Equilibrium Studies on Chromium(III) Complexes of Salicylic Acid and Salicylic Acid Derivatives in Aqueous Solution

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The complexes of chromium(III) ion formed by salicylic acid, SA(H_2L), and its derivatives (H_2L): 5-nitrosalicylic acid (5-NSA), 5-sulphosalicylic acid (5-SSA) were investigated by means of potentiometry and spectroscopy, at 25 °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(III) ion to SA and its derivatives in 1 : 1 mole ratio occurs, CrL^+ type complex is formed. In the excess of ligand, the coordination of the second ligand molecule is somewhat hindered; as a result CrL(HL) type complex occurs. Their existences were verified and their formation constants were determined. At near neutral pH, CrL(OH) and CrL(HL)$(OH)^-$ type hydroxo complexes formed by hydrolytic equilibria and their formation constants were also defined. The stabilities of Cr(III) complexes of SA and its derivatives decrease in the following order: SA>5-SSA>5-NSA. The formation constants of Cr(III) complexes of SA and its derivatives are in comparable ranges with the corresponding complexes of the 2,*x*-dihydroxybenzoic acid (2,*x*-DHBA) of Cr(III) ion. The stabilities of SA complexes for V(IV), Cr(III) and Fe(III) ions that have similar ionic radii, increase in the order VOL<CrL^+<FeL^+. It is worthwhile noting that the binding ability of Cr(III) to salicylate ion is four orders of magnitude higher than to transferin, which is a blood serum protein and is associated with insulin action.

Key words chromium; salicylic acid; salicylic acid derivative; potentiometry; stability constant

Chromium(III) is one of the most stable, generally and biologically important oxidation state of chromium with d^3 configuration. The hexaaqua chromium(III) ion, $[Cr(H_2O)_6]^{3+}$, is acidic (pK_a=4) and the hydroxo ions that are formed by hydrolytic equilibria, $Cr(OH)^{2+}$, $Cr(OH)_2^+$, condense to give polymeric hydroxo bridged or polynuclear complexes of the type $[Cr_x(OH)_y(H_2O)_z]^{n+}$ at near neutral pH.[1)] Drljaca and Spicca[2)] studied the mechanisms and factors which influence the rates of the acid cleavage of trimers and tetramers of Cr(III) ion as a function of hydrogen ion concentration and temperature. Stefanowicz *et al.*[3)] also established that the stable state of equilibria between hydrated Cr(III) ion, various ligands, and the resulting complex compounds were achieved rather slowly. Therefore, in the investigations of Cr(III) ion hydrolysis, they took into account the influence of time, temperature, Cr(III) concentration, and the ionic strength of the solution. They also determined the formation constants of the hydroxo complex species for mononuclear mode until chromium(III) hydroxide precipitates and also reported the influence of the absolute pH value upon the hydrolysis. They applied the curve fitting method in equilibrium state calculations in their research.

There is no evidence for any toxic effects of Cr(III), which is an essential trace element in mammals (required daily intake 50—200 μg) and it was shown that Cr(III) is required for proper carbohydrate and lipid metabolism in mammals.[1,4—6)] Vincent reviewed the function of Cr(III) in glucose metabolism associated with insulin action.[6)] In the "low-molecular-weight Cr binding substance" (LMWCr), an oligopeptide, a tetranuclear Cr(III) carboxylate complex maybe present. In humans, Fe(III) and Cr(III) ions that have similar charge and ionic radii should bind relatively tightly to the transferin, which is a blood serum protein. *In vitro* studies of the addition of Cr(III) ions to isolated transferrin reveal that Cr(III) readily binds to the two-metal binding sites. However, only Cr(III) ions at one site can be displaced by Fe(III) ion at near neutral pH and below pH *ca.* 6. Recent reports on the effects of insulin on Fe(III) transport and diabetes suggest that transferrin may actually be the major physiological chromium transport agent.

On the other hand, in surface waters uncomplexed Cr(III) ion partly oxidizes to Cr(VI) ion that is toxic and possesses mutagenic and carcinogenic activity.[7)] Most of the soluble chromium in surface waters may be present as Cr(VI) ion and a small amount as organic complexes of Cr(III) ion. It is well known that chromium pollution in surface waters occurs due to waste water from the electroplating, leather tanning, and textile industries and solid waste from the chemical manufacture of chromium compounds when disposed in landfill sites. The removal of Cr(III) ion from polluted surface water would be possible by complexation either with natural or synthetic ligands.[7—10)] The most important class of complexing agents that occur naturally are the humic subtances that contain the humic acids. The main chelating groups of humic acids are the carboxyl and phenolic groups of salicylates; they present heterogeneous compositions that depend on the chemistry of how they were generated.

Salicylic acid (SA) and its derivatives (H_2L) are also biologically important ligands. Its well known and most widely used drug aspirin reduces the risk of many diseases associated with aging and is used in the treatment of rheumatic fever, pain, and the prevention of thrombosis in the vascular system. On the other hand, a search of the literature revealed that there are many studies which deal with SA complexes of various metal ions.[11—22)] Anderson *et al.*[14)] and Singh *et al.*[16)] included Cr(III) ion in their investigations of the 5-sulphosalicylate (5-SSA) complexes of various metal ions which form hydrolytic species. They successfully determined the formation constant of 1 : 1 Cr(III) : 5-SSA complex; but they were interested in neither hydrolytic equilibria of this complex nor the 1 : 2 Cr(III) : 5-SSA complex.

There were three aims of the present work, the first of

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which was to evaluate the stochiometries and determine the formation constants of the Cr(III) complexes of SA, 5-NSA, and 5-SSA. Thus, it would be possible to compare these formation constants with the corresponding values for the 2,*x*-DHBA (x=4, 5, 6) complexes since we have already determined the complex species present in systems containing Cr(III) ion and 2,*x*-DHBA by potentiometry and spectrophotometry.[18] As a result of this study, the behaviours of Cr(III), oxovanadium(IV),[17] and Fe(III)[11,12] ions towards (SA) and its derivatives can also be determined since they have similar ionic radii. The second aim was to investigate the pH ranges by means of species distribution curves, in which the complexes of Cr(III) and SA or SA derivatives can exist. Thus, the stabilities of Cr(III) : transferrin[6] and Cr(III) : SA or SA derivatives complexes can be compared, and these results can serve as a framework for further studies to test the role of Cr(III) ion in metabolism in mammals that involves salicylates of aspirin, and the influences of SA or SA derivatives on transferrin and Cr(III) transport in insulin action can be investigated. The third aim was to suggest suitable synthetic ligands in order to remove Cr(III) pollutants in the Nilufer River, which flows through the Bursa plain, that are present in the waste water of leather and electroplating factories.

Experimental

Materials All chemicals used in this research were of analytical reagent grade. The bidentate ligands, SA (Merck), 5-NSA (Aldrich, 99% purity) and 5-SSA (Sigma, 99% purity), were the highest quality used available as received; the purities of the ligands were further checked by the Gran method.[23] The stock solution of Cr(III) was prepared for potentiometric measurement by dissolving the proper amounts of $Cr(NO_3)_3 \cdot 9H_2O$ (Merck) in a small excess of 10^{-2} M HNO_3 (Merck, 100% purity, d=1.52) to avoid hydrolysis as described previously.[18] The supporting electrolyte was 0.1 M KNO_3 to adjust the ionic strength. For spectroscopic measurements, $CrCl_3 \cdot 6H_2O$ was dissolved in 10^{-2} M HCl and the ionic strength was adjusted to 0.1 M by 0.1 M KCl.

Potentiometric Measurements The details of the apparatus and procedure were described in previous publications.[18,24,25] The experimental method consisted of potentiometric titration of SA and its derivatives, H_2L (for simplicity charge in 5-SSA is omitted) in the absence of and in the presence of Cr(III) ion. At least three different potentiometric titrations were carried out for H_2L and Cr(III) : H_2L systems in which the Cr(III) concentrations were in the 1.97×10^{-3}—7.88×10^{-3} M range and in different mole ratios. The concentration of free acid in the Cr(III) solution was systematically checked by potentiometric titrations before each series of experiments. In acidic medium, the reaction was considerably faster than in neutral or basic solutions. Because of kinetic inertness of the Cr(III) ion, the resulting complex compounds are achieved rather slowly. Therefore, at least one overnight period (24 h) is required for pH equilibrium to be reached, after each addition of NaOH into the Cr(III)-ligand mixture.

Spectroscopic Measurements The UV and VIS absorption spectra were taken using a Shimadzu UV-2100 spectrophotometer to define the existence of deprotonated SA, SA derivatives and their Cr(III) complexes at different pH values, as a function of wavelengths. The stochiometries of these complexes were then determined by taking spectra of Cr(III) systems which include Cr(III) ion and SA or its derivatives in definite mole ratios in the 290—410 nm range. Job's method was applied whenever possible in order to confirm the results of the potentiometry.[24]

Calculations The potentiometric titration curves of three ligands and their complexes with Cr(III) ions were investigated by mathematical analysis. The calculated protonation constants (K) were introduced into the necessary equations and then the formation constants of the Cr(III) complexes of SA or SA derivatives, (β), were calculated by the RANA computer program.[25] For each system, the best complex that accounts for the experimental data was assumed. Non-linear least-squares analysis of the data in terms of assumed reactions gave a satisfactory fit in the buffer regions of complexes in different mole ratios of Cr(III) and ligands. The Log K and Log β values were the averages of at least ten calculated values in the defined regions (Table 1). In order to draw the speciation and formation curves the concentrations of the various species and $\bar{n}$ values were also calculated using the RANA computer program.

Results and Discussion

Proton Complexes of Salicylic Acid and its Derivatives Two protons of SA and its derivatives dissociate in the measurable range. In these ligands only carboxyl groups can loose protons in acidic medium, but it was proved by detailed potentiometric and spectrophotometric measurements[28] that the dissociation of the phenolic OH can be detected and determined only with a large experimental error due to the strong intramolecular hydrogen bond between the COO^- and OH group.[9,27,28] Therefore, the potentiometric titrations were performed to define only the protonation constants of HL^- ions and the results are tabulated in Table 1 (row 1). Our $\log K_{HL^-}$ values are in a comparable range with values that were defined by Martell[13] and Migal *et al.*[26] However, we introduced literature values for $\log K_{L^-}$ in our calculations due to the above explained difficulties in the determination of $\log K_{L^-}$ values. As a result of the electron-withdrawing actions of phenoxide, nitro and sulpho groups, the sums of the log protonation constants (pK's) of SA, 5-SSA, and 5-NSA decreases in the order SA>5-SSA>5-NSA and this order indicates the hardness of these bidentate donors.

Cr(III) Complexes of Salicylic Acid and Its Derivatives, Potentiometric Investigations H_2L ligands alone and then Cr(III) : H_2L systems at (1 : 1) and (1 : 2) mole ratios were investigated potentiometrically. The potentiometric titrations started with a base solution at pH *ca.* 2.4 and continued up to pH *ca.* 6.5 either in 1 : 1 and 1 : 2 mole ratios. Since the precipitation of hydrolytic complexes was started, the titration curves could not be drawn after pH=7.0. Well-defined inflection points were noticed at m=2.0 and at m=3.0 for 1 : 1 mol ratios (m is moles of base added per mole of ligand; Fig. 1, curve II, only the curves obtained for one concentration of SA are shown). The formation of CrL^+ type complex was considered by neutralization of carboxyl and phenolic protons in m=0.0—2.0 range (Table 1, row 3); then the occurrence of CrL(OH) type complexes by hydrolytic reactions of CrL^+ type complexes was assumed in m=2.0—3.0 range (Table 1, row 4). The existences of these complexes were verified by taking into account the related equilibria. The calculated formation constants (β) of the suggested complexes are tabulated in Table 1. We can compare only the literature values of $\log \beta$ that were found for 1 : 1 Cr(III) : 5-SSA complex; our $\log \beta$ value is higher than the corresponding $\log \beta$ values of Anderson *et al.*[14] and Singh *et al.*[16] (Table 1, row 3). These discrepancies could be related to differences in the ionic media and other working conditions since our ionic medium was 0.1 M KNO_3.

In the case of 1 : 2 mole ratios of three Cr(III) : H_2L systems; the first and second inflections were observed at m=3.0 and around m=4.0, respectively. Attempts to calculate the formation constants of CrL_2^- type complexes from data obtained for values of "m" less than 3.0 (pH=2.4—4.0 range) were unsuccessful. The occurrences of CrL(HL) and $CrL(HL)(OH)^-$ type complexes in m=0.0—3.0 and m=3.0—4.0 ranges, respectively, might be taken into account (Table 1, rows 5, 6). The potentiometric titration results verified our suppositions by calculations. Cr(III) ion with d^3 electronic configuration can compete with two moles of hydro-

Table 1. Equilibrium Constants of Proton Complexes ($\log K$) and Formation Constants ($\log \beta$) of Cr(III), VO^{2+}(IV) and Fe(III) : SA, 5-SSA and 5-NSA Complexes at 25±0.0 °C and I=0.1 M KNO_3

Row	Equilibrium	SA	5-NSA	5-SSA
	Proton complexes	Log K	Log K	Log K
1	$HL^- + H^+ \rightleftharpoons H_2L$	2.81[13] 2.77±0.03[a]	2.20[13] 1.92±0.01[a]	2.47[26] 2.48±0.02[a]
2	$L^{2-} + H^+ \rightleftharpoons HL^-$	13.4[13]	10.11[13]	11.87[26]
	Cr(III) complexes	Log β	Log β	Log β 9.56[16]
3	$Cr^{3+} + L^{2-} \rightleftharpoons CrL^+$	13.27±0.06[a]	8.94±0.06[a]	9.79±0.03[a]
4	$CrL^+ + OH^- \rightleftharpoons CrL(OH)$	5.90±0.07[a]	5.43±0.06[a]	5.73±0.06[a]
5	$Cr^{3+} + L^{2-} + HL^- \rightleftharpoons CrL(HL)$	15.23±0.07[a]	10.87±0.04[a]	11.80±0.04[a]
6	$CrL(HL) + OH^- \rightleftharpoons CrL(HL)(OH)^-$	6.30±0.06[a]	6.23±0.04[a]	5.81±0.08[a]
	VO^{2+} Complexes			
7	$VO^{2+} + L^{2-} \rightleftharpoons VOL$	12.97±0.02[17]	—	11.71[33]
8	$VO^{2+} + 2L^{2-} \rightleftharpoons VOL_2^{2-}$	22.81±0.09[17]	—	20.6[33]
9	$VOL + OH^- \rightleftharpoons VOL(OH)^-$	6.32[17]		
	Fe^{3+} Complexes			
	$Fe^{3+} + L^{2-} \rightleftharpoons FeL^+$	16.3[31]	14.34[32]	14.60[34]
	$Fe^{3+} + 2L^{2-} \rightleftharpoons FeL_2^-$	28.25[31]	—	25.15[34]

a) This work.

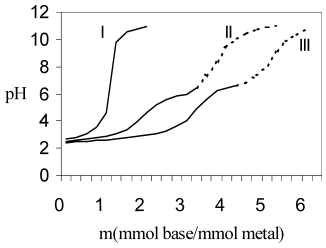

Fig. 1. Potentiometric Titration Curves of Cr(III) Complexes of SA in 0.1 mol L^- KNO_3 Ionic Medium at 25 °C

I: SA alone (T_L=1.974×10^{-3} mol L^-); II: Cr(III)–SA system in 1 : 1 mol ratio (T_{Cr}=T_L=1.974×10^{-3} mol L^-); III: Cr(III)–SA system in 1 : 2 mol ratio (T_{Cr}=1.974×10^{-3}, T_L=3.948×10^{-3} mol L^-).

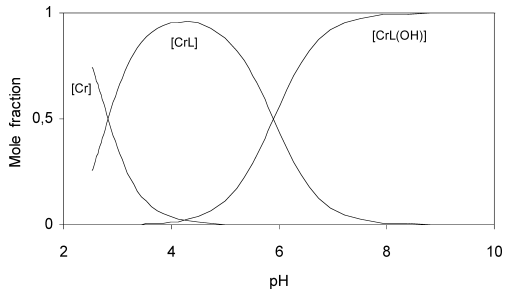

Fig. 2. Species Distribution Curves of Cr(III) : SA System in 1 : 1 Mole Ratio as a Function of pH, for a Solution Initially Containing 3.94×10^{-4} mol L^- SA and 1.97×10^{-3} mol L^- Cr(III) Ion at 25 °C and I=0.1 mol L^- KNO_3 Ionic Medium

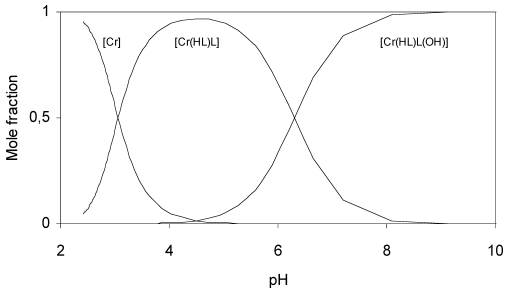

Fig. 3. Species Distribution Curves of Cr(III) : SA System in 1 : 2 Mole Ratio as a Function of pH, for a Solution Initially Containing 3.94×10^{-4} mol L^- SA and 1.97×10^{-3} mol L^- Cr(III) Ion at 25 °C and I=0.1 mol L^- KNO_3 Ionic Medium

gen ions of the first mole of H_2L ligand, however, the complete coordination of the second mole of H_2L ligand to CrL^+ coordination ion does not take place. The coordination of the second ligand molecule to CrL^+ ion is hindered due to electrostatic reasons. Therefore, Cr(III) ion can coordinate only HL^- forms of the second mole of ligand rather than the L^{2-} forms for pH<3.0. As a result, CrL(HL) seems to be formed. This might be due to the higher affinity of Cr(III) ion for carboxylate groups in acidic medium. The same behaviour was observed in SA complexes of uranyl (UO^{2+})[29] and Al(III) complexes of 2,*x*-DHBA.[9] However, the prevelance of one of the two possibilities in SA and its derivatives towards Cr(III) ion depends on the pH of the solution and the charge/radius ratio of the metal ion.[9,13]

The species distribution curves (as an illustration, that for the system Cr(III) : SA in 1 : 1 mole ratio is given in Fig. 2) show that the major species in the acidic pH range in all systems are mono complex CrL^+; but in the basic pH range CrL^+ complex presumably loses a proton from a coordinated water molecule and it becomes CrL(OH) type species. In the case of a 1 : 2 mole ratio, the major species in the acidic pH in all systems (only for system Cr(III) : SA in a 1 : 2 mole ratio is given in Fig. 3) are CrL(HL) type complex, while in basic pH CrL(HL)(OH) complex is formed by hydrolytic equilibria.

In order to verify the potentiometric data for Cr(III) : SA and SA derivatives, the degree of formation ($\tilde{n}$) values were determined and then the formation curves were drawn in a (1 : 2) mole ratio–log ligand concentration *versus* $\tilde{n}$ (Fig. 4). They have one plateau at $\tilde{n}\cong$1.0 and then they reach up to $\tilde{n}\cong$1.87 ($\tilde{n}$<2), which suggests that Cr(III) ion coordinates one mole of SA in the L^{2-} form (Table 1, row 3). However, this coordination continues by deprotonation of a second mole of SA to form (HL^-) ion with a protonated phenol

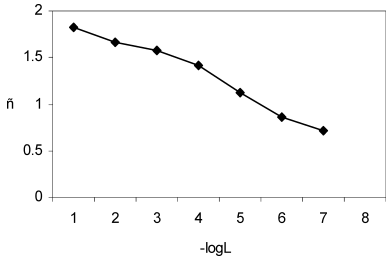

Fig. 4. Degree of Formation, $\tilde{n}$, as a Function of $-\log L$ in 1 : 2 Mole Ratio of Cr(III)–SA System

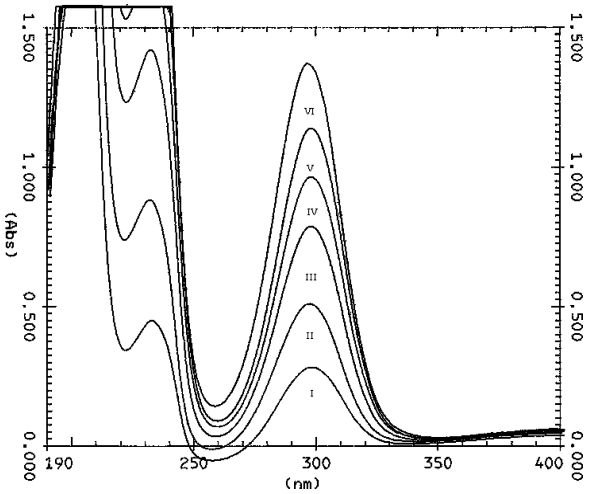

Fig. 5. Absorption Spectra of a Set of Solutions of Cr(III) Complex of SA in 0.1 mol L^- KCl Ionic Medium at 25 °C

The solutions all contain Cr(III) ion in 1.6×10^{-3} mol L^- plus SA in 1.6×10^{-3} mol L^-. pH values (for solutions in order of decreasing intensity at 326 nm): 4.410, 4.203, 4.008, 3.804, 3.612 and 3.401.

group.

Spectrophotometric Investigations The pH dependent changes in absorbances for each ligand were determined from the titration curves of ligands alone in order to select convenient pH values. The electronic spectra of SA and its derivatives in 2×10^{-4} M L^- concentration at pH=4.0 were then taken. The maximum absorption of SA alone was observed at λ=295 nm, of 5-NSA alone at λ=320 nm, and of 5-SSA alone at λ=295 nm. The potentiometric results were defined in terms of CrL^+ type coordination ions existing in a pH=3.4—4.4 range. Therefore, the spectra for each Cr(III) : H_2L system were taken at the pH range of 3.4—4.4, and thus the changes in absorbance values with pH values were investigated. The most appropriate working wavelengths for each 1 : 1 Cr(III) : H_2L complex were defined and found to be λ=326 nm for 1 : 1 Cr(III) : SA complex; λ=410 nm is for 1 : 1 Cr(III) : 5-NSA complex, and λ=325 nm for 1 : 1 Cr(III) : 5-SSA complex (Fig. 5: only the spectra of Cr(III) : SA system in 1 : 1 mole ratio is given). Their Job's plots were drawn at these wavelengths for the solutions of Cr(III) : SA and derivatives in which the mole fractions of Cr(III) ions were (X_M=0.0—1.0) range (Fig. 6: only for Cr(III) : SA system is given). In all of the Job's plots of Cr(III) : H_2L systems in a 1 : 1 mole ratio the stochiometries of the formed complex ions at pH=4.0 correspond to X_M=0.5, indicating that CrL^+ type complexes exist. Thus, it is evident that the spectroscopic data fit very well with the potentiometric results.

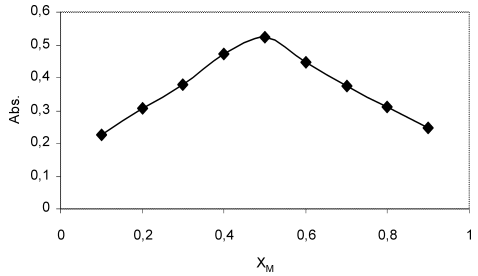

Fig. 6. Job's Plot for Cr(III)–SA System in 1 : 1 Mole Ratio at pH=4.0 at λ=326 nm

Conclusion

Over the acidic pH range, the coordination of Cr(III) ion to SA and its derivatives in a 1 : 1 mole ratio occurs presumably *via* salicylate sites (COO^-, O^-) and CrL^+ type complexes occur since a carboxylate group can act as the anchoring site for Cr(III) ion in these complexes. In the excess of ligand, the coordination of only one mole of SA and its derivatives can take place through salicylate (COO^-, O^-) sites, but coordination of the second ligand molecule is somewhat hindered and the binding of HL^- ion is accomplished. SA and its derivatives as bidentate ligands have high affinities for Cr(III) ion. SA with the highest sum of protonation constants forms the strongest complex and the stabilities of Cr(III) complexes of SA and its derivatives decrease in the following order: SA>5-SSA>5-NSA. At near neutral pH values, CrL(OH) and $CrL(HL)(OH)^-$ type hydroxo complexes also formed by hydrolytic equilibria and their formation contants were also calculated. The stochiometries of the formed complexes were defined from the spectroscopic results continuous variation method was applied; the occurrences of CrL^+ type complexes were verified.

The similarities between SA, SA derivatives and 2,*x*-DHBA ligands were noticed in their Cr(III)-binding capabilities; the salicylate sets are more effective binding sites over the acidic pH range.[18] Although 2,*x*-DHBA ligands have three acidic functional groups (H_3L), the coordination of these ligands to Cr(III) ion takes place by the dissociations of only two protons[18] in such a manner that the separate phenolic OH groups in *X* positions of 2,*x*-DHBA ligands are not coordinated and they exist as phenolic OH groups. The less acidic phenolic OH and COOH of the salicylic acid and of its derivatives dissociate and coordinate to Cr(III) ion. Thus, the formation of $Cr(HL)^+$ and $Cr(HL)(H_2L)$ type complexes is accomplished in 1 : 1 and 1 : 2 mole ratios, respectively. The formation constants of 2,*x*-DHBA complexes of Cr(III) are in comparable ranges with the corresponding SA and SA derivatives that have similar electron withdrawing substituents. Therefore the removal of Cr(III) from polluted water can be performed either by SA, SA derivatives, or 2,*x*-DHBA ligands in acidic media.

On the other hand, the behaviour of Cr(III) ion towards (SA) and its derivatives could also be compared with SA complexes of oxovanadium(IV) and Fe(III) ion. Since V(III) is a d^2 ion, Cr(III) is a d^3 ion and Fe(III) and in high spin complexes it is a d^5 ion. They have ionic radii of 0.78 Å, 0.76 Å, and 0.79 Å, respectively,[1] for a coordination number

six. VO^{2+} ion is formed by rapid oxidation of V(III) in air. These three transition metal ions that have similar ionic radii, form rather strong complexes with SA and its derivatives; while Fe(III) and VO^{2+} can coordinate one and two moles of SA. The stabilities of complexes of H_2L type ligands with VO^{2+}, Cr(III), and Fe(III) aqua ions[11,12,17] increase in the order $VOL < CrL^+ < FeL^+$ (Irwing–Williams Order). On the other hand, VO^{2+} ion also has a tendency to form hydroxo species like Cr(III) ion in aqueous solution.[17]

The effective binding constant of Cr(III) to isolated transferrin which is blood serum protein and associated with insulin action, was determined by Vincent *et al.*[30] as $\log K_1 = 10.15$ and $\log K_2 = 5.31$. They have isolated, in *in vitro* studies, Cr(III) : transferrin complex in which the binding of transferrin to Cr(III) occurs, below pH 6, only from one site. It means the coordination ability of Cr(III) to salicylate from two sites is four orders of magnitude higher than the binding ability of Cr(III) to transferin ie, Cr(III) ion will prefer to coordinate SA from salicylate sites, instead of transferrin. This property of Cr(III) ion towards transferrin is very important since it is clear that in the explanation of the role of Cr(III) in metabolism the stability of Cr(III) : SA complexes should be considered.

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