixture: **(A)** Dopa and **(B)** Catechol, (a) 0.25, (b) 0.375 and (c) 0.50 mmol, respectively.

Modeling strategy: The approximate protonation constants of L-dopa and catechol were calculated with the computer program SCPHD [23]. The best fit chemical model for each system investigated was arrived at using MINIQUAD75 [24]. The variation of stepwise protonation constants was analyzed on electrostatic grounds on the basis of solute-solute and solute-solvent interactions.

RESULTS AND DISCUSSION

Secondary Formation Functions: Secondary 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 and polymeric species, respectively. Plots of $\bar{n}H$ versus pH for different concentrations of ligand (formation curves) should overlap if there is no formation of polymeric species. The present study overlapping formation curves for dopa and catechol (Figure 2) rule out the polymerization of the ligand molecules. The pH values at half integral values of $\bar{n}H$ correspond to the protonation constants of the ligands. Three half integrals (0.5, 1.5 and 2.5) in the case of dopa corresponding to log K_1, log K_2 and log K_3 values and only one half integral (0.5) in the case of catechol corresponding to log K_1 value. Three values are observed (Fig. 2A) in the case of dopa but only one value for catechol (Fig. 2B) because log K_2 is out of the pH range of the study for the latter. The presence of three and one protonation-deprotonation equilibria in the pH range of present study.

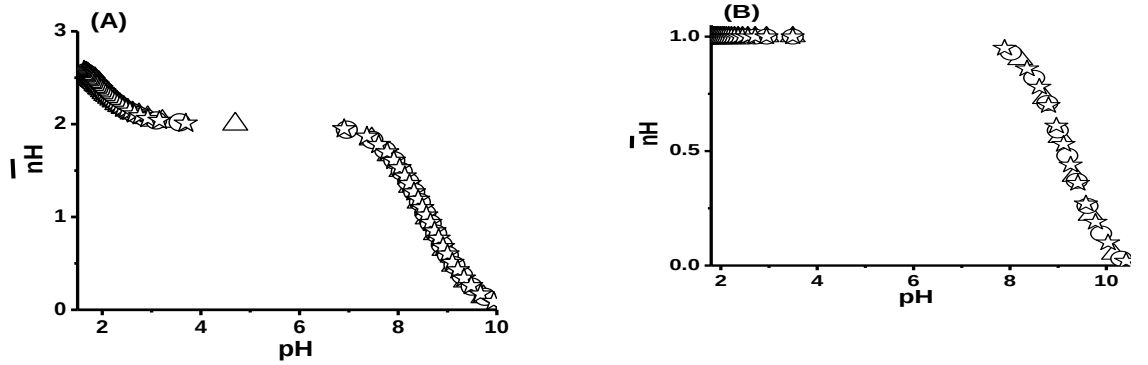

Figure 2. Plots of $\bar{n}H$ versus **pH** in 2.0% v/v TX100-water mixture, (A) Dopa (B) Catechol.

The plots of **a** versus pH are given in Figure 3. 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** (Figure 3A) is +3, which clearly infers that dopa has three dissociable (one carboxyl and two phenolic) protons. The corresponding value for catechol (Figure 3B) is +1, which indicates that catechol has one dissociable (phenolic) proton. The second phenolic proton is out of the pH range of study.

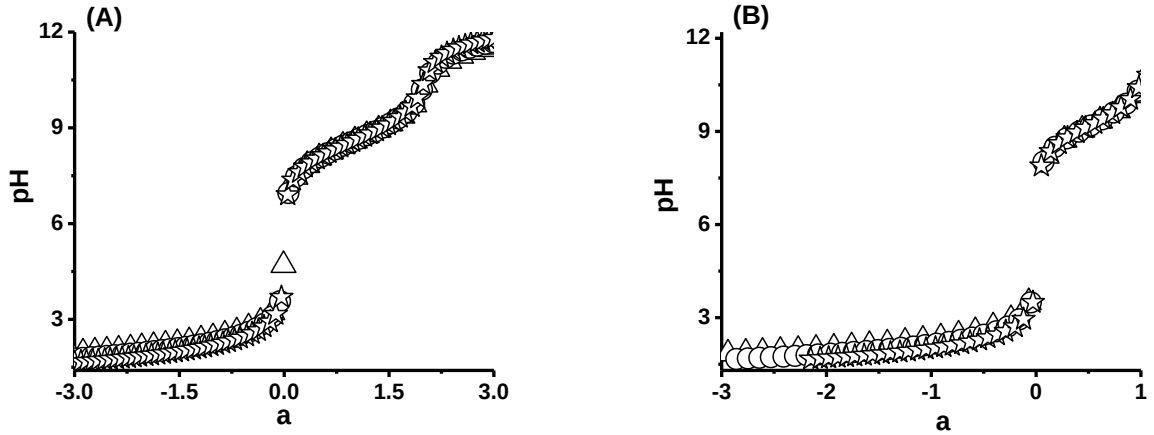

Figure 3. Plots of **pH** versus **a** in 1.5% v/v TX100-water mixture, (A) Dopa (B) Catechol.

Protonation equilibria: Dopa contains two ionizable phenolic protons (catecholate) in addition to carboxylic and amino protons. Its neutral ligand form is a tribasic acid, H_3L, with four potential co-ordination centers. So dopa possesses four protonation constants corresponding to four protons in H_4L^+ form. The first proton has a very high affinity for L^{3-} ion to coordinate phenolate ion (log K~13). The next two protons coordinate to the other phenolate oxygen and the amine nitrogen. These two formation reactions overlap. The fourth proton to coordinate is the carboxyl proton (log K~2). From spectroscopic evidence Martin [25,26] and Gergely et al [27] concluded that the amine group has higher affinity for protons than the second phenolate oxygen which was criticized by Jameson [28]. He interpreted that the phenolate oxygen protonated first (log K_{OH} = 9.76) followed by the amine nitrogen (log K_{NH3+} = 8.93). The uncertainty was resolved by a proton NMR study in D_2O solution [29]. This study identified the second phenolic group of dopa to be more acidic (log K_{OH} = 8.78) than the amino group (log K_{NH3+} = 9.76). Other literature values reported [30-36] allowed the calculation of recommended protonation constants at 25°C and I = 0.1 to 0.2 M to be log K_{HL} = 13.4, log K_{H2L} = 9.84, log K_{H3L} = 8.77 and log K_{H4L} = 2.21. Catechol contains two ionizable phenolic protons (catecholate). Its neutral ligand form is a dibasic acid, with two potential co-ordination centers. So catechol possesses two protonation constants corresponding to two protons in H_2L form. From the various literature [37-45] protonation constant values reported at 18°-26°C and I = 0.06 to 0.15 M phenolate oxygen protonated first (log K_{OH} = 9.21) and second phenolate oxygen protonated (log K_{OH}~13). In present study only one protonation constant value is reported. The second protonation constant value is out of pH range (log K_{OH}~13) in the present study.

The analysis of alkalimetric titration data of dopa and catechol in TX100-water media show that the acido-basic equilibria are active in the pH range 1.60-10.50 and 7.00-10.00, respectively. The best fit models that contain the type of species and log values of overall formation constants (log β) along with some of the important statistical parameters of the present study are given in table 1. A very low standard deviation (SD) in log β values, U_{corr} (sum of the squares of deviations in concentrations of ligand and hydrogen ion at all experimental data points corrected for degree of freedom) indicate that the experimental data can be represented by the model. Small values of mean, standard deviation and mean deviation for the systems corroborate that the residuals are around a zero mean with little dispersion.

Table 1. Parameters of best fit chemical models of acido-basic equilibria of Dopa and Catechol in aqua-TX100 mixtures. Temperature = 303 K, Ionic strength=0.16 mol dm^{-3}.

% v/v TX100	log β_1(SD)	log β_2(SD)	log β_3(SD)	NP	U_{corr}	Skew-ness	χ^2	Kurtosis	R-factor
L-Dopa (pH range 1.60-3.00 & 7.00-10.50)									
0.0	9.91(9)	18.74(1)	21.10(1)	145	1.70	0.90	39.16	5.46	0.004
0.5	9.15(1)	17.43(6)	19.45(9)	92	0.82	-0.64	10.96	3.82	0.003
1.0	9.01(1)	17.28(1)	19.41(1)	124	1.70	0.92	11.94	5.62	0.004
1.5	9.10(8)	17.39(8)	19.52(1)	109	1.43	1.38	16.28	7.68	0.005
2.0	8.98(2)	17.18(2)	18.94(3)	111	7.11	0.71	11.44	4.75	0.041
2.5	8.94(1)	17.15(1)	19.37(2)	123	7.60	1.02	21.64	5.48	0.021
Catechol (pH range 7.00-10.00)									
0.0	9.25(9)	-	-	28	2.16	1.94	14.57	7.71	0.016
0.5	9.22(1)	-	-	27	5.59	1.47	4.96	5.22	0.025
1.0	9.20(2)	-	-	30	13.45	0.74	5.07	3.13	0.039
1.5	9.18(2)	-	-	25	12.60	1.27	6.96	4.72	0.038
2.0	9.16(1)	-	-	25	7.80	0.89	3.76	3.32	0.030
2.5	9.13(1)	-	-	28	7.60	1.81	16.86	5.86	0.030

Residual Analysis: 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 [20]. 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 dopa and catechol in TX100-water mixtures, as discussed below.

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 χ^2 calculated is less than the table value, the model is accepted.

Crystallographic R-test: Hamilton's R factor ratio test [46] 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 1 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 1 are between –0.64 to 1.38 for dopa, and 0.74 to 1.94 for catechol. 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 leptokurtic pattern in dopa and catechol.

Effect of systematic errors on best fit model: Any variation in the concentrations of ingredients like alkali, mineral acid and ligand affects the magnitudes of protonation constants. Such parameters are called influential or dangerous parameters. 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 influential parameters. The results of a typical system given in table 2 emphasize that the errors in the concentrations of alkali and mineral acid affect the protonation constants more than that of the ligand.

Table 2. Effect of errors in influential parameters on the protonation constants in 1.5% v/v aqua- TX100 mixture.

Ingredient	% Error	log β (SD)			
		L- Dopa			catechol
		LH	LH_2	LH_3	LH
	0	9.10(8)	17.39(8)	19.52(1)	9.18(2)
Acid	-5	8.85(2)	16.98(2)	28.77(3)	8.94(3)
	-2	9.00(1)	17.22(1)	19.22(1)	9.09(2)
	+2	9.20(9)	17.56(9)	19.82(1)	9.28(2)
	+5	9.36(1)	17.82(1)	20.29(2)	9.43(3)
Alkali	-5	9.50(1)	17.98(1)	20.33(2)	9.49(2)
	-2	9.26(9)	17.61(9)	19.83(1)	9.30(2)
	+2	8.95(1)	17.18(1)	19.23(2)	9.07(2)
	+5	8.72(3)	16.90(2)	18.83(4)	8.89(4)
Ligand	-5	8.96(1)	17.27(1)	19.45(2)	9.13(2)
	-2	9.05(9)	17.34(9)	19.49(1)	9.16(2)
	+2	9.16(7)	17.44(7)	19.55(1)	9.20(2)
	+5	9.24(6)	17.51(7)	19.60(1)	9.23(1)
logF	-5	9.10(8)	17.38(8)	19.48(1)	9.15(2)
	-2	9.10(8)	17.38(8)	19.50(1)	9.17(2)
	+2	9.14(1)	17.46(1)	19.79(2)	9.20(2)
	+5	9.11(9)	17.40(9)	19.57(1)	9.21(2)
Volume	-5	9.10(9)	17.39(9)	19.56(1)	9.17(2)
	-2	9.10(8)	17.39(8)	19.54(1)	9.17(2)
	+2	9.10(8)	17.39(7)	19.50(1)	9.17(2)
	+5	9.10(8)	17.39(8)	19.48(1)	9.17(2)

Effect of micelles: The apparent shift in the magnitude of protonation constants in micellar media compared to aqueous solution (Figure 3) was attributed to the creation of concentration gradient of protons between the interface and the bulk solution [47] Further the presence of micelles is known to alter the dielectric constant of the medium, which has direct influence on the protonation deprotonation equilibria [48-50]. The effect of dielectric constant on the protonation equilibria of dopa in dioxan-water mixture was reported earlier in our laboratory [51] where the log values of protonation constants of dopa increased linearly with decreasing dielectric constant of the medium.

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 [52]. According to this treatment, the energy of electrostatic interaction or the logarithm of step-wise protonation constant (log K) should vary linearly as a function of the mole fraction of the medium. Such linear variation of the protonation constants of dopa (Figure 4A) in TX100-water mixture shows the dominance of electrostatic interactions.

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 [53-55]. The effective dielectric constant of TX-100 is 36 [56]. The surfactant concentration maintained in the present study is below critical micellar concentration, so that micelles are ensured in the solution. The ionic charge increases during protonation of phenolate ion. The charge increases dielectric constant increase of the medium. Hence the magnitude of the protonation constants must decrease as the surfactant concentration decreases. The log K value of catechol linearly decrease with mole fraction of the medium (Figure 4B). This may be because catechol has no associable protons.

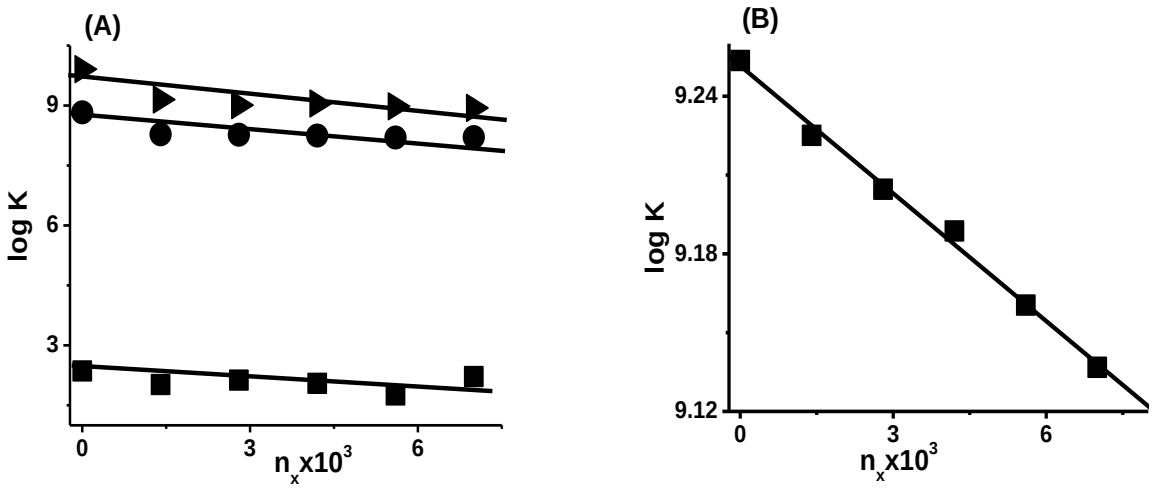

Figure 4. Variation of stepwise protonation constant (log K) with mole fraction of TX100 in TX100-water mixture. (A) Dopa, (B) Catechol, (■) log K_1, (●) log K_2, (►) log K_3.

Distribution diagrams: The distribution plots (Figure 5) produced using the protonation constants from the best fit models (Table 1) show the existence of LH_4^+, LH_3, LH_2^- and LH^{2-} in the case of dopa and LH_2 and LH^- in the case of catechol in different pH ranges. The LH_4^+ species is predominant at low pH. As the pH increases its concentration decrease exponentially and becomes almost zero at pH = 5. The LH_3 and LH_2^- species of dopa maximum concentration at pH = 6 and 9. In case of catechol LH_2 species concentration decrease and becomes almost zero at pH = 11. The LH^{2-} (dopa) and LH^- (catechol) species concentration progressively increases and attains the maximum at higher pH values.

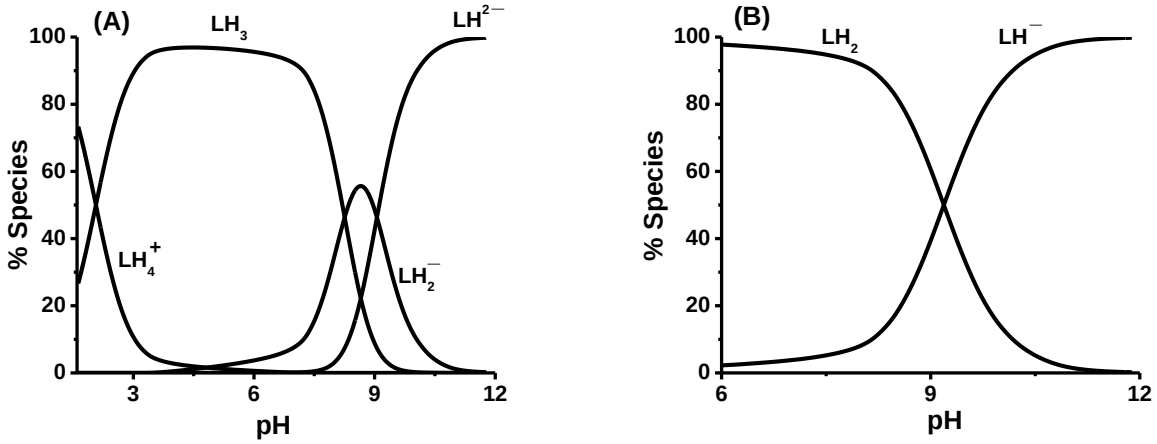

Figure 5. Species distribution diagrams of (A) Dopa, (B) Catechol in 1.5% v/v TX100-water mixture.

Alkali is added to the titrand containing the ligands, the protonated forms of the ligands lose their protons. In the pH range of study, dopa loses carboxylic, phenolic and amino protons successively. The second phenolic proton is lost at pH greater than 13.0. Hence, under present experimental conditions the most deprotonated form of dopa is LH^{2-}. Similarly the second phenolic proton of catechol is lost at pH greater than 13.0. In the present study, the pH range is 8.0-10.0 the most deprotonated form of catechol is LH^{-}. So only one protonation constant is reported. The corresponding protonation-deprotonation equilibria are shown in Figure 6.

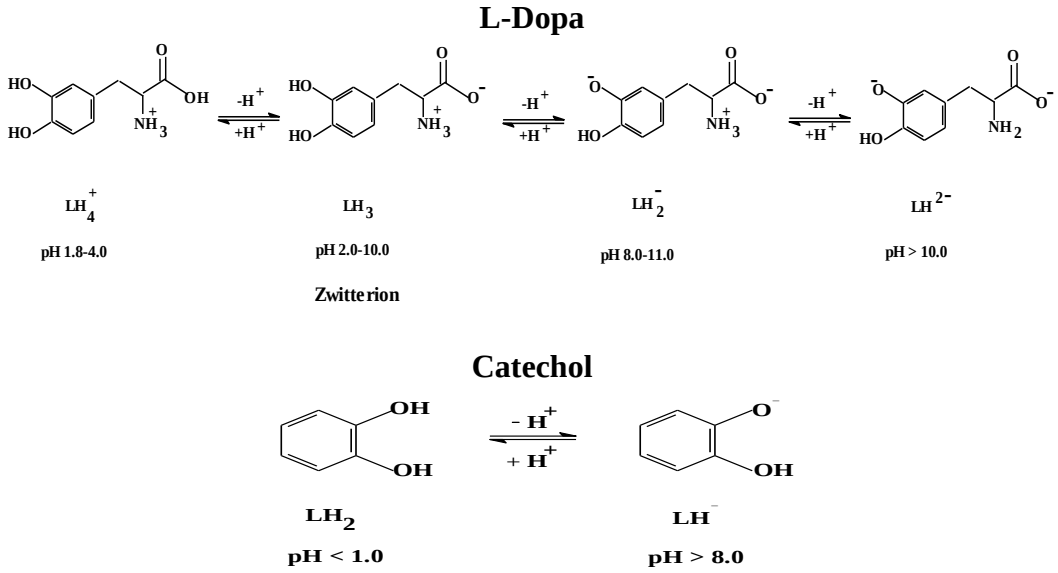

Figure 6. Protonation-deprotonation equilibria of Dopa and Catechol.

APPLICATIONS

The protonation equilibria is also helpful in understanding the metal-ligand equilibria associated with these ligands. Hence speciation study of essential metal ion complexes is useful to understand the role played by the active site cavities in biological molecules and the bonding behavior of protein residues with metal ions.

CONCLUSIONS

1. The overlapping formation curves for different concentrations of the ligands indicated that no condensed species are formed.
2. The half $\bar{n}H$ values of L-dopa and Catechol indicated that they have three and one protonation constants, respectively.
3. The linear variation of step wise protonation constants of dopa and catechol with mole fraction of TX100–water mixtures confirmed the dominance of electrostatic forces over non-electrostatic forces of on the protonation–deprotonation equilibria.
4. The effect of systematic errors in the influential parameters shows that the errors in the concentrations of alkali and ligand will affect the protonation constants more than that of the mineral acid.

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