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Complexes of Chromium(III) with 2,3-Dihydroxynaphthalene-6-sulfonic Acid and 4,5-Dihydroxynaphthalene-2,7-disulfonic Acid in Aqueous Solution

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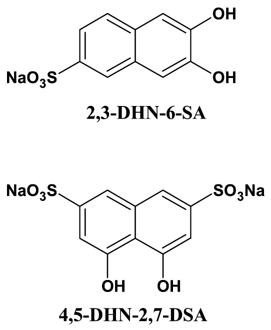
The chromium(III) complex species formed, in acidic and basic solutions at 25.0±0.1 °C, between Cr(III) and 2,3-dihydroxynaphthalene-6-sulfonic acid (2,3-DHN-6-SA, H_2L^{2-}) and 4,5-dihydroxynaphthalene-2,7-disulfonic acid (4,5-DHN-2,7-DSA, H_2L^-) were determined. Over the acidic pH range, the coordination of 2,3-DHN-6-SA and 4,5-DHN-2,7-DSA to Cr(III) in 1 : 1 mole ratio occurs, and CrL and CrL^- type complexes are formed. At near neutral pH, $CrL(OH)^-$ and $CrL(OH)^{2-}$ type hydroxo complexes are formed. The acid-dissociation constants of ligands and the formation constants of chromium(III) complexes were determined in 0.1 M KNO_3 ionic medium by potentiometric titration using the BEST computer program. Thus, the removing capacities of these ligands could be examined by calculating the equilibrium concentration of Cr(III) that exists in the discharge water of various industries since Cr(III) ions are the main pollutants present during waste water treatment in our city, Bursa.

Key words chromium; formation constant; potentiometry; water pollutant

Chromium exists with variable valance and certain chromium species, such as Cr(III) and CrO_4^{2-}, have different toxicity. While Cr(III) is not toxic, CrO_4^{2-} is highly toxic.[1] The coordination chemistry of Cr(III) is problematic, due to its inert character. Despite this, the hexaaqua Cr(III), $Cr(H_2O)_6^{3+}$ contributes to many hydrolytic equilibria.[2—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 mammals.[7] The introduction of CrO_4^{2-} into biological systems likely exerts its effects due to the degeneration of Cr(III) bound in a special site from which it will not exchange.[1]

We continue our studies on the complex equilibria between Cr(III) with 2,3-dihydroxynaphthalene-6-sulfonic acid (2,3-DHN-6-SA) and 4,5-dihydroxynaphthalene-2,7-disulfonic acid (4,5-DHN-2,7-DSA). The structural formulas of the studied ligands are shown in Fig. 1. Some reports on binary complex formation abilities are available in the literature for various metal ions.[8—11] Currently our main aim is to investigate the binding abilities of 2,3-DHN-6-SA and 4,5-DHN-2,7-DSA to Cr(III) and to determine the formation constants of their complexes.

In previous studies, we demonstrated the coordination of salicylic acid and its derivatives, and hydroxynaphthoic acids to Cr(III); and we also described the stabilities of various complex species of Cr(III).



2,3-DHN-6-SA

4,5-DHN-2,7-DSA

Fig. 1. Structural Formula of the Ligands Studied

The stoichiometric protonation constants of these two ligands and the stoichiometric stability constants of Cr(III)–hydroxynaphthalene complexes were calculated. Since we have already reported that Cr(III) with Cr(VI) is one of the main pollutants during waste water treatment in Bursa[12]; our goal is to increase the number of available ligands necessary to remove Cr(III) from polluted water.

Experimental

Chemicals and Solutions 2,3-DHN-6-SA (sodium salt, Sigma) and 4,5-DHN-2,7-DSA (disodium salt, Sigma) were of analytical reagent grade; all other chemicals were purchased from Merck and were used as received. The purities of the ligands were further checked by the Gran method.[13] The stock solution of Cr(III) was prepared for potentiometric measurement by dissolving the proper amounts of $Cr(NO_3)_3 \cdot 9H_2O$ (98%, Merck) in a small excess of 0.1 M HNO_3 (100% purity, d=1.52) to prevent hydrolysis as described previously.[14] The concentration of free acid in the Cr(III) 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 by EDTA titration according to the Schwarzenbach method.[15] The supporting electrolyte was 0.1 M KNO_3 in potentiometric studies, while for spectroscopic measurements $CrCl_3 \cdot 6H_2O$ was dissolved in 0.1 M HCl and the ionic strength was adjusted to 0.1 M by KCl. The Cr(III) complexes were formed at 70—75 °C and then the potentiometric titration and spectrophotometric measurements were carried out 1—2 h later.

Potentiometric Measurements Potentiometric measurements were performed 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.*[16] 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, and the reproducible values were found to be 13.76. The acid-dissociation constants of 2,3-DHN-6-SA and 4,5-DHN-2,7-DSA were determined by potentiometric titration of 50 cm^3 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

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prevent the partial oxidations of these ligands "quasi-equilibrium" titrations were performed in the 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(III)–H_2L^{2-} (or H_2L^-) systems in which the Cr(III) concentrations were in the (2.02—4.04) 10^{-3} M range and molar ratios of Cr(III) to ligand were 1 : 1, 1 : 2.

Spectroscopic Measurements The absorption spectra of ligands alone and Cr(III)–H_2L^{2-} (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). Job's method of Continuous Variation[17] was applied to define the stoichiometries of the complex species. The solutions were allowed to equilibriate overnight in 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 refines the equilibrium constants of H^+ and Cr(III) 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 titrations.[18] Mathematical analysis of the data comprising at least four titrations was performed and the averages of protonation and formation constants obtained from the BEST program are tabulated in Table 1.

Results and Discussion

2,3-DHN-6-SA Complexes The potentiometric titration curves of a 1 : 1 mole ratio of Cr(III)-2,3-DHN-6-SA exhibits an inflection point at m (mmol base/mmol metal)$=2.0$ and $m=4.0$ (Fig. 2, curve II). The formation of a CrL type complex of Cr(III) with 2,3-DHN-6-SA in the $m=0.0$—2.0 range, may be inferred from the drops in the buffer regions of the titration curves and from the inflection point at $m=2.0$. Further, the extended hydrolysis of the CrL complex between $m=2.0$—4.0 may be proposed from the inflection point at $m=4.0$. Moreover, continued drops of pH readings after $m=2.0$ suggest that hydrolysis of a CrL type complex is initiated in the system.

Table 1. Equilibrium Constants of Proton Complexes (log K) and Formation Constants (log β) of Cr(III) : 2,3-DHN-6-SA and 4,5-DHN-2,7-DSA Complexes at 25±0.1 °C and 0.1 M KNO_3

Row	Equilibrium	2,3-DHN-6-SA	4,5-DHN-2,7-DSA
	Proton complexes 2,3-DHN-6-SA	Log K	Log K
1	$L^{3-}+H^+ \rightleftharpoons HL^{2-}$	12.00±0.3[2)] 12.09±0.4[a)]	
2	$HL^{2-}+H^+ \rightleftharpoons H_2L^-$	8.09±0.04[2)] 8.10±0.05[a)]	
	4,5-DHN-2,7-DSA		
3	$L^{4-}+H^+ \rightleftharpoons HL^{3-}$		15.60±0.06[2)] —
4	$HL^{3-}+H^+ \rightleftharpoons H_2L^{2-}$		5.35±0.05[2)] 5.37±0.04[a)]
	Cr(III) complexes	Log β	Log β
5	$Cr^{3+}+L^{3-} \rightleftharpoons CrL$	12.32±0.08[a)]	
6	$CrL+OH^- \rightleftharpoons CrL(OH)^-$	5.38±0.08[a)]	
7	$Cr^{3+}+L^{4-} \rightleftharpoons CrL^-$		13.17±0.08[a)]
8	$CrL^-+OH^- \rightleftharpoons CrL(OH)^{2-}$		5.64±0.08[a)]

a) This work.

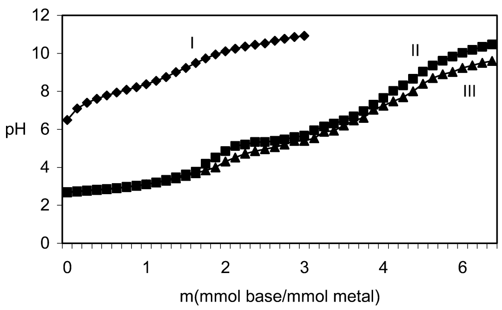

Fig. 2. Potentiometric Titration Curves of Cr(III) Complexes of 2,3-DHN-6-SA in 0.1 M KNO_3 at 25 °C

I: 2,3-DHN-6-SA alone ($T_L=2.02\times10^{-3}$ M); II: (1 : 1) molar ratio of Cr(III) to 2,3-DHN-6-SA ($T_{Cr}=T_L=2.02\times10^{-3}$ M); III: (1 : 2) molar ratio of Cr(III) to 2,3-DHN-6-SA ($T_{Cr}=2.02\times10^{-3}$ M, $T_L=4.04\times10^{-3}$ M).

The potentiometric titration curves of Cr(III)–2,3-DHN-6-SA in a 1 : 2 mole ratio show first inflection points at $m=2.0$, and a second inflection at $m=4.0$ (Fig. 2, curve III). As a result, the formation of CrL type complex for different mole ratios was taken into account (Table 1, row 5). In all of these titrations the process of equilibration was slow after the addition of two equivalents of OH^- per mole of Cr(III) and the drifts in pH readings at the pH$=6.0$—8.0 range. The occurrence of $CrL(OH)^-$ type complex was assumed.

The occurrence of CrL type complex in all mole ratios other than the 1 : 1 mole ratio was verified by introducing 236 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 162 pH values measured in all mole ratios (Table 1).

The major species in defined pH ranges were defined by means of the distribution diagram. They are Cr(III), CrL and $CrL(OH)^-$ (Fig. 3).

In order to validate the existence of CrL type complex the stoichiometry of the formed complex was investigated spectroscopically. Solutions of 2,3-DHN-6-SA alone, and 1 : 1 and 1 : 2 mole ratios of Cr(III) and 2,3-DHN-6-SA were prepared at pH$=4.5$ in 0.1 M KCl ionic medium since it was noticed that CrL type complex ions exist in the pH$=4.0$—6.0 range, therefore the spectrum of each Cr(III)–2,3-DHN-6-SA system exhibits the coordination of naphtol oxygen atoms as evidenced by observation of charge transfer between these donors and Cr(III) (Fig. 4). The conformities of this Cr(III)–2,3-DHN-6-SA system to Beer's law were checked within the chosen concentration range. Job's diagrams were drawn at $\lambda=350$ nm regardless of their mole ratios for the solution of Cr(III)–2,3-DHN-6-SA system in which the mole fractions (X_M) of Cr(III) were in the ($X_M=0.00$—1.00) range (Fig. 5). In Job's plot, the stoichiometries of the formed complex ion at pH$=4.5$ corresponded to $X_M=0.5$ indicating a 1 : 1 molar

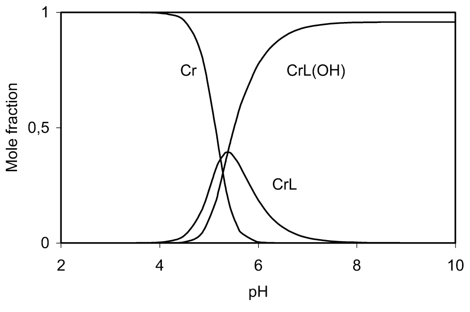

Fig. 3. Species Distribution Curves of the 2,3-DHN-6-SA System and Cr(III) as a Function of $-\log[H^+]$, for a Solution Initially Containing 2.02×10^{-3} M 2,3-DHN-6-SA and 2.02×10^{-3} M Cr(III)

25 °C and I$=0.1$ M KNO_3.

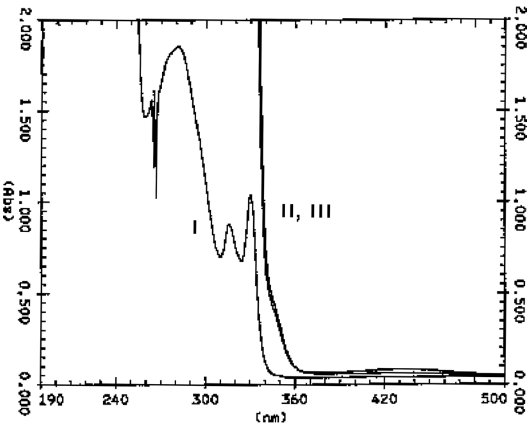

Fig. 4. Absorption Spectra of Cr(III) Complexes of 2,3-DHN-6-SA in 0.1 M KCl at 25 °C (pH=4.0)

I: 2,3-DHN-6-SA alone ($T_L=1\times10^{-4}$ M; $X_M=0.0$); II: (1 : 1) Cr(III) : 2,3-DHN-6-SA ($T_{Cr}=T_L=1\times10^{-4}$ M; $X_M=0.5$); III: (1 : 2) Cr(III) : 2,3-DHN-6-SA ($T_{Cr}=1\times10^{-4}$ M, $T_L=2\times10^{-4}$ M; $X_M=0.33$).

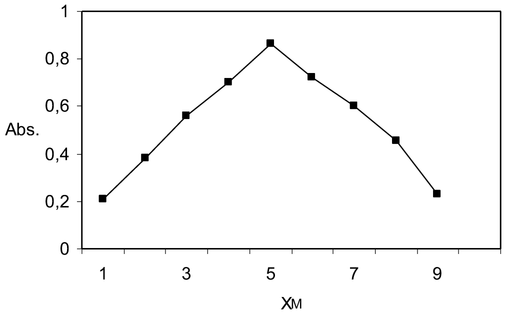

Fig. 5. Job's Plot for Cr(III)–2,3-DHN-6-SA Complexes at $\lambda=350$ nm and at pH=4.0

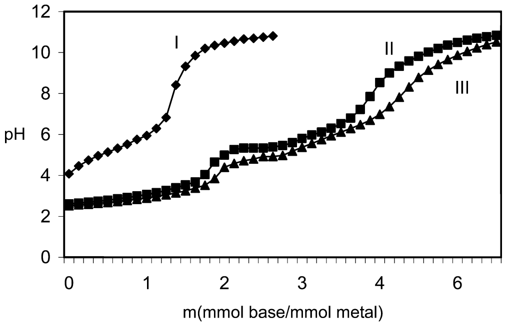

Fig. 6. Potentiometric Titration Curves of Cr(III) Complexes of 4,5-DHN-2,7-DSA in 0.1 M KNO_3 at 25 °C

I: 4,5-DHN-2,7-DSA alone ($T_L=2.02\times10^{-3}$ M); II: (1 : 1) molar ratio of Cr(III) to 4,5-DHN-2,7-DSA ($T_{Cr}=T_L=2.02\times10^{-3}$ M); III: (1 : 2) molar ratio of Cr(III) to 4,5-DHN-2,7-DSA ($T_{Cr}=2.02\times10^{-3}$ M, $T_L=4.04\times10^{-3}$ M).

ratio of Cr(III) to 2,3-DHN-6-SA.

4,5-DHN-2,7-DSA Complexes In the potentiometric titrations of the Cr(III)–4,5-DHN-2,7-DSA 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 $CrL(OH)^{2-}$ complexes were determined (Table 1).

The potentiometric titration curves of Cr(III)–4,5-DHN-2,7-DSA in 1 : 2 ratio show first inflection points at $m=2.0$, and a second inflection at $m=4.0$ (Fig. 6, curve III).

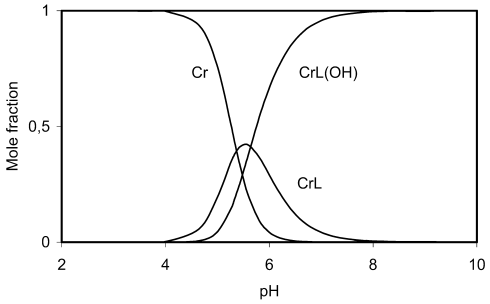

Fig. 7. Species Distribution Curves of the 4,5-DHN-2,7-DSA System and Cr(III) Ion as a Function of $-\log[H^+]$, for a Solution Initially Containing 2.02×10^{-3} M 4,5-DHN-2,7-DSA and 2.02×10^{-3} M Cr(III)

25 °C and I=0.1 M KNO_3.

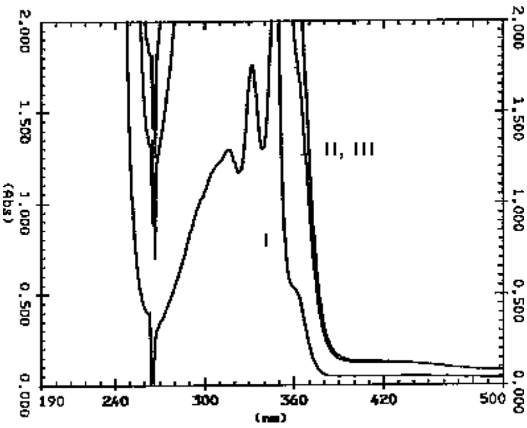

Fig. 8. Absorption Spectra of Cr(III) Complexes of 4,5-DHN-2,7-DSA in 0.1 M KCl at 25 °C (pH=4.0)

I: 4,5-DHN-2,7-DSA alone ($T_L=1\times10^{-4}$ M; $X_M=0.0$); II: (1 : 1) Cr(III) : 4,5-DHN-2,7-DSA ($T_{Cr}=T_L=1\times10^{-4}$ M; $X_M=0.5$); III: (1 : 2) Cr(III) : 4,5-DHN-2,7-DSA ($T_{Cr}=1\times10^{-4}$ M, $T_L=2\times10^{-4}$ M; $X_M=0.33$).

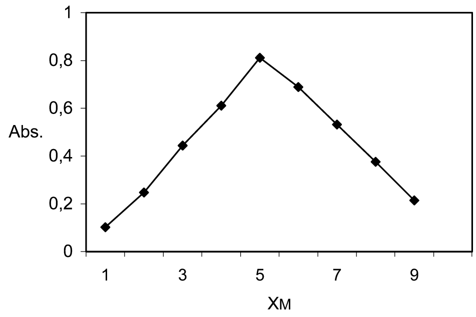

Fig. 9. Job's Plot for Cr(III)–4,5-DHN-2,7-DSA Complexes at $\lambda=380$ nm and at pH=4.0

The major species in defined pH ranges were defined by means of the distribution diagram. They are Cr(III), CrL^- and $CrL(OH)^{2-}$ (Fig. 7).

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 $\lambda=380$ nm regardless of their mole ratios for the solution of Cr(III)–4,5-DHN-2,7-DSA system in which the mole fractions (X_M) of Cr(III) were in the ($X_M=0.00$—1.00) range (Fig. 9). In Job's plot, the stoichiometries of the formed complex ion at pH=4.5 correspond to $X_M=0.5$ indicating a 1 : 1 molar ratio of Cr(III) to 4,5-DHN-2,7-DSA.

Complexation of Cr(III) in Discharge Water The Nilufer River flows in the Bursa plain and is polluted by Cr(III) and Cr(VI) because of leather tanneries and textile and electroplating industries. We performed our research project[12,19—21] from 1996—1998 to define the total Cr, Cr(III) and Cr(VI) concentrations in the river. The total chromium concentrations measured were 0.970—0.090 mg/l range. The Cr(III) concentration should not exceed 0.150 mg/l for highly polluted classes of water according to the water pollution control regulations of Turkey.[19,22] The equilibrium concentration of Cr(III) that exists in 2,3-DHN-6-SA or 4,5-DHN-2,7-DSA complex equilibria was found to be a 1 : 1 mole ratio of Cr(III) to the ligands systems. Thus, the removing capacities of these two ligands were found by means of defined formation constants in this study. We proved that the level of Cr(III) in discharge water could be decreased from 1.148 M to 2.34×10^{-12} M by the addition of 4,5-DHN-2,7-DSA at a 1 : 1 mole ratio in the acidic pH range of 4.00—7.00.[19]

Conclusion

At near neutral pH values, $CrL(OH)^-$ and $CrL(OH)^{2-}$ type hydroxo complexes were also formed by hydrolytic equilibria and their formation constants were also calculated. The stochiometries of the formed complexes were defined from the spectroscopic continuous variation method that was applied; the occurrences of CrL and CrL^- type complexes were verified.

Over the acidic pH range the binding of these H_2L^{2-} and H_2L^- ligands to Cr(III) in a 1 : 1 mole ratio takes place, presumably *via* (O^-, O^-) sites and ML, ML^- type complexes are formed.

The results of Cr(III) speciation studies for complexes of Cr(III) ion formed by 2,3-DHN-6-SA or 4,5-DHN-2,7-DSA indicate that Cr(III) ion can be removed from discharge water in acidic medium. Thus, the level of Cr(III) can be decreased roughly 10^{12} times by the addition of 4,5-DHN-2,7-DSA into the discharge water of leather tanneries, at a 1 : 1 mole ratio.

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