Ternary Complexs: Equilibrium Studies of Mixed-ligand Complexes of Neodymium Ion with Carboxylic and Phenolic Acids in Aqueous Medium

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The stability constants of simple and mixed ligand systems of neodymium ion with bidentate ligands such as carboxylic and phenolic acids are studied in an aqueous medium by pH metric titrations at 30±0.1 °C and at an ionic strength of 0.1 M ($NaClO_4$). Neodymium forms 1 : 1 complexes with succinic, adipic, itaconic, malonic, and 3,5-dinitrosalicylic acids and 1 : 1 and 1 : 2 complexes with phthalic, 5-sulfo-, and 4-hydroxysalicylic acids. Ternary complexes of neodymium with these acids when (i) both the ligands are carboxylic acids, (ii) one is carboxylic and the other a phenolic acid, (iii) both ligands are phenolic acids, are studied by potentiometry. The stability constants of these complexes are compared with those of binary complexes. The results have been discussed on the basis of the magnitudes of $\Delta \log K$, K_{DXY}, and $\log \beta_{XY} - 1/2[\log \beta_{XX} + \log \beta_{YY}]$, and also from the comparison of K_{2YX} and K_{MX_1} or K_{2XY} and K_{MY_1}. The values of K_{2YX} are directly related to the acid dissociation constant of the secondary ligand. The overall stability (β_{XY}) is found to be depending on the binary stabilities and the basicities of the ligands.

The simple chelates of lanthanoides with carboxylic and phenolic acids have been studied extensively, though not much work has been reported on the mixed ligand chelates of the lanthanides with these acids. As regards Nd(III), its mixed-ligand chelates with *meso-* and *dl*-tartaric acid have been investigated by Ramamoorthy and Manning.1) We have reported earlier the formation of mixed-ligand chelates of UO_2^{2+} and Cu^{2+} with bidentate carboxylic and phenolic acids by simultaneous equilibria.2,3) Nd(III) forms 1 : 1 complexes with carboxylic acids and 1 : 1 and 1 : 2 complexes with phenolic acids. The present work was undertaken to investigate whether the mixed-ligand chelates of Nd(III) with these acids are formed in a stepwise or a simultaneous equilibrium when (i) both the ligands are carboxylic acids, (ii) one is carboxylic and the other is phenolic acid, and (iii) both the ligands are phenolic acids. The calculations of various other factors were done, and the values obtained were utilized to understand some structural aspects of the mixed ligand chelates.

Experimental

Neodymium perchlorate was prepared by the standard procedure. The concentration of Nd(III) in original solution was estimated as Nd_2O_3. Succinic, adipic, itaconic, malonic, phthalic, 5-sulfo-, 3,5-dinitrosalicylic acids, and 4-hydroxysalicylic acids were of B.D.H.(AnalaR) grade. They were recrystallized and their purity was checked by their melting points. All the solutions were prepared in double-distilled water. The details of the measurements of pH are given in earlier paper.4)

Titrations. The experimental procedure involved, the potentiometric titrations of carbonate-free solutions of (i) free $HClO_4$(4.40×10^{-3} M), (ii) free $HClO_4$(4.40×10^{-3} M)+ligand(X) (2.00×10^{-3} M), (iii) free $HClO_4$(4.40×10^{-3} M)+ligand(X) (2.00×10^{-3} M)+Nd(III) (2.00×10^{-3} M) (M), (iv) free $HClO_4$(4.40×10^{-3} M)+ligand(Y) (2.00×10^{-3} M), (v) free $HClO_4$(4.40×10^{-3} M)+ligand(Y) (2.00×10^{-3} M)+Nd(III) (2.00×10^{-3} M), (vi) free $HClO_4$(4.40×10^{-3} M)+ligand(X) (2.00×10^{-3} M)+ligand(Y) (2.00×10^{-3} M)+Nd(III) (2.00×10^{-3} M), where the X and Y stands for two respective ligands. The ionic strength of solutions was maintained constant at 0.1 M by the addition of the appropriate amount of 1 M sodium perchlorate solution. The titrations were carried out in an inert atmosphere by bubbling oxygen-free nitrogen gas through an assembly containing the electrodes to keep out CO_2.

Results

Simple Systems. The proton-ligand formation number $\bar{n}_A$ was calculated by the method of Irving and Rossotti.5) The preliminary values of pK_1 and pK_2 were calculated from the proton-ligand formation curves. The pointwise method was used for the calculations of accurate pK values. These are presented in Table 1. The metal-ligand formation number, $\bar{n}$ were calculated by the Irving and Rossotti's expression.6) The maximum value of $\bar{n}$ before the pH of precipitation as observed in metal complex titration was 1.9 for phthalic, 5-sulfo-, and 4-hydroxysalicylic acids and 1.0 for succinic, adipic, malonic, and 3,5-dinitrosalicylic acids, showing thereby the ligands belonging to the first set form both 1 : 1 and 1 : 2 complexes and those to the other form only 1 : 1 complex. The pL values were calculated and the formation curves were constructed by plotting pL *vs.* $\bar{n}$. The log-K_1 and log K_2 were calculated initially by half-integral method and finally by the method of pointwise calculations. Since the difference in log K_1 and log K_2 was less than 1.7 in number of cases, their accurate values were calculated by the method of least squares. It is observed that neodymium forms only 1 : 1 complex with succinic, adipic, itaconic, malonic, and 3,5-dinitrosalicylic acids and both 1 : 1 and 1 : 2 complexes with phthalic, 5-sulfo-, and 4-hydroxysalicylic acids. The reported values of log K_1 and log K_2 for phthalic, 5-sulfo-, and 4-hydroxysalicylic acids7,8) are in good agreement with our values.

In aqueous solution neodymium ion is present as $[Nd(H_2O)_6]^{3+}$, $[Nd(H_2O)_8]^{3+}$ and $[Nd(H_2O)_9]^{3+}$.9) The metal chelate is formed due to the simultaneous replacement of water molecules from the coordination sphere of neodymium ion with formation of Nd–O bonds. The chelates formed are mainly entropy stabilized as the lanthanide chelates are generally supposed to be ionic in nature.

TABLE 1. DISSOCIATION CONSTANTS (pK_1 AND pK_2) OF LIGANDS AND STABILITY CONSTANTS ($\log K_1$ AND $\log K_2$) OF NEODYMIUM COMPLEXES
$t=30\ ^\circ C$ $\mu=0.1\ M\ (NaClO_4)$

Ligand acid	pK_1		pK_2		$\log K_1$[a]		$\log K_2$[b]	
	Obsd	Lit	Obsd	Lit	Obsd	Lit	Obsd	Lit
Succinic	3.82±0.04	3.86(2) 4.00(7)	5.22±0.03	5.22(2) 5.21(7)	3.38	—	—	—
Adipic	4.14±0.02	4.12(2) 4.28(7)	5.06±0.03	5.03(2) 5.06(7)	2.90	—	—	—
Itaconic	3.62±0.04	3.68(7)	5.11±0.03	5.14(7) 5.06(7)	3.77	—	—	—
Malonic	2.86±0.02	2.66(7)	5.28±0.03	5.32(7) 5.27(7)	4.21	—	—	—
Phthalic	2.80±0.03	2.80(2)	4.92±0.04	4.92(2) 5.00(7)	4.22	4.22(7)	3.25	3.25(7)
5-Sulfosalicylic	2.63±0.02	2.49(7)	12.10±0.02	12.00(7)	7.39	7.39(7)	5.62	5.62(7)
3,5-Dinitrosalicylic	1.31±0.02	1.31(2)	7.02±0.02	7.00(2)	4.44	4.44(8)	—	—
4-Hydroxysalicylic	3.33±0.02	3.33(2) 3.31(7)	14.20	14.20(2)	10.91	—	9.75	—

a) $\log K_{MX_1}/\log K_{MY_1}$. b) $\log K_{MX_2}/\log K_{MY_2}$.

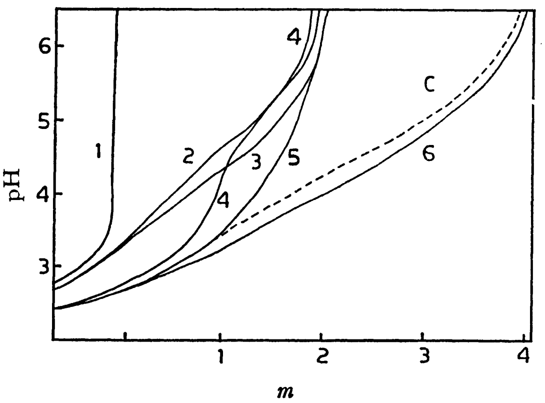

Fig. 1. Neodymium ion-succinic acid-malonic acid system. $\mu=0.1(NaClO_4)$, $t=30\ ^\circ C$, pH titration curves of a system (i) $HClO_4$(1), (ii) $HClO_4$+succinic acid(2), (iii) $HClO_4$+succinic acid+neodymium ion(3), (iv) $HClO_4$+malonic acid(4), (v) $HClO_4$+malonic acid+neodymium ion(5), and (vi) $HClO_4$+succinic acid+malonic acid+neodymium ion(6) against 0.22 M sodium hydroxide, c=composite curve.

Mixed-ligand Systems. The formation of a mixed ligand complex was concluded initially from qualitative evidence by noting the pH of precipitation for MX, MY and MYX for the titration curves III, V and VI respectively. It was observed that the pH of precipitation for the mixed ligand system was either the same or higher than that of the simple ligand system. The formation of a mixed ligand chelate was confirmed by comparing the mixed ligand curve with the composite curve. The latter curve was drawn theoretically by the graphical addition of 1 : 1 MX curve to the titration curve of free ligand Y. If there is any interaction between NdX and Y the composite curve should be displaced from the experimental curve. The deviation of the composite curve from the mixed ligand titration one was observed in each case. The nature of the complex equilibrium was investigated according to the method suggested by Carey and Martell.[10]

The pH titration curves for a representative system are shown in Fig. 1. The moles of base added after the neutralization of $HClO_4$ are presented as *m*.

The procedure adopted to understand the complexation equilibria is discussed for a representative system. For all the remaining systems the conclusions drawn regarding the complexation were on the basis of the considerations given above. The final complexation reactions are given in a consolidated form.

Carboxylic–Carboxylic Acid Systems.

i) Neodymium-succinic (H_2Y)–adipic (H_2X) acid.
ii) Neodymium-succinic (H_2Y)–malonic (H_2X) acid.
iii) Neodymium-succinic (H_2Y)–itaconic (H_2X) acid.
iv) Neodymium-succinic (H_2Y)–phthalic (H_2X) acid.

The pH values of precipitation for four mixed ligand systems i—iv were 7.0, 6.8, 7.0 and 6.6 respectively, while those of Nd(III)–succinic acid, Nd(III)–adipic acid, Nd(III)–malonic acid, Nd(III)–itaconic acid, and Nd(III)–phthalic acid were 7.2, 7.1, 6.9, 7.0, and 6.8 respectively. All the carboxylic acids individually form 1 : 1 complex with neodymium except phthalic acid which forms both 1 : 1 and 1 : 2 complexes in the pH range 3—5. The deviation of the mixed ligand curve from the composite curve was from m=0—4 for the systems i, ii, and iii and m=0—3 for the system iv. The horizontal difference between the mixed ligand complex curve and the composite one remained nearly constant in all the systems, in the pH range 3—6, except in the case of succinic–phthalic acids, wherein the composite curve was towards right-hand side of the mixed ligand titration curve above pH 5. The formation of a mixed ligand chelate by a simultaneous equilibrium for i—iii can be shown as:

$$Nd^{3+} + H_2X + H_2Y \rightleftharpoons Nd(X)(Y)^- + 4H^+$$

In succinic–phthalic acid the mixed ligand titration curve was towards right hand side of the composite curve between m=0—3 and, therefore, the complexa-

TABLE 2. THE MIXED LIGAND SYSTEMS OF Nd^{3+}-ligand(Y)-ligand(X) WITH THE COMPLEXATION EQUILIBRIA $t=30$ °C; $\mu=0.1$ M ($NaClO_4$).

Acid system	Complexation equilibria
1. Malonic-adipic[a]	$Nd^{3+} + H_2X + H_2Y \rightleftharpoons Nd(X)(Y)^- + 4H^+$
2. Malonic-itaconic	
3. Phthalic-adipic	
4. Phthalic-itaconic	$Nd^{3+} + H_2X + H_2Y \rightleftharpoons Nd(HX)(Y) + 3H^+$
5. Phthalic-malonic	$Nd^{3+} + HX^- + HY^- \rightleftharpoons Nd(X)(Y)^- + 2H^+$
6. Succinic-3,5-dinitrosalicylic	$Nd^{3+} + HX^- + H_2Y \rightleftharpoons Nd(X)(Y)^- + 3H^+$
7. Malonic-3,5-dinitrosalicylic	$Nd^{3+} + HX^- + H_2Y \rightleftharpoons Nd(HX)(Y) + 2H^+$
8. Phthalic-3,5-dinitrosalicylic	$Nd^{3+} + HX^- + HY^- \rightleftharpoons Nd(X)(Y)^- + 2H^+$
9. Succinic-5-sulfosalicylic	$Nd^{3+} + H_2X^- + H_2Y \rightleftharpoons Nd(HX)(HY) + 2H^+$
10. Malonic-5-sulfosalicylic	
11. Phthalic-5-sulfosalicylic	
12. 5-sulfo-3,5-dinitrosalicylic	$Nd^{3+} + HX^- + HY^{2-} \rightleftharpoons Nd(X)(HY)^- + H^+$
13. 5-sulfo-4-hydroxysalicylic	$Nd^{3+} + H_3X + HY^{2-} \rightleftharpoons Nd(H_2X)(Y)^- + 2H^+$
14. 3,5-dinitro-4-hydroxysalicylic	$Nd^{3+} + H_3X + HY^- \rightleftharpoons Nd(H_2X)(Y) + 2H^+$

a) Y stands for malonic and X stands for adipic.

tion is represented as:

$$Nd^{3+} + H_2Y + H_2Y \rightleftharpoons Nd(X)(HY) + 3H^+$$

In the titrations of the neodymium ion mixed ligand systems against standard sodium hydroxide, the following possible equilibria along with disproportionation reactions are given in Table 2.

In all the cases the equilibria

$$K_{MX_1} = K(M+X \rightleftharpoons MX),$$
$$K_{MX_2} = K(MX+X \rightleftharpoons MX_2),$$
$$K_{MY_1} = K(M+Y \rightleftharpoons MY),$$
$$K_{MY_2} = K(MY+Y \rightleftharpoons MY_2),$$
$$K_{2XY} = K(MX+Y \rightleftharpoons MXY),$$
$$K_{2YX} = K(MY+X \rightleftharpoons MXY), \text{ and}$$
$$\beta_{XY} = K(M+X+Y \rightleftharpoons MXY),$$

must be involved.

The disproportionation constants

$$K_{DXY} = K(MX+MY \rightleftharpoons MXY+M),$$
$$K_{DXY} = K(MX_2+MY \rightleftharpoons MXY+MX),$$
$$K_{DXY} = K(MX+MY_2 \rightleftharpoons MXY+MY), \text{ and}$$
$$K_{DXY} = K(MX_2+MY_2 \rightleftharpoons 2MXY),$$

corresponding to the systems are calculated.

The distinguishable cases depend on the relative value of K_{MX_1}, K_{MX_2}, $\cdots$, β_{XY}. In all the cases $\beta_{XY}= K_{MX_1}\cdot K_{2XY}=K_{MY_1}\cdot K_{2YX}$.

The procedure adopted and the mathematical expressions used for the calculations of the stability constants of mixed-ligand chelates were given earlier.[11] All the mathematical calculations were done on the DCM Moscal 1400 electronic calculator. The β_{XY} values are presented in Table 3.

The stability of ternary complex is conveniently characterized by the following two ways. One is based on the difference of stability constants (logarithmic values), $\Delta\log K$, and the second on the disproportionation constant, $\log K_{DXY}$.

$$\Delta\log K = \log K_{MY_1} - \log K_{2XY}$$

Generally, $K_{MY_1}>K_{MY_2}$ because more coordinating positions are normally available for bonding of the first ligand to a metal ion than for the second ligand. The addition of ligand Y to MX should also show the same trend. Evidently, $K_{MY_1}>K_{2XY}$ or $\Delta\log K$ is positive. $\Delta\log K$ can also be calculated by the expression:

$$\Delta\log K = \log K_{MX_1} + \log K_{MY_1} - \log\beta_{XY}.$$

The positive $\Delta\log K$ value of ternary system indicates that primary ligand anion and secondary ligand anions preferentially form binary complexes to ternary complexes.

From the above expression it follows that the influence of both ligands in a ternary complex is mutual and of the same size. Both ligands are either stabilized or destablished in their coordination to the same metal ion. This is connected with the fact that the difference, $\Delta\log K$, is the result from the subtraction of two constants, and, therefore, also a constant which corresponds to the equation.

$$MX + MY \rightleftharpoons MXY + M$$

Obviously, the observation of positive values for $\Delta\log K$ would indicate that the equation is more on its right side.[12]

Based on the statistical considerations, mixed ligand chelate formation by these disproportionation reactions is favored, if $\log K_{DXY}>0.6$ log units.[12] The comparison of equilibrium constants $\log K_{2XY}$ and $\log K_{MY_2}$, can be made to find out whether the primary diacid ligand prefers to coordinate to 1 : 1 binary complex of the same ligand. The factors concerning the higher or lower stability of ternary complexes as compared to the binary complexes can also be observed from the $\log\beta_{XY}-1/2[\log\beta_{XX}+\log\beta_{YY}]$.

In short, the tendency of the formation of a ternary chelate can be examined from the magnitude of a) $\Delta\log K$, b) $\log K_{DXY}$, c) comparison of $\log K_{2XY}$ and $\log K_{MY_2}$ or $\log K_{2YX}$ and $\log K_{MX_2}$ and d) the magnitude of $\log\beta_{XY}-1/2[\log\beta_{XX}+\log\beta_{YY}]$.

The mixed ligand chelate is formed due to the

Table 3. Logarithms of equilibrium constants of ternary complexes of neodymium ion
$t=30\ ^\circ C$ $\mu=0.1\ M\ (NaClO_4)$

Acid systems	β_{XY}	K_{DXY}*	K_{2XY}	K_{2YX}	$\Delta\log K$	$\log\beta_{XY}-[\log K_{MX_1}+\log K_{MY_1}]$
Succinic-adipic	6.53	+0.25	3.26	3.15	−0.25	+0.25
Succinic-malonic	7.48	−0.11	3.27	4.10	+0.11	−0.11
Succinic-itaconic	7.41	+0.26	4.64	4.03	−0.26	+0.26
Succinic-phthalic	7.15	+0.52 −0.45**	2.93	3.77	+0.45	+0.03[a]
Malonic-itaconic	8.21	+0.23	4.44	4.00	−0.23	+0.23
Malonic-adipic	6.74	−0.37	3.84	2.52	+0.37	−0.37
Phthalic-malonic	7.39	−0.07 −1.05**	3.14	3.18	+1.03	−0.55[b]
Phthalic-itaconic	8.18	+1.16 +0.19**	3.96	4.41	−0.19	+0.68[b]
Phthalic-adipic	6.62	+0.47	2.40	3.72	+0.50	−0.02[b]
Succinic-5-sulfosalicylic	8.66	−0.35 −2.11**	1.27	5.28	+2.11	−1.22[a]
Malonic-5-sulfosalicylic	9.42	−0.42 −2.18**	2.03	5.21	+2.18	−1.29[a]
Phthalic-5-sulfosalicylic	8.74	−2.97 −3.00@	1.35	4.52	+2.87	−1.50[c]
Succinic-3,5-dinitrosalicylic	8.25	+0.43	3.81	4.87	−0.43	+0.43
Malonic-3,5-dinitrosalicylic	8.52	−0.14	4.08	4.31	+0.13	−0.13
Phthalic-3,5-dinitrosalicylic	8.22	+0.53 −0.44**	3.78	4.00	+0.44	+0.05[b]
5-Sulfo-3,5-dinitrosalicylic	11.58	+1.52 −0.25**	7.14	4.19	+0.25	+0.64[b]
5-Sulfo-4-hydroxysalicylic	17.56	−0.74 +2.39@	6.59	10.17	+0.80	+0.69[c]
3,5-Dinitro-4-hydroxysalicylic	12.45	−2.95 −1.74**	1.74	8.00	+2.96	−2.35[a]

The accuracy of β_{XY} values was between 0.05 to 0.10.
$K_{DXY}{}^{*}=K(MX+MY \rightleftharpoons MXY+M)$; $a=\log\beta_{XY}-[1/2\log\beta_{XX}+\log K_{MY_1}]$
$K_{DXY}{}^{**}=K(MX_2+MY \rightleftharpoons MXY+MX)$ $b=\log\beta_{XY}-[\log K_{MX_1}+1/2\log\beta_{YY}]$
$=K(MX+MY_2 \rightleftharpoons MXY+MY)$ $c=\log\beta_{XY}-1/2[\log\beta_{XX}+\log\beta_{YY}]$
$K_{DXY}{}^{@}=K(MX_2+MY_2 \rightleftharpoons 2MXY)$.

simultaneous or stepwise replacement of four water molecules from the coordination sphere of the Nd^{3+} ion with the formation of four Nd–O bonds. The carboxylate oxygen is not directly bound to the benzene nucleus like the phenolate oxygen. The carboxylate oxygen may, therefore, adjust stereochemically more easily than the phenolate ion which is directly attached to the benzene nucleus. Greater strain in the Nd–O bond is, therefore, expected when the phenolate oxygen is coordinated to the metal ion than when the coordination takes place through the carboxylate oxygen. Further the electronegativity of phenolate oxygen will be higher than that of carboxylate oxygen. The Coulombic repulsion between the end oxygens will, therefore, be stronger when both ligands are phenolic acids than when they are carboxylic acids. Thus, the value of Δlog K should be higher when both the ligands are phenolic acids than when both the ligands are carboxylic acids, and the intermediate value is expected when one is a carboxylic acid and the other a phenolic acid. The observed values of Δlog K do not strictly fit into this pattern. This behavior can be scrutinized critically, if the values of the factors given in a, b, c and d are examined.

Carboxylic–Carboxylic Acid Systems. a) Δlog K is negative for succinic–adipic, succinic–itaconic, malonic–itaconic, and phthalic–itaconic systems. The formation of the mixed-ligand chelates over the binary complexes in these cases is thus favored. On the other hand, systems like succinic–malonic, succinic–phthalic, phthalic–malonic, malonic–adipic, and phthalic–adipic have positive Δlog K. The value in the case of phthalic–malonic being significantly higher than the other remaining systems.

b) $\log K_{DXY}<0.6$ log units for all the systems except phthalic–itaconic acid system. The ternary complexation in the case of phthalic–itaconic acid system is thus favored by this equilibrium $MX+MY \rightleftharpoons MXY+M$.

c) $\log K_{2XY}>\log K_{MY_2}$ for phthalic–malonic and phthalic–adipic acid systems.

d) $\log\beta_{XY}-1/2[\log\beta_{XX}+\log\beta_{YY}]$ is positive for succinic–adipic, succinic–itaconic, malonic–itaconic, and phthalic–itaconic which is complementary to the values of Δlog K obtained for these systems and, therefore, confirm the conclusions drawn earlier.

In the series examined, the magnitude of Δlog K is maximum for phthalic–malonic system. For this system log K_{DXY} is not favorable to the mixed ligand chelate formation, similarly log K_{2XY}<log K_{MY_2}, but log K_{2YX}>log K_{MX_2}. This is the only factor which is favorable for the ternary complex formation. In the case of phthalic–itaconic the factors 'a' and 'b' are favorable to the formation of ternary complexes. For phthalic–adipic 'b' is favorable but 'c' is very much unfavorable giving a positive value of Δlog K. In the carboxylic–carboxylic acid systems, except phthalic acid, no other carboxylic acid forms 1:2 complex independently. The 1 : 1 : 1 mixed-ligand complexation occurs in a pH region where normally 1 : 1 complexes are formed by these acids. This may be probably the reason, for the presence of mixed chelate formation in these cases.

Carboxylic–Phenolic Acid Systems.

a) Δlog K are all positive except succinic–3,5-dinitrosalicylic acid system.

b) log K_{DXY} is not favorable for ternary complex formation.

c) log K_{2YX}<log K_{MY_2} for ternary chelates with 5-sulfosalicylic acid is primary ligands. The value of Δlog K is positive and higher than any of the systems belonging to group 1. In the case of succinic–3,5-dinitrosalicylic acid log K_{DXY}=0.43 which is quite close to 0.6 log units. These two ligands independently do not form 1 : 2 chelates. The value of Δlog K and log $\beta_{XY}-1/2$[log β_{XX}+log β_{YY}] are favorable to the ternary complex formation. In the case of phthalic–3,5-dinitrosalicylic acid system, phthalic acid forms a 1 : 2 complex. The factors a, b, and d are not favorable for malonic–3,5-dinitrosalicylic acid system. Similar is the case for phthalic–3,5-dinitrosalicylic acid system, but because of a positive value of a disproportionation reaction, a slightly higher value of Δlog K was obtained for this system than malonic–3,5-dinitrosalicylic acid system.

Phenolic–Phenolic Acid Systems.

a) Δlog K is positive for all the three systems. The magnitude of Δlog K follows the order Nd^{3+}-3,5-dinitrosalicylic–4-hydroxysalicylic > Nd^{3+}-5-sulfosalicylic–4-hydroxysalicylic>Nd^{3+}-5-sulfosalicylic–3,5-dinitrosalicylic acid systems.

b) log K_{DXY}>0.6 for 5-sulfo–3,5-dinitrosalicylic acid and 5-sulfo–4-hydroxysalicylic acid system.

c) log K_{2YX}>log K_{MX_2} for 5-sulfo–4-hydroxysalicylic acid. log K_{2YX}<log K_{MX_2} for 3,5-dinitro–4-hydroxysalicylic and log K_{2XY}>log K_{MY_2} for 5-sulfo–3,5-dinitrosalicylic and 5-sulfo–4-hydroxysalicylic acid.

d) log $\beta_{XY}-1/2$[log β_{XX}+log β_{YY}] is positive for 5-sulfo–3,5-dinitrosalicylic and 5-sulfo–4-hydroxysalicylic acid and negative for 3,5-dinitro–4-hydroxysalicylic acid system.

In this series, except Nd^{3+}-3,5-dinitro–4-hydroxysalicylic acid the 'b' factor is much favorable to the remaining two systems, despite of Δlog K being positive for them. The mixed-ligand chelation therefore, occurs mainly by the reaction

$$MX_2 + MY_2 \rightleftharpoons 2MXY, \text{ and}$$

$$MX + MY_2 \rightleftharpoons MXY + MY,$$

in the case of 5-sulfo–4-hydroxy- and 5-sulfo–3,5-dinitrosalicylic acid systems respectively. Only 3,5-dinitrosalicylic acid does not form a 1 : 2 complex. In the presence of 4-hydroxysalicylic acid it forms 1 : 1 : 1 chelate in a pH region at which it forms a 1 : 1 complex. In the case of 3,5-dinitrosalicylic acid, the absence of 1 : 2 complex may be due to the steric hindrance of the earlier attached ligand to the incoming ligand anion. The secondary ligand like 4-hydroxysalicylic acid or 5-sulfosalicylic acid which do not afford steric hindrance like 3,5-dinitrosalicylic acid may, therefore, attach to the 1 : 1 complex of Nd^{3+}-3,5-dinitrosalicylic acid to form a 1 : 1 : 1 complex.

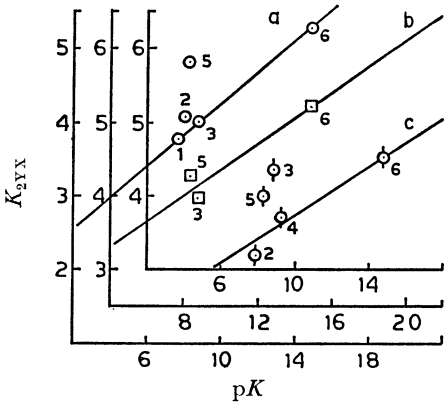

Fig. 2. Relation between log K_{2YX} and the product of the acid dissociation constants of the ligands for neodymium dibasic–dibasic systems.

(a) Neodymium ion-succinic acid(Y)-ligand(X), (b) neodymium ion-malonic acid(Y)-ligand(X), (c) neodymium ion-phthalic acid(Y)-ligand(X); ligand(X): (1) phthalic acid, (2) malonic acid, (3) itaconic acid, (4) adipic acid, (5) 3,5-dinitrosalicylic acid, (6) 5-sulfosalicylic acid. μ=0.1 M ($NaClO_4$), t=30 °C.

In the case of 3,5-dinitrosalicylic–4-hydroxysalicylic acid system the factors b, c, and d are not favorable which has resulted in a significantly large value of Δlog K.

The mixed-ligand chelates are formed in a simultaneous equilibria. The replacement of four water molecules from the hydration sphere of Nd^{3+} ion simultaneously by the two ligands would make the reaction 'entropy stabilized'. An additional factor in favor of the mixed ligand chelates, of some systems are the charge cancellation of the metal ion and the ligand to form a neutral complex.[11–14)]

The order of log K_{2YX} is given as:

i) 5-sulfo>3,5-dinitro>itaconic>adipic when the primary ligands are succinic, malonic and phthalic acids.

ii) 4-hydroxy>3,5-dinitrosalicylic acid when 5-sulfosalicylic acid is a primary ligand. This is also the order of the basicities of the ligands. The plots of log K_{2XY} *vs.* ΣpK (Fig. 2) gave a satisfactory direct relationship between these two quantities. However, the points corresponding to adipic acid system deviated from the straight line, which may be due to the ring size effect.[11)] We have already established the direct relationship between these two quantities for mixed-ligand chelates of vanadyl ion.[16)] In the present investigation, the formation of ternary complexes of

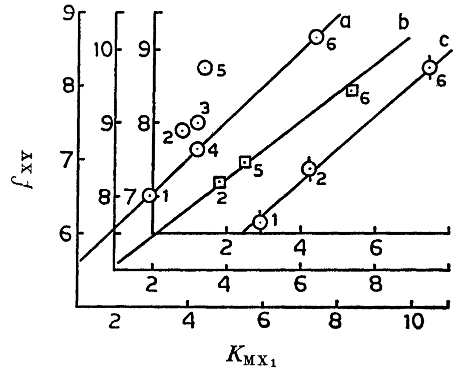

Fig. 3. Relation between β_{XY} and log K_{MX_1} of ternary complexes of neodymium ion. (a) neodymiun ion-succinic acid(Y)-ligand(X), (b) neodymium ion-malonic acid(Y)-ligand(X), (c) neodymium ion-phthalic acid(Y)-ligand(X), ligand(X): (1) adipic acid, (2) itaconic acid-malonic acid (c), (3) malonic acid (4) phthalic acid, (5) 3,5-dinitrosalicylic acid, (6)-5-sulfosalicylic acid. μ=0.1 M ($NaClO_4$), t= 30 °C.

the neodymium ion has been found to be depending on the basicities of the ligand.

The plots of β_{XY} *vs.* K_{MX_2} (Fig. 3) gave straight lines which are parallel. The values of overall stability constants β_{XY} for these systems are as:

5-sulfo > 3,5-dinitro > malonic > phthalic > itaconic > adipic when primary ligands are succinic, malonic and phthalic acids. This is in accordance to the stabilities of 1 : 1 binary complexes. This observation is in good agreement with the earlier work.[14-17]

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