

Shift in pKa of 1,10-Phenanthroline in TBAB and PEG-400 Micellar Media: A Potentiometric Study

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Abstract

The acid-base equilibrium of 1,10-phenanthroline (1,10-phen) in the presence of polyethylene glycol 400 (PEG-400, non-ionic) and tetrabutylammonium bromide (TBAB, ionic) micellar media has been studied by Calvin-Wilson titration technique at different mole fractions (0.5% - 2.5%) of PEG-400 and TBAB micellar solutions at an ionic strength of 0.16 mol dm⁻³ NaCl and at a temperature of 298 K. The pH metric data were subjected to SCPHD program to obtain correction factor and K_w which were given as initial inputs for MINQUAD75 program to refine protonation constants. HySS program was then used to generate the species distribution diagrams versus pH using the results obtained from the MINQUAD75 program and SIM run data. The difference in values of protonation constants in aqueous medium (logβ₁ = 4.93 & logβ₂ = 6.22) and in the micellar media (PEG-400, logβ₁ = 4.89 & logβ₂ = 5.91 and TBAB, logβ₁ = 4.84 & logβ₂ = 5.73) is attributed to different intrinsic solvent characteristics of micelles. In case of ionic surfactants, the electrostatic micellar surface is an additional contributing factor.

Keywords

Protonation Equilibria, 1,10-Phenanthroline, MINQUAD75, PEG-400, TBAB Micelles

1. Introduction

1,10-phenanthroline (1,10-phen) is a neutral hetero cyclic bidentate ligand

which forms coloured stable metal complexes that are insoluble in water and soluble in organic solvents [1]. Several reports are published in literature on the use of 1,10-phen as a chromogenic reagent for spectroscopic determinations of metal ions in low concentrations [1] [2]. Since high concentrations of 1,10-phen are insoluble in water, organic solvents are used either for determination or extraction. However, Green chemistry requires the elimination of toxic organic solvents from various analytical procedures [3]. So surfactants are used in place of organic solvents, and the surfactant modified procedures are more sensitive, selective and accurate compared to earlier methods [4]. Surfactants are amphiphilic compounds having hydrophilic head and hydrophobic tail and above a certain concentration form into aggregates called micelles. These micelles have the ability to solubilize a variety of compounds, polar to non-polar [5]. When a solute is incorporated into a micelle, equilibria like acid-base and metal ligand are affected due to a combination of electrostatic and micro environmental factors [6]-[14]. In order to study these changes in micellar systems, 1,10-phen has been taken as a probe in the presence of two surfactants of different nature, one non-ionic, polyethylene glycol 400 (PEG-400) and one ionic, tetrabutylammonium bromide (TBAB). The results are reported in this paper.

2. Materials and Methods

2.1. Materials

All solutions were made in doubly distilled water through which nitrogen gas was purged to expel dissolved gases (oxygen or carbon dioxide). All chemicals used were of analytical reagent grade. A solution of $0.05 \text{ mol}\cdot\text{dm}^{-3}$ 1,10-phen (Sigma-Aldrich, India), was prepared in $0.05 \text{ mol}\cdot\text{dm}^{-3}$ HCl. A $\sim 0.4 \text{ mol}\cdot\text{dm}^{-3}$ of sodium hydroxide (Merck, India) was prepared and standardized against potassium hydrogen phthalate. It was regularly Gran-titrated [14] [15] to check the absence of carbonates. A solution of $0.2 \text{ mol}\cdot\text{dm}^{-3}$ hydrochloric acid (Merck, India), prepared by successive dilutions was standardized against a standard solution of $0.4 \text{ mol}\cdot\text{dm}^{-3}$ NaOH. PEG-400 (Merck, India) and TBAB (Merck, India) were used as received from which, 0.5% - 2.5% (v/v) solutions have been prepared. A $2.0 \text{ mol}\cdot\text{dm}^{-3}$ solution of sodium chloride (Merck, India) was prepared to maintain an ionic strength of $0.16 \text{ mol}\cdot\text{dm}^{-3}$.

2.2. Methods

Potentiometric titrations were carried out using Metrohm 877 titrimo plus auto-titrator (Switzerland) (readability 0.001) in conjunction with a combination electrode (0 - 14 pH range) for pH measurements at a temperature of 298 K. The electrode was calibrated with $0.1 \text{ mol}\cdot\text{dm}^{-3}$ potassium hydrogen phthalate solution (pH 4.01) in the acidic region and $0.05 \text{ mol}\cdot\text{dm}^{-3}$ borax solution (pH 9.18) in the basic region. Three replicate titrations were always conducted and it was observed that the three measurements differ by not more than 0.02 units.

After calibrating the glass electrode by freshly prepared potassium hydrogen

phthalate ($0.1 \text{ mol}\cdot\text{dm}^{-3}$) and borax ($0.05 \text{ mol}\cdot\text{dm}^{-3}$) solutions, it was equilibrated in a well stirred 0.5% PEG-400 water solution containing inert electrolyte. Complete equilibration of the glass electrode was checked through titration of the strong acid with alkali at regular intervals prior to alkalimetric titrations. Whenever the experiments were conducted in different percentage of surfactants, the electrodes were equilibrated in that particular surfactant percentage.

In each titration, the titrand consisted of requisite volumes of hydrochloric acid, sodium chloride and the ligand, the values of which were calculated based on achieving total fixed ionic strength of $0.16 \text{ mol}\cdot\text{dm}^{-3}$ in a total volume of 50 mL. Alkalimetric titrations were then conducted by adding 0.05 mL of $0.4 \text{ mol}\cdot\text{dm}^{-3}$ NaOH. The titrations were conducted in both the surfactants at various concentrations of the surfactants (0.5% - 2.5% v/v) and at different concentrations of 1,10-phen [14] [15] (0.25, 0.375 and 0.50 mmol).

3. Results and Discussion

3.1. Data Acquisition and Analysis

Calvin-Wilson titration technique as modified by Irving and Rossotti [16] was used for the determination of protonation constants in micellar media. After each addition of NaOH, the pH meter reading was recorded. The pH metric titration data for 1,10-phen in the two micellar media, TBAB and PEG-400 were obtained from origin 8.5 as shown in **Figure 1**.

The effect of variations in the asymmetric potential, 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 and K_w obtained from SCPHD [17] program, which was developed in this laboratory. The correction factor and K_w were used as initial estimates for MINIQAD75 program [18] to determine the protonation constants of the ligand. **Table 1** contains two protonation constants $\log K_1$ and $\log K_2$ corresponding to LH^+ and LH_2^{2+} .

3.2. Protonation Constants

The acid-base equilibria of 1,10-phen in TBAB- and PEG-400-water mixtures (0.0% - 2.5% v/v) were found to be in the pH range of 1.6 - 7.0 and 1.48 - 7.0, respectively. The best fit models containing the type of species and overall formation constants ($\log\beta$) along with some of the important statistical parameters are given in **Table 2**.

Distribution Diagrams:

The species distribution plots (**Figure 2**) were generated by giving the protonation constants from the best fit models (**Table 2**) as input in to HySS [22], which show the existence of LH_2^{2+} and LH^+ for 1,10-phen in different pH ranges. The LH_2^{2+} species is predominant at low pH. As the pH increases its concentration decreases exponentially. The LH^+ species exists in the pH range 1.5 - 6.0 and L species exists above pH 3.0.

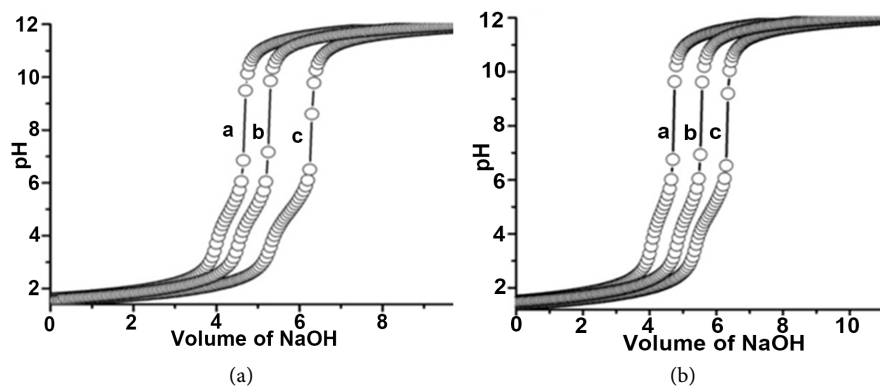


Figure 1. Alkalimetric titration curves in 1.5% (v/v) (a) TBAB-water mixtures and (b) PEG-400-water mixtures: 1,10-phenanthroline; (a) 0.25, (b) 0.375 and (c) 0.50 mmol, respectively.

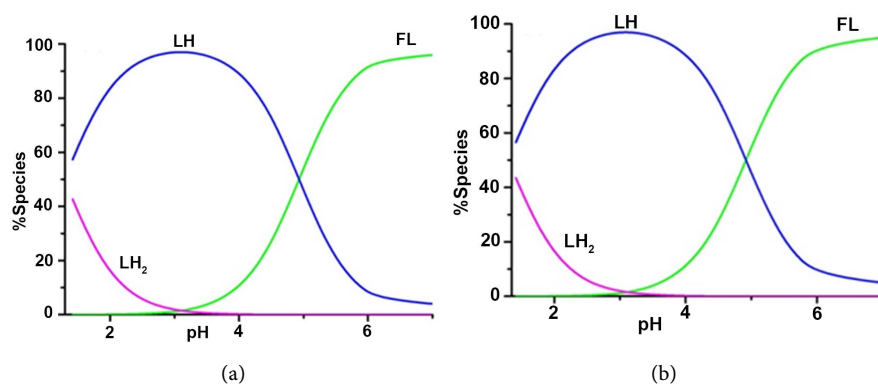


Figure 2. Species distribution diagrams of 1,10-phenanthroline in (a) 1.5% w/v TBAB-water and (b) 1.5% v/v PEG-400-water mixtures.

Table 1. Comparison of protonation constants of 1,10-phen in PEG-400 and TBAB along with literature values.

Log K_1	Log K_2	Solvent	Method	Reference
4.86	1.5	Aqueous	potentiometric	[19]
5.00	--	Dioxan-water (10%)	potentiometric	[20]
4.97	--	Glycol-water (10%)	potentiometric	[21]
4.93	1.29	Aqueous	Potentiometric	Present study
4.84	0.89	TBAB (ionic micellar)	Potentiometric	Present study
4.89	1.02	PEG-400 (non-ionic micellar)	Potentiometric	Present study

Effect of Systematic Errors on Best Fit Model:

A very low standard deviations (SD) in $\log \beta$ values and U_{corr} (sum of squares of residuals in all mass-balance equations) obtained in the present study indicate that the experimental data can be represented by the best fit model.

MINIQUAD75 or other similar programs do not have any built in provision to recognize or overcome these errors. An investigation was conducted by

Table 2. Best fit chemical model of protonation equilibria of 1,10-phen in micellar media. Temp. 298 K, Ionic strength 0.16 mol-dm⁻³.

Surfactants%	Log β_{mlh} (SD)		NP	U _{corr}	Skewness	χ^2	R-Factor	Kurtosis	pH-Range
	011	012							
TBAB									
0.0	4.93(1)	6.16(4)	90	1.0	0.27	9.87	0.0050	3.04	1.6 - 7.0
0.5	4.92(1)	6.11(2)	106	1.9	0.24	23.17	0.0108	2.10	1.9 - 7.0
1.0	4.90(1)	5.87(2)	90	1.4	0.02	19.38	0.0058	2.81	1.61 - 7.0
1.5	4.84(2)	5.73(3)	89	1.4	0.19	5.91	0.0056	3.76	1.54 - 7.0
2.0	4.70(2)	5.65(6)	50	2.0	0.14	8.32	0.01240	1.87	1.72 - 7.0
2.5	4.68(4)	Rejected	26	1.7	0.27	10.77	0.04806	2.48	2.0 - 7.0
PEG-400									
0.0	4.93(1)	6.16(4)	90	1.0	0.27	9.87	0.0050	3.04	1.6 - 7.0
0.5	4.84(1)	5.83(2)	86	0.7	0.16	2.42	0.0046	2.52	1.6 - 7.0
1.0	4.88(2)	5.88(2)	99	0.9	0.22	12.10	0.0042	3.12	1.5 - 7.0
1.5	4.89(3)	5.91(2)	105	0.8	0.15	14.08	0.0036	4.46	1.45 - 7.0
2.0	4.93(2)	5.94(2)	51	1.3	-0.05	2.00	0.0094	2.50	1.95 - 7.0
2.5	4.94(2)	5.99(3)	64	1.08	-0.06	9.75	0.0069	3.03	1.96 - 7.0

deliberately introducing errors in the influential parameters. The outcomes of a typical system (**Table 3**) show that the incorporated errors in the concentrations of alkali and mineral acid affect the protonation constants more than that of the ligand concentration.

Effect of Micelles:

Micelles are known to have an anisotropic water distribution within their structure. The water concentration decreases from the surface towards the core of the micelle which is totally hydrophobic. As a result, the microviscosity, micropolarity and degree of hydration are not uniform in the micelle [8] [9].

The position of solute depends on its polarity and is the primary factor which affects the acid-base equilibria. Non polar molecules are stabilized in the micellar core, substances with intermediate polarity are distributed along the surfactant molecules in the intermediate positions and highly polar compounds at the surface.

In the case of ionic surfactants where the head group is either positively or negatively charged in addition to this micro environmental factor, electrostatic effects also become an important parameter. There is an ion-pair formation between oppositely charged solute species and head group of surfactant [10] [11] [12].

The effect of PEG-400, a non-ionic surfactant and TBAB, anionic surfactant on the acid base equilibria of 1,10-phen has been studied. **Table 4** shows that the log K_1 value is much lower in TBAB compared to PEG-400 and aqueous

Table 3. Effect of errors in concentrations of components of titration mixtures on the protonation constants of 1,10-phenanthroline.

Ingredient	% Error	$\log \beta_{\text{mlh}}$ (SD)			
		TBAB		PEG-400	
		0 11	012	011	012
Alkali	0	4.84 (2)	5.73 (3)	4.89 (3)	5.91 (3)
	-5	5.69 (11)	6.97 (12)	6.09 (18)	7.64 (19)
	+5	3.94 (11)	5.10 (11)	3.46 (12)	4.84 (12)
	-2	5.15 (6)	6.21 (4)	5.35 (4)	6.55 (6)
	+2	4.53 (5)	5.23 (8)	4.50 (4)	5.34 (6)
Acid	-5	4.01 (11)	Rejected	2.60 (6)	Rejected
	+5	5.73 (9)	7.55 (10)	5.92 (12)	7.92 (13)
	-2	4.59 (3)	5.32 (5)	4.50 (5)	5.91 (6)
	+2	5.21 (3)	6.58 (4)	5.27 (4)	6.70 (5)
	-5	4.96 (2)	6.14 (2)	4.94 (2)	6.11 (2)
Ligand	+5	4.85 (1)	5.57 (3)	4.82 (2)	5.62 (3)
	-2	4.92 (1)	5.98 (2)	4.91 (2)	5.97 (2)
	+2	4.88 (1)	5.76 (2)	4.86 (2)	5.78 (2)

Table 4. Protonation equilibria of 1,10-phen and its step-wise protonation constants.

S.No.	Protonation equilibria of 1,10-phen	Step-wise protonation constants	Water	PEG-400	TBAB
1		Log K_1	4.93	4.89	4.84
2		Log K_2	1.29	0.99	0.89

medium. This is because the LH^+ form is destabilized more in the presence of TBAB compared to PEG-400, neutral surfactant due to electrostatic repulsions by cationic head group of the micelle. This facilitates the dissociation of LH^+ to L decreasing the corresponding protonation constant. In the case of PEG-400, this electrostatic effect is absent and polarity effect is the only factor which plays a major role. The dielectric constant of micellar phase is lower than that of water and so when 1,10-phen is solubilized, L form is more stabilized, the association equilibrium is shifted to the left and protonation constant decreases.

Further protonation leads to the formation of LH_2^{2+} , which is also affected by micellar media. Relatively lower values of $\log K_2$ were observed in TBAB and

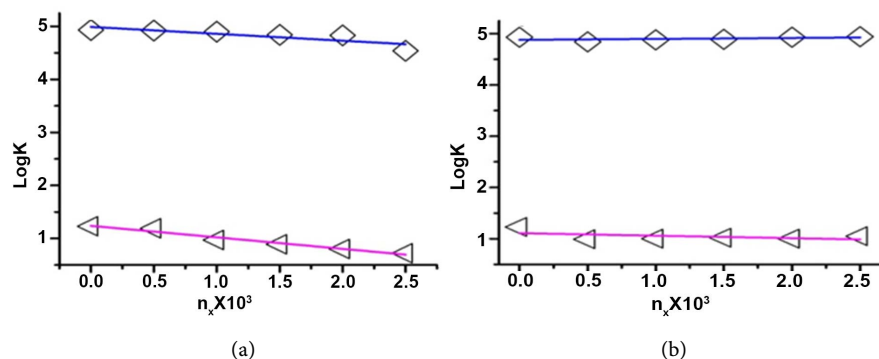


Figure 3. Variation of stepwise protonation constant ($\log K$) of 1,10-phen with mole fraction of surfactant. (a) TBAB and (b) PEG-400; (Δ) $\log K_1$, (\diamond) $\log K_2$.

PEG-400 compared to water. In the case of TBAB, the LH_2^{2+} form is less favorable and hence decreases the protonation constants. In the case of PEG-400, the surface charge effects are absent but due to lower dielectric constant compared to water, the LH^+ form is more preferred. This accounts for the lower formation constant. Both the $\log K_1$ and $\log K_2$ decrease with increase in percentage of TBAB while there is not much of variation in the case of PEG-400 (Figure 3). This is because of extra stabilization/destabilization of the charged species in the case of TBAB which is absent in PEG-400.

4. Conclusions

- In this study, successful determination of two $\log \beta$ values for 1,10-phenanthroline was possible at low pH using the Calvin-Wilson titration technique and MINIQUAD75 program.
- 1,10-phen exists as LH_2^{2+} at low pH and gets deprotonated with the formation of LH^+ and L with increasing pH of the titration mixture.
- Effect of systematic errors in the influential parameters shows that the errors in the concentrations of alkali and mineral acid were found to affect the protonation constants more than that of the ligand did.
- $\log \beta$ values of 1,10-phen in both the micellar media are found to be less than in water. They are much lower in the ionic micellar medium TBAB compared to those in PEG-400.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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