

Formation Constants of Chromium(III) Complexes with 8-Hydroxyquinoline and 8-Hydroxyquinoline-5-sulfonic Acid

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The complexes of Cr^{3+} ion formed by 8-hydroxyquinoline (HQ, HL) and 8-hydroxyquinoline-5-sulfonic acid (HQ-5-SA, H_2L) were investigated by means of potentiometry and spectroscopy at 25.0 ± 0.1 °C and in ionic strength of 0.1 M KNO_3 and 0.1 M KCl , respectively. Over the acidic pH range, the coordination of Cr^{3+} ion to HQ and HQ-5-SA in 1:1 mole ratios occur, CrL^{2+} and CrL^+ type complexes are formed. At near neutral pH, $\text{CrL}(\text{OH})^+$ and $\text{CrL}(\text{OH})$ type hydroxo complexes formed. All the data can be explained with the formation of only binary and mixed hydroxo Cr^{3+} complexes of these ligands. The formation constants were determined using the BEST computer program in 0.1 M KNO_3 ionic medium. The stoichiometries of Cr^{3+} complexes formed with these ligands were defined and their formation constants were determined. Thus, the removing capacities of these ligands could be examined by calculating the equilibrium concentration of Cr^{3+} that exists in the discharge water of various industries since Cr^{3+} ions are the main pollutants present during waste water treatment in Bursa city of Turkey.

Key Words: Chromium, 8-Hydroxyquinoline, Formation constants, Water pollutant.

INTRODUCTION

Chromium exists with variable valance and certain chromium species, such as Cr^{3+} ions and CrO_4^{2-} anion, have different toxicity. While Cr^{3+} is not toxic, CrO_4^{2-} is highly toxic¹. The coordination chemistry of Cr^{3+} is problematic, due to its inert character. Despite this, the hexaaqua Cr^{3+} , $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ contribute to many hydrolytic equilibria²⁻⁶. The biologically important (or proposed to be important) form of chromium is the trivalent ion and is required for proper carbohydrate and lipid metabolism in mammals⁷. The introduction of CrO_4^{2-} into biological systems likely exerts its effects due to the denaturation of Cr^{3+} bound in a special site from which it will not exchange¹.

8-Hydroxyquinoline (HQ, oxine), most frequently used in analytical chemistry, particularly for the description of the chelate compounds, which may be oxinates^{8,9}.

8-Hydroxyquinoline and its derivatives have found extensive applications as analytical reagents in absorption spectrophotometry, fluorometry, solvent extraction and partition chromatography because of their ability to form complexes with many

metal ions. 8-Hydroxyquinoline and its derivatives are also used as fungicides, amoebicides, bactericides and insecticides^{10,11}. Recently, much attention has been focused on the development of chemosensors for the selective and efficient detection of chemically and biologically important ionic species using 8-hydroxyquinoline¹²⁻²⁰.

In present studies, the complex equilibria between Cr^{3+} with 8-hydroxyquinoline (HQ) and 8-hydroxyquinoline-5-sulfonic acid (HQ-5-SA) are described (Fig. 1). Some reports on binary complex formation abilities are available in the literature for various metal ions^{2,3}.

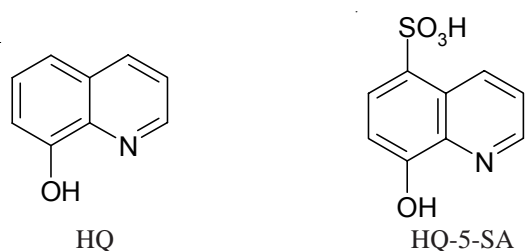


Fig. 1. Structural formulas of the ligands

In previous studies, the coordination of Cr^{3+} to salicylic acid, hydroxynaphthoic acid and its stabilities of various complex of Cr^{3+} were described²¹.

The stoichiometric protonation constants of these two ligands and the stability constants of Cr^{3+} -hydroxyquinolate complexes were calculated. Since, Cr^{3+} with Cr^{6+} are the main pollutants found during wastewater treatment²¹ in Bursa city of Turkey, it is aimed to explore the possibility of available ligands required to remove Cr^{3+} effectively from polluted water.

EXPERIMENTAL

8-Hydroxyquinoline (HQ) and 8-hydroxyquinoline-5-sulfonic acid (HQ-5-SA) (Aldrich) were of analytical reagent grade. The other chemicals procured from Merck and were used as received. The purities of the ligands were further checked by the Gran method²². The stock solution of Cr^{3+} was prepared for potentiometric measurement by dissolving the proper amounts of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98 %, Merck) in a small excess of 0.1 M HNO_3 (100 % purity, $d = 1.52$) to prevent hydrolysis as described previously²³. The concentration of free acid in the Cr^{3+} solution was systematically checked by potentiometric titrations before each series of experiments. 0.1 M sodium hydroxide solution was prepared as a carbonate-free solution by dissolving in doubly distilled water and was standardized against potassium hydrogen phthalate. It was standardized with EDTA titration by the method of Schwarzenbach method²⁴. The supporting electrolyte was 0.1 M KNO_3 in potentiometric studies. For spectroscopic measurements $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 0.1 M HCl and the ionic strength was adjusted to 0.1 M by KCl .

Potentiometric measurements: Potentiometric measurements were made using an automatic titration apparatus (Schott, Hofheim, Germany) equipped with a water-jacketed vessel and a combined pH electrode. Before each experiment the potentiometric cell was standardized in acetic acid buffer (Merck) and dilute hydrochloric acid (Merck) for the measurement of hydrogen ion concentration rather than its activity according to Irving *et al.*²⁵. In the calibration step of the pH meter, the pH reproducibility is < 0.005 units in the acidic pH region and < 0.015 units in the basic pH region. The autoprotolysis constant, K_w , was determined from dilute HCl solution titrations in 0.1 M KNO_3 , the reproducible values were found to be 13.76. The formation constants of the proton and Cr^{3+} complexes of HQ and HQ-5-SA were determined by potentiometric titration of 50 cm³ samples at 25.0 ± 0.1 °C. The titrations were performed within the limits $3 \leq pH \leq 10$ under a purified nitrogen (99.99 %, Bos, Turkey) atmosphere to prevent oxidation of the ligands. At least 10 ± 1 min passed between each pH reading to reach thermodynamic equilibrium in acidic solution. However, in order to prevent the partial oxidations of these ligands "quasi-equilibrium" titrations were performed in basic pH region with the waiting time to record the pH readings never being more than 15 min. At least four different potentiometric titrations were performed for each ligand studied; the first one was carried out with the ligand alone; the others were for Cr^{3+} -HL (or H_2L) systems in which the Cr^{3+} concentrations were in the (2.24-4.48) 10^{-3} M range and molar ratios of Cr^{3+} to ligand were 1:1, 1:2.

Spectroscopic measurements: The absorption spectra of ligands alone and Cr^{3+} -HL (or H_2L) systems in different mole ratios were taken at defined pH values and wavelength ranges on a Shimadzu GDU-20C spectrophotometer (Kyoto, Japan). In order to define the stoichiometries of the complex species Job's method of Continuous Variation was applied²⁶. The solutions were allowed to equilibrate overnight under a nitrogen atmosphere at 25.0 ± 0.1 °C.

Data treatment: The results of potentiometric titrations were evaluated using the computer programme BEST, which computes and refine the equilibrium constants of H^+ and Cr^{3+} complexes of these two ligands and provides the standard deviation of the fit (σ_{fit}) between the observed and calculated pH values obtained by potentiometric titrations²⁷. The mathematical analysis of the data comprising at least four titrations was performed and the averages of protonation and formation constants obtained from BEST program are tabulated in Table-1.

RESULTS AND DISCUSSION

8-Hydroxyquinoline (HQ) complexes: The potentiometric titration curves of a 1:1 mole ratio of Cr^{2+} -HQ exhibits an inflection point at m (mmole base/mmole metal) = 1.0 and $m = 3.0$ (Fig. 2, curve II). The formation of a CrL^{2+} type complex of Cr^{3+} with HQ in the $m = 0.0$ -1.0 range, may be inferred from the drops in the buffer regions of the titration curves and from inflection point at $m = 1.0$. Further, the extended hydrolysis of the CrL^{2+} complex between $m = 1.0$ -3.0 may be proposed

TABLE-1
EQUILIBRIUM CONSTANTS OF PROTON COMPLEXES (log K) AND
FORMATION CONSTANTS (log β) OF Cr³⁺:HQ AND HQ-5-SA
COMPLEXES AT 25 ± 0.1 °C AND 0.1 M KNO₃

Row	Equilibrium	HQ	HQ-5-SA
Proton complexes		log K	log K
HQ			
1	$L^{2-} + H^+ \rightleftharpoons HL^-$	9.66 ± 0.03 [Ref. 2] 9.62 ± 0.05*	
2	$HL^- + H^+ \rightleftharpoons H_2L$	4.99 ± 0.04 [Ref. 2]	
HQ-5-SA			
3	$L^{2-} + H^+ \rightleftharpoons HL^-$		8.42 ± 0.07 [Ref. 2] 8.39 ± 0.08*
4	$HL^- + H^+ \rightleftharpoons H_2L$		3.94 ± 0.05 [Ref. 2]
Cr(III) complexes		log β	log β
5	$Cr^{3+} + L^- \rightleftharpoons CrL^{2+}$	13.72 ± 0.09*	
6	$CrL^{2+} + OH^- \rightleftharpoons CrL(OH)^+$	5.36 ± 0.09*	
7	$Cr^{3+} + L^{2-} \rightleftharpoons CrL^+$		11.45 ± 0.09*
8	$CrL^+ + OH^- \rightleftharpoons CrL(OH)$		4.28 ± 0.09*

*This work.

from the inflection point at $m = 3.0$. Moreover, continued drops on pH readings after $m = 1.0$ suggest that hydrolysis of a CrL^{2+} type complex is initiated in the system.

The potentiometric titration curves of Cr³⁺-HQ in 1:2 mole ratio show first inflection points at $m = 1.0$ and second inflection at $m = 3.0$. (Fig. 2, curves III). As a result, the formation of CrL^{2+} type complex for different mole ratios was taken into account (Table-1, row 5). In all of these titrations the process of equilibrates were slow after the addition of two equivalents OH⁻ per mole of Cr³⁺ and the drifts on pH readings in pH = 6.0-8.0 range. The occurrences of $[CrL(OH)]^+$ type complex was assumed.

The occurrence of CrL^{2+} type complex, besides 1:1 mole ratio in all mole ratios was verified by introducing 2.16 pH values into the BEST computer program and its formation constant was defined (Table-1).

The existence of $[CrL(OH)]^+$ type complex was considered and its formation constant was found by introducing 1.38 pH values measured in all mole ratios (Table-1).

By means of the distribution diagram the major species in defined pH ranges were defined. They are Cr³⁺, CrL^{2+} and $[CrL(OH)]^+$ (Fig. 3).

In order to validate the existence of CrL^{2+} type complex the stoichiometry of the formed complex was investigated spectroscopically. Solutions of HQ alone, 1:1 and 1:2 mole ratios of Cr³⁺ and HQ were prepared at pH = 4.0 were prepared in 0.1 M

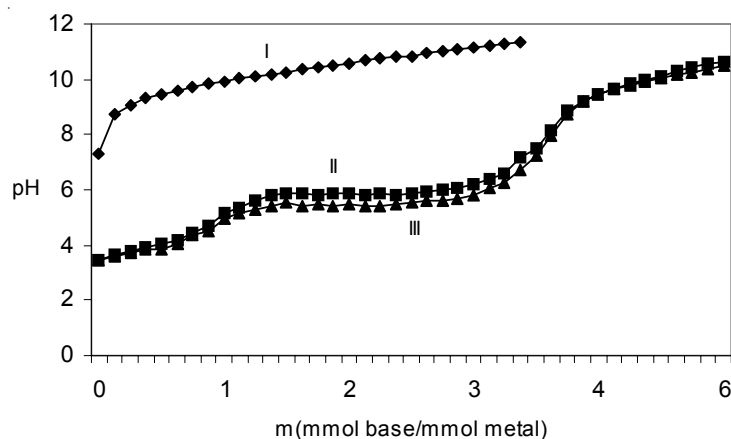


Fig. 2. Potentiometric titration curves of Cr^{3+} complexes of HQ in $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ at $25 \text{ }^\circ\text{C}$
 I: HQ alone ($T_L = 2.24 \times 10^{-3} \text{ mol L}^{-1}$);
 II: (1:1) molar ratio of Cr^{3+} to HQ ($T_{\text{Cr}} = T_L = 2.24 \times 10^{-3} \text{ mol L}^{-1}$);
 III: (1:2) molar ratio of Cr^{3+} to HQ ($T_{\text{Cr}} = 2.24 \times 10^{-3} \text{ mol L}^{-1}$, $T_L = 4.48 \times 10^{-3} \text{ mol L}^{-1}$)

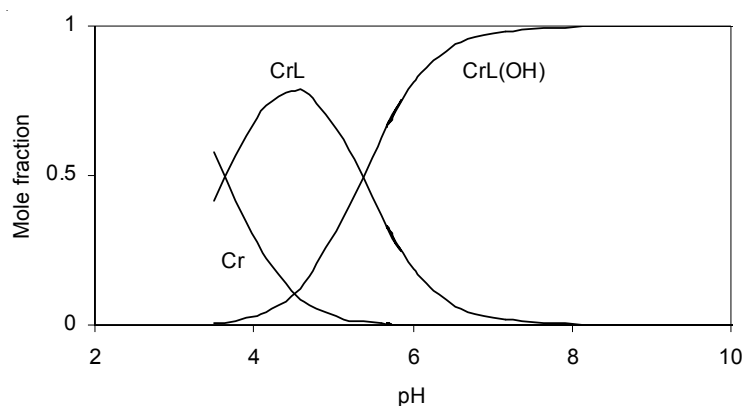


Fig. 3. Species distribution curves of the HQ system and Cr^{3+} ion as a function of $-\log [\text{H}^+]$, for a solution initially containing $2.24 \times 10^{-3} \text{ mol L}^{-1} \text{ HQ}$ and $2.24 \times 10^{-3} \text{ mol L}^{-1} \text{ Cr}^{3+}$ ion $25 \text{ }^\circ\text{C}$ and $I = 0.1 \text{ mol L}^{-1} \text{ KNO}_3$

KCl ionic medium. Since it was noticed that CrL^{2+} type complex ion exist in $\text{pH} = 4.0\text{--}6.0$ range, therefore the spectrum of each Cr^{3+} -HQ system exhibits the coordination of hydroxyquinolate oxygen atoms as evidenced by observation of charge transfer between these donors and Cr^{3+} (Fig. 4). The conformities of this Cr^{3+} -HQ systems to Beer's law were checked within the chosen concentration range. Job's diagrams were drawn at $\lambda = 420 \text{ nm}$ regardless of their mole ratios for the solution of Cr^{3+} -HQ system in which the mole fractions (X_M) of Cr^{3+} were in ($X_M = 0.00\text{--}1.00$) range (Fig. 5). In Job's plot, the stoichiometries of the formed complex ion at $\text{pH} = 4.0$ correspond to $X_M = 0.5$ indicating a 1:1 molar ratio of Cr^{3+} to HQ.

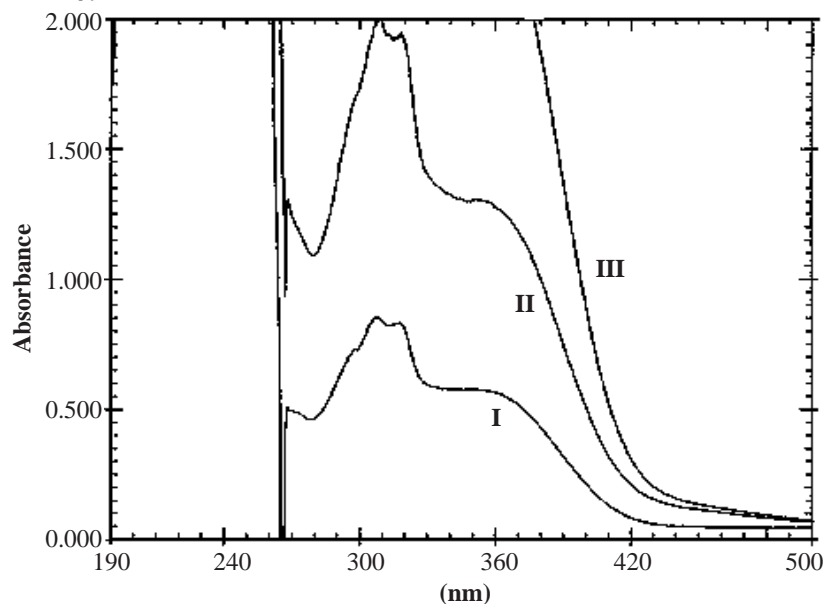


Fig. 4. Absorption spectra of Cr^{3+} complexes of HQ in 0.1 mol L^{-1} KCl at $25 \text{ }^\circ\text{C}$ ($\text{pH} = 4.0$)
 I: HQ alone ($T_L = 1 \times 10^{-4} \text{ mol L}^{-1}$; $X_M = 0.0$)
 II: (1:1) Cr^{3+} : HQ ($T_{\text{Cr}} = T_L = 1 \times 10^{-4} \text{ mol L}^{-1}$; $X_M = 0.5$)
 III: (1:2) Cr^{3+} : HQ ($T_{\text{Cr}} = 1 \times 10^{-4} \text{ mol L}^{-1}$, $T_L = 2 \times 10^{-4} \text{ mol L}^{-1}$; $X_M = 0.33$)

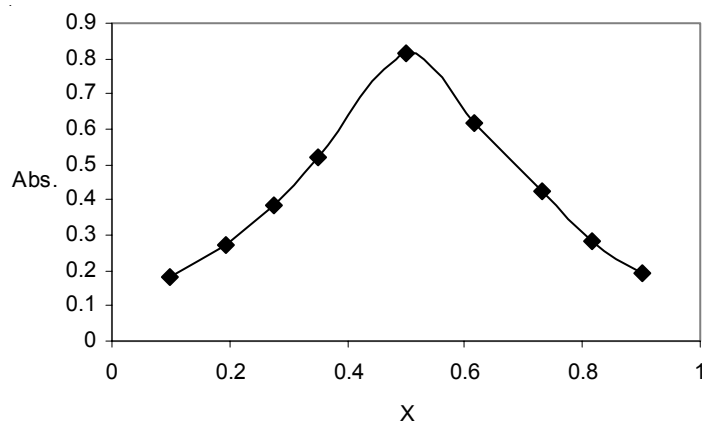


Fig. 5. Job's plot for Cr^{3+} -HQ complexes at $\lambda = 420 \text{ nm}$ and at $\text{pH} = 4.0$

8-Hydroxyquinoline-5-sulfonic acid (HQ-5-SA) complexes: In the potentiometric titrations of the Cr^{3+} -HQ-5-SA system for a 1:1 mole ratio, inflections were found at $m = 2.0$ and around $m = 4.0$ (Fig. 6, curve II). The drifts in pH readings were around $m = 2.0$. The stability constants of CrL^+ and $\text{CrL}(\text{OH})$ complexes were determined (Table-1).

The potentiometric titration curves of Cr^{3+} -HQ-5-SA in 1:2 ratio show first inflection points at $m = 2.0$ and second inflection at $m = 4.0$ (Fig. 6, curves III).

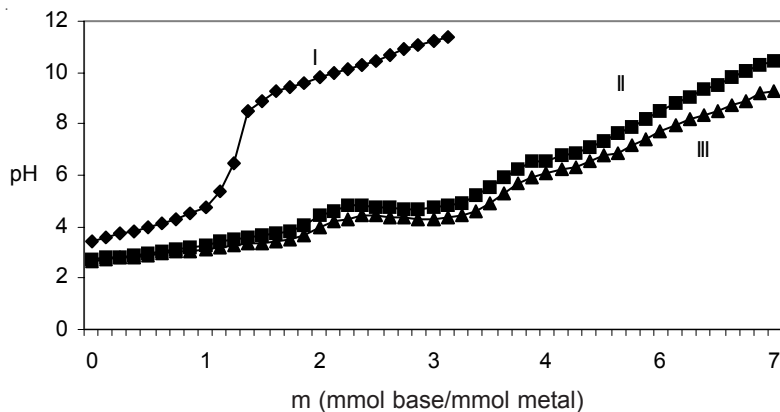


Fig. 6. Potentiometric titration curves of Cr^{3+} complexes of HQ-5-SA in $0.1 \text{ mol L}^{-1} \text{ KNO}_3$ at $25 \text{ }^\circ\text{C}$

I: HQ-5-SA alone ($T_L = 2.24 \times 10^{-3} \text{ mol L}^{-1}$);

II: (1:1) molar ratio of Cr^{3+} to HQ-5-SA ($T_{\text{Cr}} = T_L = 2.24 \times 10^{-3} \text{ mol L}^{-1}$);

III: (1:2) molar ratio of Cr^{3+} to HQ-5-SA ($T_{\text{Cr}} = 2.24 \times 10^{-3} \text{ mol L}^{-1}$, $T_L = 4.48 \times 10^{-3} \text{ mol L}^{-1}$)

By means of the distribution diagram the major species in defined pH ranges were defined. They are Cr^{3+} , CrL^+ and $[\text{CrL}(\text{OH})]$ (Fig. 7).

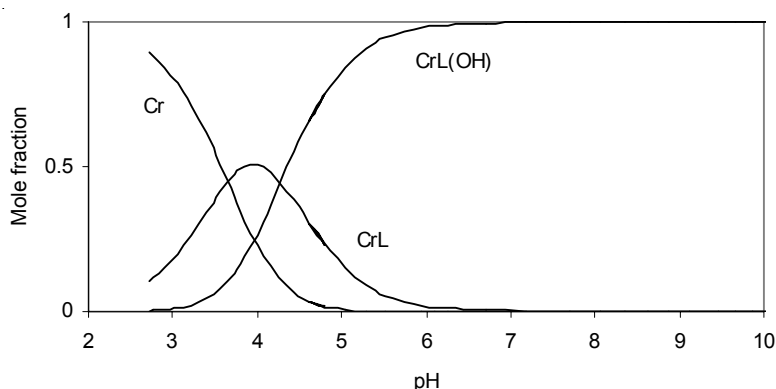


Fig. 7. Species distribution curves of the HQ-5-SA system and Cr^{3+} ion as a function of $-\log [\text{H}^+]$, for a solution initially containing $2.24 \times 10^{-3} \text{ mol L}^{-1}$ HQ-5-SA and $2.24 \times 10^{-3} \text{ mol L}^{-1} \text{ Cr}^{3+}$ ion, $25 \text{ }^\circ\text{C}$ and $I = 0.1 \text{ mol L}^{-1} \text{ KNO}_3$

In order to validate the existence of a CrL^+ type complex, the stoichiometry of the formed complex was investigated spectroscopically (Fig. 8). Job's diagrams were drawn at $\lambda = 390 \text{ nm}$ regardless of their mole ratios for the solution of Cr^{3+} -HQ-5-SA system in which the mole fractions (X_M) of Cr^{3+} were in ($X_M = 0.00$ - 1.00) range (Fig. 9). In Job's plot, the stoichiometries of the formed complex ion at $\text{pH} = 4.0$ correspond to $X_M = 0.5$ indicating a 1:1 molar ratio of Cr^{3+} to HQ-5-SA.

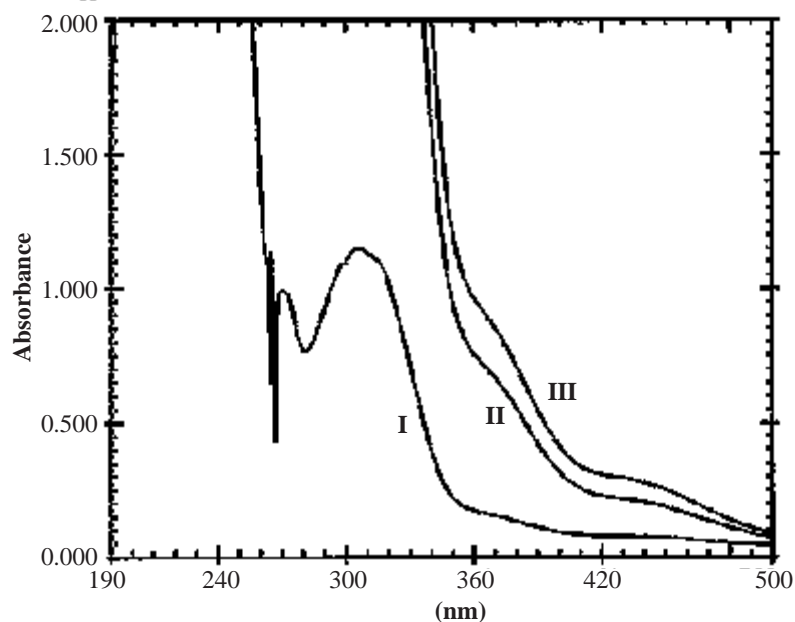


Fig. 8. Absorption spectra of Cr^{3+} complexes of HQ-5-SA in 0.1 mol L^{-1} KCl at $25 \text{ }^\circ\text{C}$ ($\text{pH} = 4.0$)
 I: HQ-5-SA alone ($T_L = 1 \times 10^{-4} \text{ mol L}^{-1}$; $X_M = 0.0$)
 II: (1:1) Cr^{3+} : HQ-5-SA ($T_{\text{Cr}} = T_L = 1 \times 10^{-4} \text{ mol L}^{-1}$; $X_M = 0.5$)
 III: (1:2) Cr^{3+} : HQ-5-SA ($T_{\text{Cr}} = 1 \times 10^{-4} \text{ mol L}^{-1}$, $T_L = 2 \times 10^{-4} \text{ mol L}^{-1}$; $X_M = 0.33$)

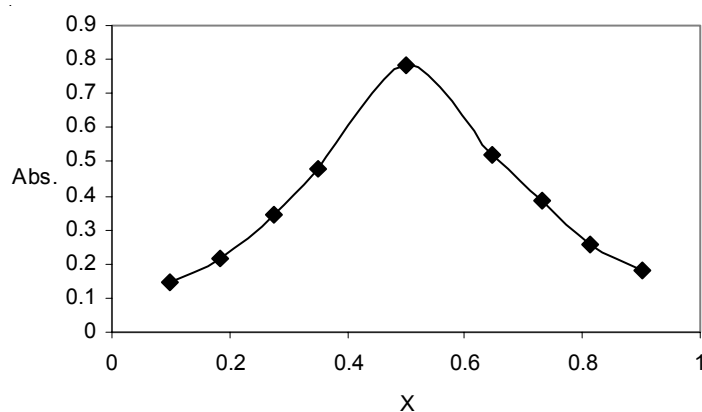


Fig. 9. Job's plot for Cr^{3+} -HQ-5-SA complexes at $\lambda = 390 \text{ nm}$ and at $\text{pH} = 4.0$

Complexation of Cr^{3+} in discharge water: Nilufer river flows in the Bursa plain and is polluted by Cr^{3+} and Cr^{6+} because of leather tanneries and textile and electroplating industries. We performed our research projects^{21,28-31} from 1996-1998 to define the total Cr, Cr^{3+} and Cr^{6+} concentrations in Nilufer river. The total chromium concentrations varied in the (0.970-0.090) mg/L range. The Cr^{3+} concentration should

not exceed 0.150 mg/L for highly polluted classes of water according to the water pollution control regulations of Turkey^{28,32}. The equilibrium concentration of Cr³⁺ that exists in HQ or HQ-5-SA complex equilibria were found to be 1:1 mole ratio of Cr³⁺ to the ligands systems. Thus, the removing capacities of these two ligands were found by means of defined formation constants in this study. It is proved that the level of Cr³⁺ in discharge water could be decreased from 1.148 mol/L to 4.28×10^{-12} mol/L by the addition of HQ at a 1:1 mole ratio in the acidic pH range of 4.00-7.00²⁸.

Conclusion

At near neutral pH values, CrL(OH)⁺ and CrL(OH) type hydroxo complexes also formed by hydrolytic equilibria and their formation constants were also calculated. The stoichiometries of the formed complexes were defined from the spectroscopic continuous variation method was applied; the occurrences of CrL²⁺ and CrL⁺ type complexes were verified.

Over the acidic pH range the binding of these HL and H₂L ligands to Cr³⁺ in 1:1 mole ratio take place, presumably *via* (O⁻) sites and ML²⁺, ML⁺ type complexes are formed.

The results of Cr³⁺ speciation studies for complexes of Cr³⁺ ion formed by HQ or HQ-5-SA indicate that Cr³⁺ ion can be removed from discharge water in acidic medium. Thus, the level of Cr³⁺ can be decreased roughly 10¹² times by the addition of HQ into the discharge water of leather tanneries, at a 1:1 mole ratio.

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