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Note

THERMODYNAMIC STABILITY CONSTANTS OF SOME COMPLEXES OF LANTHANIDES WITH 2-AMINO NICOTINIC ACID

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Hirai [1] has determined the basic ionization constants of 2-amino nicotinic acid, 2-amino isonicotinic acid and their methylethyl esters. Extensive studies have also been done on some divalent metal ion complexes of pyridine [2], 2-amino pyridine [3] and 2-amino nicotinic acid [4], but complexation of trivalent lanthanides with the biologically useful ligand [5,6] 2-amino nicotinic acid has not been reported. This paper is in continuation of the work done by Sandhu and Kalia [4] on the complexation of some divalent metal ions with 2-amino nicotinic acid. The thermodynamic stability constants of complexes of the metal ions La^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+} with 2-amino nicotinic acid have been evaluated in aqueous medium at a constant temperature of 35 ± 0.1°C but at three different ionic strengths. The Calvin—Bjerrum [7,8] pH titration technique as modified by Irving and Rossotti [9,10] has been employed for calculating the stability constants of these metal complexes.

EXPERIMENTAL

2-Amino nicotinic acid was obtained from E. Merck, Germany, and all other chemicals used were of B.D.H. Analar grade. Double-distilled water was used during all the experiments. Metal nitrate solutions (0.005 M) were prepared and standardized by EDTA titrations [11]. The fresh ligand solution (0.025 M) was prepared using double-distilled CO_2-free water just before the titration. Carbonate-free potassium hydroxide solution (0.05 M) was prepared by Vogel's method [12]. The calculated amount of potassium nitrate (1 M) was added to maintain constant ionic strength. The calculations were made below the pH value where hydrolysis of lanthanides was observed. A Toshniwal digital type pH meter (No. CL 46) with a sensitivity of ±0.01 was used to observe the pH of the solutions. Details of the procedure and calculations of $\bar{n}$, pL and thermodynamic functions have been given elsewhere [13].

RESULTS AND DISCUSSION

It has been observed that there is a slight shift of the ligand curve towards the left of the acid titration curve at low pH values. This shift is due to the interaction of the zwitterion and proton in the acid solution. At this point where the ligand titration curve crosses that of the acid titration curve, the neutralization of the —COOH group is complete. The neutralization of the second proton from the ligand is shown by the onward course followed by the ligand curve. The proton—ligand formation curve was obtained by plotting the degree of formation $\bar{n}_A$ of the proton complex against the pH value. The log ${}^{p}K_1^H$ value was obtained at the point where $\bar{n}_A$ is 0.5. The value of log ${}^{p}K_2^H$ was obtained by using the midpoint method.

$$\log {}^{p}K_1^H\, {}^{p}K_2^H = 2\ \mathrm{pH}\ (\bar{n}_A = 1)$$

The values of log ${}^{p}K_1^H$ and log ${}^{p}K_2^H$ at 35°C and at three different ionic strengths, 0.05, 0.15 and 0.25 M, are 6.32, 2.48; 6.30, 2.28; and 6.28, 2.12, respectively. The data given in Table 1 show that the log ${}^{p}K_2^H$ values for the carboxylic group are nearly the same for both anthranilic acid [14] and 2-amino nicotinic acid. But the value of log ${}^{p}K_1^H$ for the amino group of 2-amino nicotinic acid and anthranilic acid are different from each other. This may be attributed to the presence of nitrogen in the benzene ring of 2-amino nicotinic acid.

The metal—ligand stability constants were obtained by plotting $\bar{n}$ vs. pL. The value of $\bar{n}$ does not exceed one in any of the metal ions, indicating the formation of only 1 : 1 complexes. The mean log K values are summarized in Table 2.

The free energies (ΔG^0) of these complexing reactions have been calculated using the expression

$$\Delta G^0 = -RT \ln K$$
$$= -4.57\ T \log K$$

The thermodynamic stability constant, log K, was obtained by plotting log K_1 vs. ionic strength (μ) and extrapolating to zero ionic strength. The values of ΔG^0 are given in Table 2.

The values of ΔG^0 for all the reactions are negative but small, which indicates that these complexes are weak. The data show a decrease in the values of log K as the ionic strength increases. This is because, according to Hückel [15], the activity of the metal ion for its interaction with other molecular

TABLE 1

pK_a values of anthranilic acid and 2-amino nicotinic acid at 35°C and 0.25 M ionic strength

	pK^H of the —COOH group	pK^H of the —NH_3^+ group
2-Amino nicotinic acid	6.28	4.86
Anthranilic acid	2.12	2.34

TABLE 2

Log K values of the cation and free energies of complexation reactions at 35 ± 0.1°C

Cation	Property	Ionic strength				$-\Delta G^0$ (kcal mole^{-1})
		0.05 M	0.15 M	0.25 M	$\mu = 0$	
H	log $^PK_1^H$	6.32	6.30	6.28	6.33	8.91
	log $^PK_2^H$	2.48	2.28	2.12	2.58	3.63
La^{3+}	log K_1	2.85	2.82	2.75	2.86	4.03
Pr^{3+}	log K_1	2.92	2.89	2.82	2.94	4.14
Nd^{3+}	log K_1	2.97	2.94	2.86	2.99	4.21
Sm^{3+}	log K_1	3.04	2.95	2.89	3.08	4.33

ΔG^0 has been calculated from the values of thermodynamic stability constants.

species decreases with increase in ionic strength of the medium in which the reaction is being studied. Thus the stability of complexes decreased with increase in ionic strength. The thermodynamic proton—ligand stability constant has also been determined by plotting the ionic strength and log $^PK^H$. These values are given in Table 2.

It has also been observed from the titration curve that the metal—ligand curves are well separated from the ligand titration curve proving the liberation of proton due to the metal—ligand chelation.

The thermodynamic stability constants vary in the order $Sm^{3+} > Nd^{3+} > Pr^{3+} > La^{3+}$, which is in accordance with their increasing ionic sizes.

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