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Charge-Transfer Complexometric Study of Ferric Ion with 4-Chloro-2,6-bis(hydroxymethyl)phenol in a Methanol−Water System Using Spectrophotometric and Potentiometric Methods

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Complex formation between ferric ions and 4-chloro-2,6-bis(hydroxymethyl)phenol in 0.3 mole fraction of methanol and 0.10 M tetraethylammoniumbromide as inert ionic medium has been studied at 25.0 °C using spctrophotometric and potentiometric methods. This charge-transfer complex has a strong absorbance in 580 nm. Ferro ions do not have any significant interaction with this ligand. In both spectrophotometric and potentiometric methods, it was found that only the MLH_2 and MLH_3 species are formed in the pH range 2.0 to 11.5. The M:L ratio of the complex is also obtained by continuous variation and mole ratio methods, which is equal to 1:1 for this complex.

Spectrophotometric methods are in general highly sensitive and are more suitable for studying chemical equilibria in solution and have been used to infer equilibrium constants for many decades.[1−3] Although potentiometric pH titration is more convenient and more commonly used due to its simplicity of the equipment and minimal time requirements, spectrophotometry is one of the most powerful methods for the investigation of solution equilibria. In other words, the combination of these methods can confirm each other. Potentiometric methods are limited to the pH range of 2.0 to 11, whereas spectrophotometric methods are not limited to any pH range or to nonaqueous solutions.

In this study, the formation constants of the 4-chloro-2,6-bis(hydroxymethyl)phenol−ferric ion system were calculated using the BEST program[4,5] via the potentiometric method. This program is for the refinement of formation constants on complex systems containing any number of interacting components. In the spectrophotometric method, the EQUISPEC program[6] was used to calculate the formation constants of the 4-chloro-2,6-bis(hydroxymethyl)phenol−ferric ion system. This program is a computer program using the matrix-based MATLAB environment for second-order global analysis of spectrophotometric equilibrium data.

4-Chloro-2,6-bis(hydroxymethyl)phenol (the equilibria of this ligand are shown in Figure 1) is one of the significant precursors for preparation of an important series of compounds such as phloroglucid analogues, polyphenol resins, and calix-arens, whose applications have been published elsewhere.[7−12] The ferric ion has a strong interaction with this ligand, and in our knowledge, there is only one report about this ligand[13] that is used for the determination of the ferric ion in the range of (0.1 to 50) mg/L and without any explanation of how; they estimated the M:L ratio in this complex to be equal to 1:3 (ML_3). In our study, investigation of this system was obtained by potentiometric and spectrophotometric methods and its stability constants were determined. The only species that were obtained by these methods were MLH_2 and MLH_3, and the ratio of metal to ligand also was checked by continuous variation and mole ratio methods to confirm that the M:L ratio is equal to 1:1 for this complex. The ferro ion does not have any significant interaction with this ligand; that is why this ligand can be used for determination of the ferric ion in the presence of the ferro ion.

Experimental Section

Reagents. All reagents were of analytical grade from Merck except KOH, which was from Fluka. These reagents were used without further purification. The KOH solution was standardized by potassium hydrogen phthalate. Triply distilled water was used in the preparation of all solutions. 4-Chloro-2,6-bis(hydroxymethyl)phenol was synthesized according to the literature.[11] The synthesized ligand was purified by short-column chromatography, and its purity was identified by means of ^1H NMR (DMSO-d_6, 250 MHz) and Fourier transform (FT)-IR (Shimadzue, 8300).

The NMR characteristics of this compound (4-chloro-2,6-bis (hydroxymethyl) phenol) are: ^1H NMR (DMSO-d_6, 250 MHZ) δ 8.73 (s, 1H, 1 phenolic OH exchangeable with D_2O), 7.17 (s, 2H, aromatic ring), 5.09 (s, 2H, 2 benzylic OH exchangeable with D_2O), 4.52 (s, 4H, $2CH_2$)].

The FT-IR characteristics of this ligand are: υ_{max} 3600−3100 (br, OH), 3100 (m, C−H, aromatic), 2890 (m, CH_2−H, aliphatic), 1600 (s, C−C, aromatic), 1250−1150 (m, C−O, aromatic, aliphatic), 750 (s, C−Cl) cm^{-1}.

Apparatus. The absorption spectra were recorded on a Shimadzu UV-160 1PC spectrophotometer, containing a thermoelectrically temperature-controlled cell holder (TB-85 Thermo Bath Shimadzu) in the wavelength range of (400 to 900) nm, using 1-cm matched silica cells. The pH measurements were carried out with a 654 Metrohm pH meter (Metrohm Ltd, CH-9100-Hersau Switzerland) using a combined glass electrode. A 100-μL eppendorf micropipet (±0.6%) was used for the addition of a standard base to the solution.

Procedure for Determination of K_w in the Methanol−Water System. Before each experiment, it is necessary to calibrate[5,14−15] the pH meter and electrode system in terms

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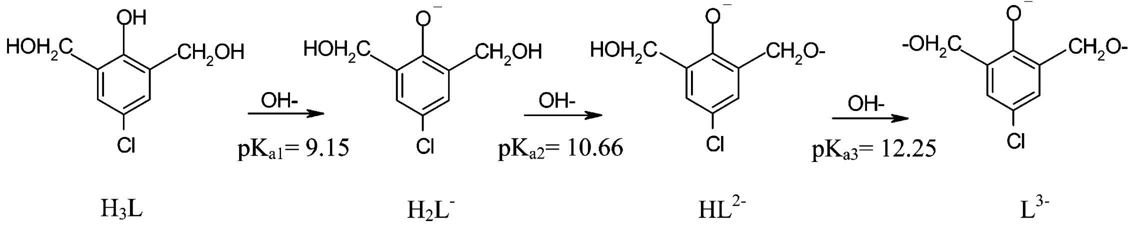

Figure 1. Equilibria for 4-chloro-2,6-bis(hydroxymethyl)phenol.

Table 1. Experimental Conditions of the Experiments Performed in Potentiometric Study at μ =0.10 M TEAB, t = (25.0 ± 0.1) °C in 0.3 Mole Fraction of Methanol

sample	M:L Ratio	C_L(M)	C_M (M)	pH range
A	1:1	3.40×10^{-3}	3.30×10^{-3}	2.51−3.97
B	1:2	6.95×10^{-3}	3.44×10^{-3}	2.59−4.00
C	1:3	3.00×10^{-3}	1.02×10^{-3}	2.92−4.05
D	1:3	8.90×10^{-4}	3.00×10^{-4}	3.28−4.05
E	1:10	1.01×10^{-2}	1.11×10^{-3}	2.80−4.01
F	1:5	1.01×10^{-3}	1.80×10^{-4}	3.57−11.20
G	1:10	1.02×10^{-3}	1.05×10^{-4}	3.67−11.25
H	1:13	1.04×10^{-3}	7.95×10^{-5}	3.80−11.21

of pH. For determination of K_w in the methanol−water mixture,[16] at ionic strength 0.10 M TEAB and $t = 25.0$ °C, the cell was charged with 5.0 mL of 0.10 M HCl, the appropriate amount of TEAB (to have 0.10 M TEAB in 50.0 mL of solution), and the appropriated volumes of methanol and water until the total volume was equal to 50.0 mL. The cell was capped (letting inert gas flow), equilibrated until pH drifts < 0.001 unit/5 min (usually between 5 min and 0.5 h), and titrated with standard KOH (which is prepared in 0.3 mole fraction of methanol). The ion product ($K_w = [H^+][OH^-]$) was determined by several series of $[OH^-]$ and pH measurements (the pH was measured from the pH meter, while $[OH^-]$ was calculated from the amount of base added to solution). K_w and then pK_w were calculated. The pK_w value that was obtained was 13.92 for a 0.3 mole fraction of methanol.

Procedure for Determination of pK$_a$ via Potentiometry.[16] The acidity constants were determined by titrating 50.0 mL of (2.00×10^{-3} to 2.00×10^{-2}) M analyte with KOH in each medium, and the ionic strength of the solution was adjusted by 0.10 M TEAB. The temperature was maintained at 25.0 °C by circulation of thermostated water through the jacket. Before doing each titration, the solution was allowed to equilibrate until pH drifts < 0.001 unit/5 min was obtained. N_2 gas was pumped through the solution to remove CO_2. During the titration, the pumping of N_2 was continued above the solution. To obtain each pK_a value, at least five titrations were made, and each titration had almost 44 points (in the pH range 5.5−11.5). It took 1−2 min to reach the equilibrium at each titration point, but around the equivalent point, it took a longer time to reach to the equilibrium. PKAS Martell's computer program[14] has been used to calculate the acidity constants of the 4-chloro-2,6-bis(hydroxymethyl)phenol, and these values are given in Figure 1.

Procedure for Calculation of Stability Constant. In this study, a different M:L solution ratio was examined as shown in Table 1. Typical concentrations of experimental solutions are in the order of 2.00×10^{-5} M to 2.00×10^{-4} M metal ions, and several times the molar equivalent concentrations of ligand in 50 mL of solution. The ionic strength of each solution was adjusted to 0.10 M by the addition of the appropriate amount of TEAB. The temperature was maintained at (25.0 ± 0.1) °C by circulation of thermostated water through the jacket. Before doing each titration, the solution was allowed to equilibrate until pH drifts < 0.001 unit/5 min (usually between 5 min and half an hour) were obtained. Carbon dioxide was excluded from the reaction mixture by maintaining a slight positive pressure of purified nitrogen in reaction cell. During the titration, the pumping of N_2 was continued above the solution. A solution of carbonate-free 0.049 M KOH was used as a titrant. The pH profiles obtained were consisted of approximately 35−40 pH measurements vs moles of standard based per moles of ligand in the experimental solution. The BEST computer program[4,5] has been used to calculate the stability constants of 4-chloro-2,6-bis(hydroxymethyl)phenol with the ferric ion.

In spectrophotometric studies, several series titrations contained different M:L ratios at a constant ionic strength of 0.10 M TEAB were prepared (Table 2). The spectra (baseline corrected) of the samples were recorded from (400 to 900) nm at 1-nm intervals. The EQUISPEC program[6,16−17] was used for the determination of the stability constants.

Results and Discussion

Potentiometric Method. In potentiometry, the variable measured is $-\log [H^+]$, and it is therefore appropriate to carry out the calculations with an algorithm, which calculates pH directly and minimizes the sum of the weighted squares of $-\log [H^+]$ residuals. The program BEST has evolved into a very useful and friendly interactive program which, although basically designed to solve for the set of equilibrium constants corresponding to the model selected, has features that make it possible to explore all aspects

Table 2. Experimental Conditions of Spectrophotometric Study at μ = 0.10 M TEAB, t = (25.0 ± 0.1) °C in 0.3 Mole Fraction of Methanol

sample	M:L Ratio	C_L(M)	C_M (M)	pH range	no. spectra
A	1:1	2.10×10^{-3}	2.08×10^{-3}	1.71−4.00	18
B	1:2	4.08×10^{-3}	2.01×10^{-3}	1.69−3.91	24
C	1:3	2.97×10^{-3}	1.01×10^{-3}	1.65−3.85	25
D	1:10	1.03×10^{-2}	1.05×10^{-3}	1.70−3.85	19
E	1:20	1.50×10^{-2}	7.55×10^{-4}	1.68−4.02	23
F	1:10	5.30×10^{-4}	5.30×10^{-5}	1.85−11.02	23
G	1:20	1.50×10^{-3}	1.55×10^{-5}	1.68−4.02	30
H	1:30	2.85×10^{-3}	9.55×10^{-5}	1.68−4.02	29
I	1:67	4.83×10^{-3}	7.18×10^{-5}	1.82−11.51	35
J	0.0−1:5.4	$0.0-4.31 \times 10^{-4}$	7.18×10^{-5}	2.70	35

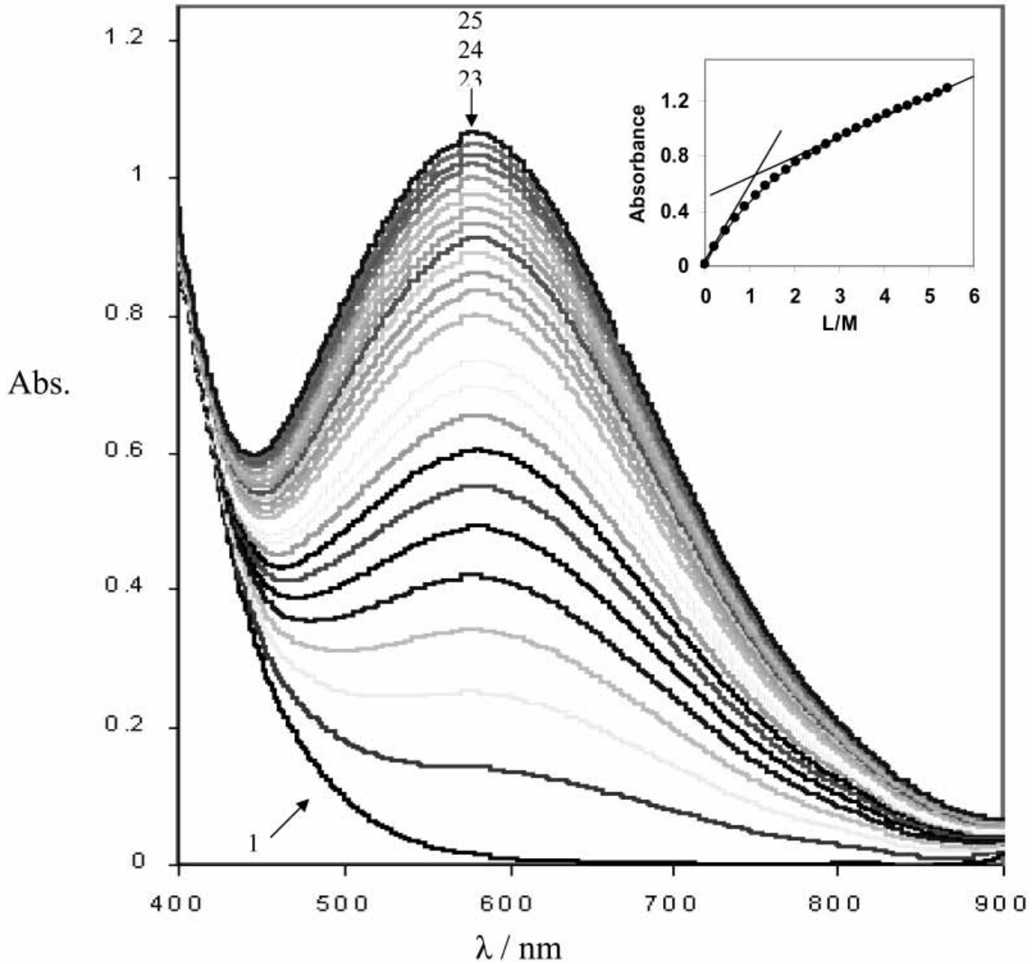

Figure 2. Spectrophotometric titration of ferric ion with ligand at pH = 2.70, L:M equal to 1:0, 2:0.22, 3:0.45, 4:0.68, 5:0.91, 6:1.13, 7:1.36, 8:1.59, 9:1.82, 10:2.04, 11:2.27, 12:2.50, 13:2.72, 14:2.95, 15:3.18, 16:3.40, 17:3.63, 18:3.86, 19:4.08, 20: 4.31, 21:4.53, 22:4.76, 23:4.99, 24:5.22, 25:5.45 (sample J in Table 2).

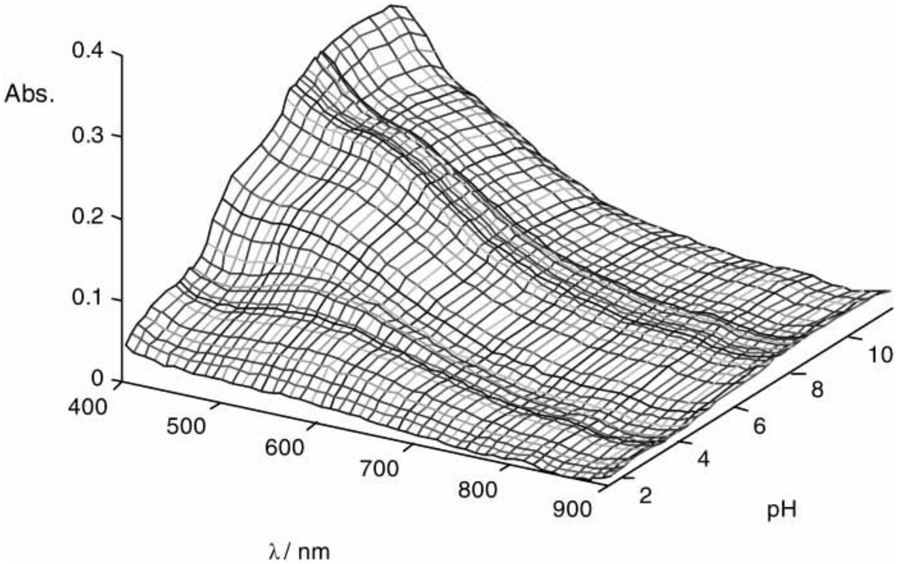

Figure 3. Visible spectra of the ferric ion with 4-chloro-2,6-bis(hydroxymethyl)phenol solutions at 0.1 M TEAB with pH ranging from 1.5 to 11.50 (sample I in Table 2).

and variations of the model. The algorithm for computing equilibrium constants in the BEST program[14] is the following sequence: (1) start with a set of known and estimated overall stability constants and compute [H$^+$] at all equilibrium points; (2) compute the weighted sum of the squares of the deviations in p[H] as in eq 1

$$U = \Sigma\, w(\mathrm{p[H]_{obs}} - \mathrm{p[H]_{calcd}})^2 \tag{1}$$

where $w = 1/(\mathrm{p[H]}_{i+1} - \mathrm{p[H]}_{i-1})^2$, a weighting factor that

Table 3. Overall Stability Constants of 4-Chloro-2,6-bis(hydroxymethyl)phenol with Ferric Ion at 0.1 M TEAB in 0.30 Mole Fraction of Methanol−Water Mixture.

log K_a	spectrophotometry	potentiometry
MLH_2	5.18 ± 0.05	5.15 ± 0.06
MLH_3	3.19 ± 0.03	3.10 ± 0.08

serves to lessen the influence of the less accurate p[H] values in the steeply sloped regions of the p[H] profile on the calculation; (3) adjust the unknown stability constants and repeat the calculations with the algorithm, which reproduces pH values according to the physicochemical model fitted and minimizes the sum of the weighted calculations until no further minimization of U (i.e., the Σ fit has been minimized) can be obtained, thus providing the final calculated β values. The standard deviation in pH units is obtained by the use of eq 2

$$\sigma_{\mathrm{fit}} = (U/N)^{1/2} \tag{2}$$

where $N = \Sigma w$. The program PKAS is a special case of the more general algorithm found in BEST, and in terms of CPU time, the algorithm in PKAS is quite fast for this special case since far fewer algebraic manipulations are made relative to the generalized treatment in BEST.

In this potentiometric study, different M:L solutions of the ligand and metal ion were examined. As Table 1 shows, solutions with more than 1.80×10^{-4} M concentration of ferric ion would be precipitated in pHs higher than 4. Because these data are not covering all of pH ranges, they are not enough for obtaining the stability constant via the potentiometric method. For this purpose, we lowered the concentration of metal ion, and then in order to have significant interaction between metal ions with the ligand, we use higher concentration of ligand relative to metal ion (i.e., M:L equal to 1:5, 1:10, 1:13). These data then were used to obtain the stability constants of the system. In this method, it was found that only the MLH_2 and MLH_3 species are formed in the pH range 2.0−11.5. The results are given in Table 3.

Spectrophotometric Method. In spectrophotometry, hard-modeling approaches solve Beer−Lambert's law assuming the fulfillment of the mass-action law and a particular chemical model, in which a set of chemical species in equilibrium are defined by their composition, stoichiometries, and equilibrium constants. By use of the EQUISPEC program, the formation constants were determined.[6,16−17] The EQUISPEC procedure is a second-order global analysis that simultaneously analyzes a number of spectrophotometric titrations with different initial concentrations; therefore, conditions for the significant formation of each species can be obtained.

In this method, the titration spectra of the ferric ion with 4-chloro-2,6-bis(hydroxymethyl)phenol (sample J in Table 2) at a pH of 2.7 are given in Figure 2. As this electronic spectra show, there is a strong peak in 580 nm. In this complex, the ferric ion is in a high-spin state and its d−d transitions are forbidden and have a very low intensity with small molar absorpitivity 0.1 L mol^{-1} cm^{-1}. Therefore, the strong peak in 580.0 nm with the calculated molar absorptivity of 0.975×10^3 L mol^{-1} cm^{-1} is related to charge-transfer complex of ferric ion with this ligand.[18,19]

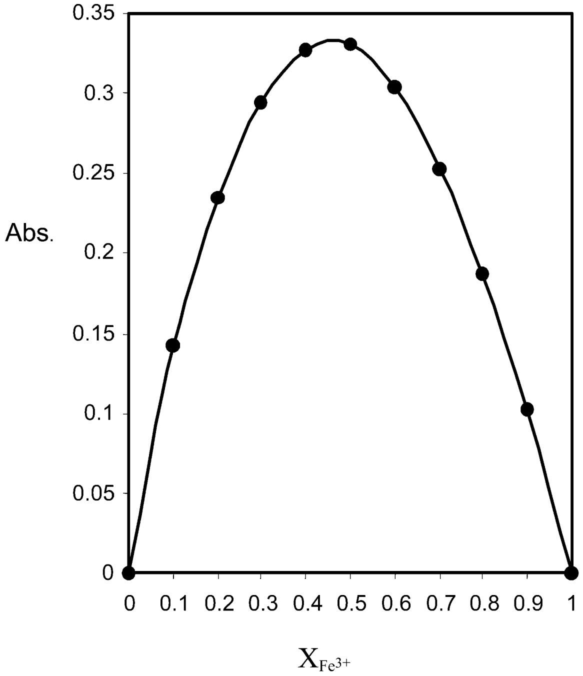

Figure 4. Continuous variation method plot of the ferric ion with 4-chloro-2,6-bis(hydroxymethyl) phenol at 580 nm and 0.10 M TEAB (each 2.0×10^{-3} M).

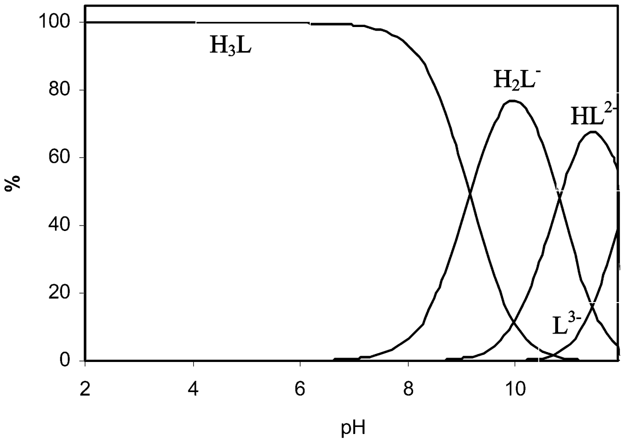

Figure 5. Distribution diagram of 4-chloro-2,6-bis(hydroxymethyl)phenol at 0.10 M TEAB in 0.30 mole fraction of methanol water mixture.

The visible spectra of the ferric ion with 4-chloro-2,6-bis(hydroxymethyl)phenol (sample I in Table 2) in different pH values are given in Figure 3. In the spectrophotometric method by using the EQUISPEC program and spectra in different mole ratios of M:L (Table 2), the stability constants of species in this system were calculated. Since in this system ferric ion precipitates as a hydroxide above pH 4.0, in order to have no precipitate and receive detectable absorbance, we obligate to use a very low concentration of ferric ion and a higher concentration of ligand during the titration of the mixture with KOH solution. By using the EQUISPEC program, the results show that only MLH_2 and MLH_3 species are present (i.e., mole ratio M:L is equal to 1:1) in this system (Table 3). The continuous variation method which is illustrated in Figure 4 and the method of mole ratio as is shown in Figure 2 also confirmed this mole ratio 1:1. The results in Table 3 show that the two methods of potentiometric and spectrophotometric are comparable and are in good agreements with each other.

The titration spectra of the ferro ion with 4-chloro-2,6-bis(hydroxymethyl)phenol does not show any significant absorbance. Therefore this ligand can also be used for determination of the ferric ion in the presence of the ferro ion in solutions.

A distribution diagram of 4-chloro-2,6-bis(hydroxymethyl)phenol in 0.3 mole fraction of methanol is shown in Figure 5. Because of low acidic constants of this compound, the H_2L^- and HL^{2-} species have a presence in high pH values. It is obvious also that the L^{3-} species should only exist in strong basic solution. As this figure shows, H_3L and H_2L^- are the main species in the pH range 2.0−10.0 and other species only exist in higher pHs.

Conclusions

In this work, we distinguish that the M:L ratio of this complex is 1:1 and the stability constants of the complexes were determined by the spectrophotometric and potentiometric methods at 25.0 °C and at an ionic strength of 0.10 M TEAB in 0.3 mole fraction of methanol. The results of the two methods are comparable with each other. This ligand has no any significant interaction with the ferro ion.

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