Formation Constants of Chromium(III), Scandium(III) and Yttrium(III) Complexes of Some Hydroxy Naphthoic Acids

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The complexes of chromium(III), scandium(III) and yttrium(III) formed by 1-hydroxy-2-naphthoic acid (1,2-HNA: H_2L) and 3-hydroxy-2-naphthoic acid (3,2-HNA: H_2L) were investigated by potentiometry and spectroscopy at 25±0.1 °C and at an ionic strength of 0.1 M KNO_3 in 50% ethanol–water (v/v) medium. The stoichiometries of these three M(III) complexes formed with these hydroxy-naphthoic acids and with hydroxo ion were defined and their formation constants were determined and compared. 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; scandium; yttrium; naphthoic acid; formation constant; water pollutant

We continue our studies on the complex equilibria between Cr(III), Sc(III), Y(III) and 1-hydroxy-2-naphthoic acid (1,2-HNA: H_2L) and 3-hydroxy-2-naphthoic acid (3,2-HNA: H_2L). We have reported the stabilities of the complexes between these metal ions and the title ligands.[1—11] The structural formulas of the studied ligands are shown in Fig. 1. There have been some reports on the Sc(III) and Y(III) complexes of hydroxy naphthoic acids[12—15]; but almost nothing is known about the complexes between Cr(III) and these two naphthoic acids. However, the stabilities and stoichiometries of the complexes formed with Cr(III), Sc(III), Y(III) and hydroxy benzoic acids were already determined by us.[4—11] It is well known that the derivatives of naphthoic acids are used as dyes and reagents for spectrophotometric measurements since they form chelates with several metal ions, whereas hydroxy carboxylic acids of the naphthalene series are far less common as ligands for complexometric studies than hydroxy benzoic acids. Some reports on binary complex formation abilities are available in the literature for various metal ions.[12—21] Currently our main aim is to investigate the binding abilities of 1,2-HNA and 3,2-HNA to Cr(III), Sc(III) and Y(III) and to determine the formation constants of their complexes.

On the other hand, the humic substances are derivatives of hydroxy naphthoic and hydroxy benzoic acids and they are found in natural ligands. They can remove environmentally mobile ions like Cu(II), Fe(III) and Al(III) that originate from various industries since humic substances are easily coordinated from oxygen donor sites to these metal ions and form very stable chelates.[22—27] Cr(III), with Cr(VI), is one of the main pollutant during waste water treatment in our city, Bursa.[28] So, the removal of Cr(III) from waste water may be possible using 1,2-HNA and 3,2-HNA ligands. Therefore, our second aim is to determine the concentration of uncomplexed Cr(III) by means of the formation constants of its 1,2-HNA and 3,2-HNA complexes as a part of our research project.

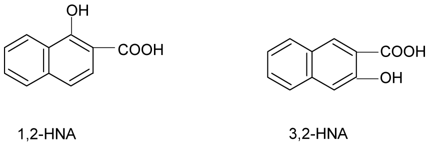

Fig. 1. Structural Formulas of the Ligands Studied

However, Bhatt *et al.*[12,13] were interested in the complex formation reactions of Sc(III) with 1,2-HNA and 3,2-HNA but they were mainly ternary complex forming systems. They obtained the stability constants of binary complexes of Sc(III) with 1,2-HNA and 3,2-HNA only at an ionic strength of 0.1 M KNO_3 in 50% (v/v) aqueous-ethanol medium by the average value method.[29,30] Y(III) and lanthanides formed with 2-hydroxy-3-naphthoic acid (2,3-HNA), 2-hydroxy-1-naphthoic acid (2,1-HNA) and 1,2-HNA were also investigated by Bhatt *et al.*[14] and Deshpande *et al.*[15] They applied only the Calvin–Bjerrum potentiometric titration technique at 25 °C and 0.1 M $NaClO_4$ ionic strength in 75% dioxane–25% (v/v) water medium. Neither Bhatt *et al.*[12—14] nor Deshpande *et al.*[15] had taken into consideration the stoichiometries of Sc(III) and Y(III) complexes and the existence of different species on their equilibria; they only determined the relative molar concentrations of complexes formed from the aqua M(III) ions with these two ligands by means of formation curves, leading to rather approximate values. Thus our third aim is introduce the reliable formation constants of complexes formed between Sc(III), Cr(III), Y(III) and these two ligands into the physical and analytical studies of these metal ions.

Experimental

Chemicals and Apparatus All chemicals were of analytical grade and purchased from Merck Company. Double distilled CO_2-free water and redistilled ethanol were used. 1,2-HNA and 3,2-HNA were obtained from Aldrich Chemical Company. They were used without further purification; their molecular weights were periodically checked by Gran titrations.[29,30]

Chromium(III) nitrate (Merck, 100% purity) and scandium(III) nitrate (Aldrich, 99.9%) solutions were prepared in known volumes of HNO_3 for potentiometry; while Cr(III) and Sc(III) chloride were dissolved in 10^{-2} M HCl for spectroscopic studies. The stock solution of yttrium(III) perchlorate was prepared from yttrium oxide in a small excess of $HClO_4$. Then all of these metal ion solutions were standardized with EDTA titration by the method of Schwarzenbach.[31]

The potentiometer used was a Schott pH meter (Hoffheim, Germany) as a part of an automatic titrator. It was calibrated to determine the hydrogen ion concentration. The procedure has been described in preceeding publications.[2—4,32,33]

Spectrophotometric measurements were performed with a Schimadzu GDU-20 C Model UV–VIS spectrophotometer (Kyoto, Japan) in order to

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define the existence of deprotonated and coordinated H_2L ligands at various pH values.

Procedure 1,2-HNA and 3,2-HNA were titrated in the absence and presence of M(III) ions with carbonate free standard NaOH solution. The ionic strengths were kept constant by 50% (v/v) aqueous-ethanol. The compositions of the various titration mixtures, the concentration of each of the components and the procedure for the pH-titrations of binary complexing systems of each metal ions were the same as those explained earlier.[2,4,33]

The potentiometric titrations were carried out at 25±0.1 °C in a jacketed cell of 100 ml capacity, under a nitrogen atmosphere and for Cr(III) and Sc(III) ions the ionic medium was 0.1 M KNO_3; while it was 0.1 M $NaClO_4$ ionic medium for Y(III) ion. However, ionic strengths were maintained at 0.1 M effectively by 0.1 M KCl, for spectroscopic measurements of Cr(III) and Sc(III) complexes; since NO_3^- ion absorbs at 313 nm, Which is in our working range. Because of the kinetic inertness of Cr(III), one should wait at least overnight for pH readings after each addition of NaOH into the Cr(III) mixtures. All potentiometric titrations were performed in triplicate. At ligand to M(III) ratios of 2.0 or greater no precipitation occurred, but at lower ratios of ligands the titration curves could be treated quantitatively only to pH *ca.* 5.50 due to the occurrence of turbidity and precipitation. Since the opacities in the titration medium were first noticed around these pH values, which were followed by the development of fine precipitates, they were explained as hydrolysis products for each M(III) : H_2L complex. The Sc(III) and Y(III) systems were titrated by waiting at least 1—3 min, because it was necessary between the additions of successive aliquots of sodium hydroxide to reach constant pH readings.

The absorption spectra of H_2L ligands alone and Sc(III) : H_2L and Cr(III) : H_2L systems in different mole ratios were recorded at defined wavelength ranges on a UV–VIS spectrophotometer. Thus the stoichiometries of the complexes were defined by Job's method of continuous variation. However, the spectroscopic investigation of Y(III) : H_2L systems was not possible.

Calculations The protonation constants of L^{2-} and of HL^- ions of H_2L ligands ($\log K$) and formation constants of their complexes ($\log \beta$) formed with Cr(III), Sc(III) and Y(III) were calculated by investigating their potentiometric titration curves; where M(III) : H_2L mole ratios generally varied from 1 : 1 to 1 : 2 and 1 : 3. All of these constants were the averages of at least twenty calculated values in the defined regions; using a RANA computer programme which was described previously.[33] The criterion used for which species are present in equilibria, is simply a model of best fit to the potentiometric data. The existence of assumed complexes was verified by taking into account the related equilibria. Non-linear least-squares analysis of the data in terms of assumed reactions gave a satisfactory result in the buffer regions of complexes in different mole ratios of M(III) ions and H_2L ligands. The values of the formation functions $\bar{n}$ (the average number of ligands attached per metal ion) were also determined by the Irving and Rossotti method.[29,30,32] The distribution curves of the various species were also drawn by calculating their concentration by means of the RANA computer program.

Results and Discussion

Potentiometric Investigations The protonation constants of 1,2-HNA, 3,2-HNA, and their various sulpho substituted derivatives were reported either in aqueous or dioxane–water, or ethanol–water mixtures.[13—16,34—36] We could easily define the protonation constants of HL^- ions of these two ligands (H_2L); but the protonation of the phenoxide (O^-) ion that is at ortho position to $-COO^-$ ion, can be detected and determined only with a large experimental error, due to the strong intramolecular hydrogen bond between the COO^- and OH groups.[26,27,33] Our results and those determined by others are tabulated for 1,2-HNA and 3,2-HNA in Tables 1 and 2, respectively, for the same ionic medium, equal temperature and ionic strengths. The measured protonation constants of COO^- ions are bigger for hydroxy naphthoic acids than naphthoic acid due to the intramolecular hydrogen bonding between the phenolic hydroxyl and carboxylate groups. Our $\log K_{HL^-}$ values belonging to 1,2-HNA and 3,2-HNA are equal to the corresponding values of Bhatt *et al.*[12—14]; but they are bigger than those of salicylic acid and its derivatives[6,11,37] and hydroxy salicylic acids[8,10]; whereas we introduced literature values[12—14] of $\log K_{L^{2-}}$ in our calculations due to the above explained difficulties in their determinations.

The potentiometric titrations of the solutions containing either Cr(III) or Sc(III) or Y(III) and one of the hydroxy naphthoic acid ligands were carried out in (1 : 1), (1 : 2) and (1 : 3) mole ratios. The potentiometric titrations yielded inflections at *m* values (mole of base per mole of metal) that are integer numbers corresponding to replacements of either carboxylic proton or phenolic protons or only proton from an aqua complex as a result of hydrolysis. The well defined inflections were observed at $m=2.0$ and $m=4.0$ in the 1 : 1 Cr(III) : 1,2-HNA system; the inflections for the 1 : 2 Cr(III) : 1,2-HNA system were at $m=3.0$ and $m=5.0$ (Fig. 2, for simplicity only Cr(III) : 1,2-HNA system is given). The coordination possible between ortho hydroxy naphthoic acids and Sc(III) or Cr(III) will be stronger as L^{2-} than monoionised HL^-. Thus the formations of several complexes were assumed according to the stoichiometries of the proposed equilibria (Tables 1, 2). ML^+ type complexes of

Table 1. Protonation Constants ($\log K$) of 1-Hydroxy-2-naphthoic Acid and Formation Constants ($\log \beta$) of Its Complexes with Cr(III), Sc(III) and Y(III) at 25.0±0.1 °C, $I=0.1\ \mathrm{mol \cdot l^{-1}}$ (KNO_3) and in 50% Ethanol–Water Medium

Equilibrium	$\log K$	$\log \beta$		
	H^+	Cr(III)	Sc(III)	Y(III)
$L^{2-}+H^+ \rightleftarrows HL^-$	11.76±0.01[12]			
$HL^-+H^+ \rightleftarrows H_2L$	3.86±0.01[a]			
	3.87±0.01[12—14]			
$M^{3+}+L^{2-} \rightleftarrows ML^+$		11.26±0.02[a]	11.96±0.03[a]	
			8.74±0.03[12]	
$ML^++HO^- \rightleftarrows ML(OH)$		5.15±0.04[a]	4.99±0.10[a]	
$M^{3+}+HL^- \rightleftarrows MHL^{2+}$				3.41±0.03[a]
$MHL^{2+}+HO^- \rightleftarrows M(HL)(OH)^+$				6.27±0.06[a]
$M^{3+}+2HL^- \rightleftarrows M(HL)_2^+$				5.96±0.03[a]
$M(HL)_2^++HO^- \rightleftarrows M(HL)_2(OH)$				6.12±0.07[a]
$M^{3+}+HL^-+L^{2-} \rightleftarrows M(HL)L$		15.82±0.06[a]		
$M(HL)L+HO^- \rightleftarrows M(HL)L(OH)^-$		5.55±0.05[a]		
$M^{3+}+2L^{2-} \rightleftarrows ML_2^-$			22.64±0.06[a]	
$M^{3+}+3L^{2-} \rightleftarrows ML_3^{3-}$			35.58±0.06[a]	

a) This work. In refs. 12—14: 50% (v/v) aqueous-ethanol medium at 25 °C and 0.1 M KNO_3 ionic strength.

Table 2. Protonation Constants (log *K*) of 3-Hydroxy-2-naphthoic Acid and Formation Constants (log β) of Its Complexes with Cr(III), Sc(III) and Y(III) at 25.0±0.1 °C, I=0.1 mol·l^{-1} (KNO$_3$) and in 50% Ethanol–Water Medium

Equilibrium	log *K*	log β		
	H$^+$	Cr(III)	Sc(III)	Y(III)
$L^{2-}+H^+ \rightleftarrows HL^-$	10.92[12—14)]			
$HL^-+H^+ \rightleftarrows H_2L$	3.56±0.01[a)]			
	3.57[12—14)]			
$M^{3+}+L^{2-} \rightleftarrows ML^+$		10.13±0.07[a)]	12.17±0.05[a)]	
			8.46±0.03[12)]	
$ML^++HO^- \rightleftarrows ML(OH)$		6.01±0.07[a)]	4.52±0.10[a)]	
$M^{3+}+HL^- \rightleftarrows MHL^{2+}$				2.88±0.04[a)]
$MHL^{2+}+HO^- \rightleftarrows M(HL)(OH)^+$				6.97±0.05[a)]
$M^{3+}+2HL^- \rightleftarrows M(HL)_2^+$				5.27±0.04[a)]
$M(HL)_2^++HO^- \rightleftarrows M(HL)_2(OH)$				6.68±0.06[a)]
$M^{3+}+HL^-+L^{2-} \rightleftarrows M(HL)L$		14.79±0.07[a)]		
$M(HL)L+HO^- \rightleftarrows M(HL)L(OH)^-$		6.28±0.08[a)]		
$M^{3+}+2L^{2-} \rightleftarrows ML_2^-$			22.12±0.08[a)]	

a) This work. In refs. 12—14: 50% (v/v) aqueous-ethanol medium at 25 °C and 0.1 M KNO$_3$ ionic strength.

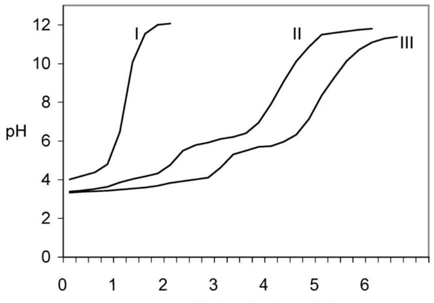

Fig. 2. Potentiometric Titration Curves of Cr(III) Complexes of 1,2-HNA in 0.1 mol·l^{-1} KNO$_3$ at 25 °C

I: 1,2-HNA alone (T_L=2.00×10^{-3} mol·l^{-}); II: (1 : 1) molar ratio of Cr(III) to 1,2HNA (T_L=2.00×10^{-3} mol·l^{-1}) ; III: (1 : 2) molar ratio of Cr(III) to 1,2-HNA (T_L=4.00×10^{-3} mol·l^{-1}).

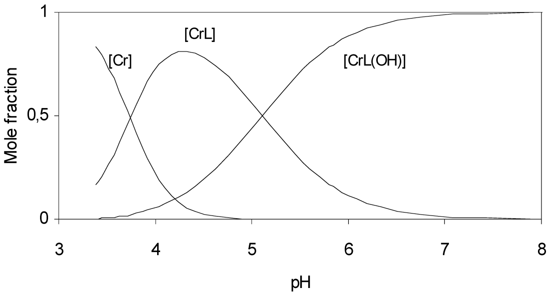

Fig. 3. Species Distribution Curves of the 1,2-HNA System and Cr(III) Ion as a Function of $-\log[H^+]$, for a Solution Initially Containing 2.00×10^{-3} mol·l^{-1} 1,2-HNA and 2.00×10^{-3} mol·l^{-1} Cr(III) Ion

T=25 °C and I=0.1 mol·l^{-1} KNO$_3$.

Cr(III) and Sc(III) form hydroxo complexes as hydrolysis products. The presumed structures for ML$^+$ and ML(OH) type hydroxo complexes resemble those of the studied salicylic and hydroxy benzoic acid complexes of Cr(III) and Sc(III) ions.[8,10,11,37)] Y(III) has a bigger ionic radius; therefore, these H$_2$L ligands with bulky structures can not approach Y(III); as a result, the dissociation of only one H$^+$ from the –COOH group of ligands occurs, which is more acidic than the –OH group, but aqua Y(III) can compete with H$_2$L ligand at this stage. Thus the –OH group is assumed to remain intact in the complex formation reaction and it forms Y(HL)$^{2+}$, Y(HL)(OH) type complexes at a 1 : 1 mole ratio (Tables 1, 2). However, the occurrence of YL$^+$ type complex was proposed[15)]; but the working conditions were not defined, they only tabulated the formation constants of ternary complexes of Y(III).[15)] The occurrences of M(HL)$^{2+}$ type complexes for La(III), Ce(III), Pr(III), Nd(III) and Sm(III) ions were also observed.[15)] This type of coordination of hydroxy carboxylic acids is not unusual for Cr(III),[37)] Y(III)[7,14)] and rare earths,[38)] in addition to these hydroxy naphthoic acids. For the 1 : 2 mole ratio of Cr(III) to H$_2$L ligand the occurrence of Cr(HL)L complex was assumed since Cr(III) can accomplish the coordination to HL$^-$ type monoprotonated and L^{2-} type deprotonated anion, as a result of d^3 electronic structure and the potentiometric titration results are in accordance with Cr(HL)L type stoichiometry. Our study revealed the formation of ScL$_2^-$ and ScL$_3^{3-}$ type complexes either with 1,2-HNA or 3,2-HNA, but Bhatt *et al.*[12,13)] could not define the stoichiometries of 1 : 2 and 1 : 3 complexes for Sc(III).

Figure 3 shows the distribution of the Cr(III) and its coordination species that occurred in the Cr(III) : 1,2-HNA system as a function of pH for defined concentrations (for simplicity only Cr(III) distribution diagram is presented). Thus, the major species resulted from Sc(III) : H$_2$L and Y(III) : H$_2$L systems in the acidic pH ranges for all systems are defined by potentiometry as: ScL, ScL$_2$, ScL$_3$, CrL, Cr(HL)L, Y(HL), Y(HL)$_2$ respectively, but in the basic pH ranges these complex species lose protons from coordinated water molecules, then they turn out to their hydroxo complexes; as a result, the occurrences of ScL(OH), CrL(OH), Cr(HL)L(OH) and Y(HL)(OH) type complexes were defined.

The degree of formation ($\tilde{n}$) values were then calculated for each M(III) : H$_2$L system and their formation curves were drawn, as an illustration only for Sc(III) : 1,2-HNA system in 1 : 3 mole ratio is given in Fig. 4; it reaches up to $\tilde{n}\cong3.0$ which indicates the coordination of up to three moles of H$_2$L ligand. In the formation curves of Cr(III) : H$_2$L and Y(III) : H$_2$L systems $\tilde{n}$ values are continuously increasing from $\tilde{n}\cong1.0$ to the maximum value of $\tilde{n}\cong2.0$ which may reflect the formations of MHL, M(HL)$_2$, M(HL)L and M(HL)(OH)$^+$ complexes.

Spectroscopic Investigations The stoichiometries of the

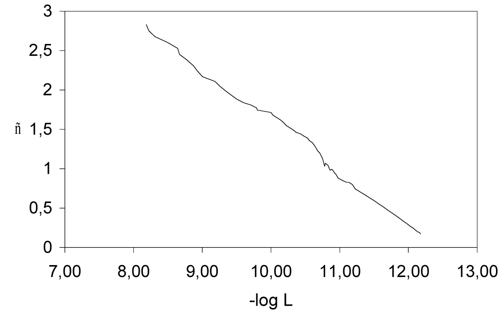

Fig. 4. Degree of Formation, $\tilde{n}$, as a Function of $-\log L$

Sc(III) : 1,2-HNA ($T_{Sc}=1.964\times10^{-3}\,mol\cdot l^{-1}$ and $T_L=5.892\times10^{-3}\,mol\cdot l^{-1}$).

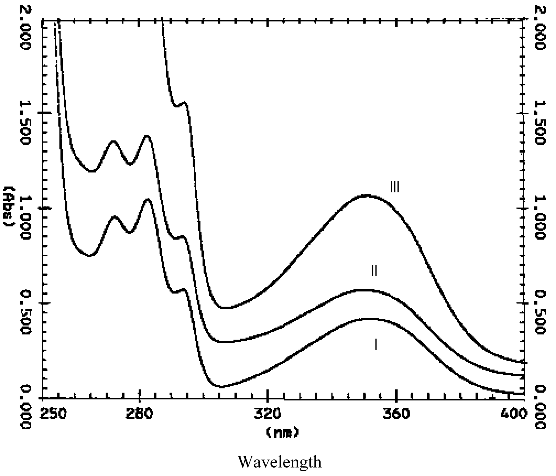

Fig. 5. Absorption Spectra of Cr(III) Complexes of 3,2-HNA in $0.1\,mol\cdot l^{-1}$ KCl at 25 °C (pH=4.0)

I: 3,2-HNA alone ($T_L=1\times10^{-4}\,mol\cdot l^{-1}$; $X_M=0.0$); II: (1 : 1) Cr(III) : 3,2-HNA ($T_{Cr}=T_L=1\times10^{-4}\,mol\cdot l^{-1}$; $X_M=0.5$); III: (1 : 2) Cr(III) : 3,2-HNA ($T_{Cr}=1\times10^{-4}\,mol\cdot l^{-1}$, $T_L=2\times10^{-4}\,mol\cdot l^{-1}$; $X_M=0.33$).

formed complexes were defined by spectroscopy. The pH dependent changes in absorbances of the ligands were correlated from the potentiometric titration curves of the ligands alone. The maximum absorptions of ligands alone were observed for 1,2-HNA at $\lambda=370\,nm$ and for 3,2-HNA at $\lambda=395\,nm$ (their pH values were 3.50). The most appropriate working wavelengths for the Cr(III) : H_2L and Sc(III) : H_2L systems were defined at pH *ca.* 3.50; they were found at $\lambda=395\,nm$ for the Sc(III) : 1,2-HNA system and for the Sc(III) : 3,2-HNA system at $\lambda=395\,nm$ in 1 : 1 mole ratios. The spectra of the Cr(III) : H_2L systems were taken at pH=4.0 in order to define the absorbances of the species which exist at $\lambda=380\,nm$ in 1 : 1 Cr(III) : 1,2-HNA system and at $\lambda=390\,nm$ in 1 : 1 Cr(III) : 3,2-HNA system (Fig. 5, the spectra of 3,2-HNA and Cr(III) : 3,2-HNA systems). Job's plots were drawn for each M(III) : H_2L system at those working wavelengths and then the stoichiometries of the complexes were defined from Job's plots (Fig. 6, it is given only for Cr(III) : 1,2-HNA system). The stoichiometries of the formed complexes correspond to $X_M=0.5$, meaning that CrL^+ or ScL^+ type complexes exist at pH=4.0 for 1 : 1 mole ratios.

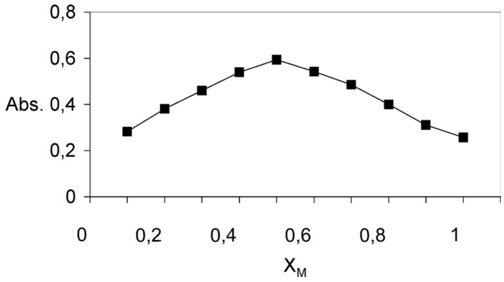

Fig. 6. Job's Plot for Cr(III) : 1,2-HNA Complexes at $\lambda=380\,nm$ and at pH=4.0

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[11,28,37,39] from 1996—1998 to define the total Cr, Cr(III) and Cr(VI) concentrations in Nilufer River. The total chromium concentrations varied in the (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.[39,40] The equilibrium concentration of Cr(III) that exists in 1,2-HNA or 3,2-HNA complex equilibria were found to be either 1 : 1 or 1 : 2 mole ratios 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 mol/l to 5.232×10^{-12} mol/l by the addition of 1,2-HNA at a 1 : 1 mole ratio in the acidic pH range of 4.00—7.00.[39]

Conclusion

I. As could be seen, the stabilities of 1 : 1 Cr(III) and Sc(III) complexes of 1,2-HNA and 3,2-HNA ligands are comparable. Cr(III), as a d^3 ion, has the smallest ionic radius (0.76 Å) while Sc(III) and Y(III) are d^0 ions and their ionic radii are 0.89 Å and 1.04 Å, respectively. As a result of comparable ionic potentials of Sc(III) and Cr(III) they may form ML^+ type complexes with these H_2L ligands. But the complexes of Y(III) is MHL type and is weaker than 1 : 1 Cr(III) and Sc(III) complexes of H_2L due to the smaller ionic potential.

II. 1,2-HNA forms more stable complexes with these three metal ions than 3,2-HNA. These results are in agreement with the overall basicity of the ligands.

III. Over the acidic pH range the binding of these H_2L ligands to Sc(III) and Cr(III) in 1 : 1 mole ratio take place, presumably *via* (COO^-, O^-) sites and ML^+ type complexes are formed. While only Sc(III) may form ML_2^- and ML_3 type complexes in higher mole ratios by simultaneous coordination of second and third moles of ligands due to the d^0 electronic structure, but Y(III) may coordinate H_2L ligands only from one site, presumably *via* COO^- site.

It was decided that there are similarities between the binding modes of Cr(III) and Y(III) complexes of H_2L ligands in 1 : 2 mole ratio since second mole of H_2L ligand is coordinated only from one site.

IV. The complexes of Cr(III), Sc(III) and Y(III) formed by these hydroxo naphthoic acids take place in hydrolytic equilibria in neutral and basic media. As a result, their monohydroxo complexes are observed.

V. The results of Cr(III) speciation studies for complexes of Cr(III) ion formed by 1,2-HNA or 3,2-HNA 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 1,2-HNA into the discharge water of leather tanneries, at a 1 : 1 mole ratio.

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