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Studies in Lanthanide Ions Complexes with Some Substituted Sulphonic Acids

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The interaction of lanthanide ions (Ca^{III}, Ce^{III}, Pr^{III}, Nd , Sm^{III} and Gd^{III}) with some substituted sulphonic acids such as (i) 1,2-dihydroxybenzene-3,5-disulphonic acid (1,2 DHB-3, 5DSA), (ii) 6,7-dihydroxynaphthalene-2-sulphonic acid (6,7-DHN-2SA), (iii) 8-amino-1-naphthol-5,7-disulphonic acid (8A-1N-5,7-DSA), (iv) 8-amino-1-naphthol-3,6-disulphonic acid (8A-1N-3,6-DSA), (v) 8-amino-1-naphthol-3,5-disulphonic acid (8A-1N-3,5-DSA), (vi) 8-amino-1-naphthol-5-sulphonic acid (8A-1N-5SA), (vii) 7-amino-1-naphthol-3-sulphonic acid (7-A-1N-3SA), (viii) 2-aminobenzenesulphonic acid (2A-BSA), and (ix) 2-amino-4-methyl-5-chlorobenzenesulphonic acid (2A-4M-5Cl-BSA) have been investigated at 30° and $\mu = 0.1\ M$ ($NaClO_4$) by Calvin-Bjerrum technique La^{III}, Ce^{III}, Pr^{III} and Gd^{III} form 1 : 1 and 1 : 2 complexes but Nd^{III} and Sm^{III} form only 1 : 1 complex with all the sulphonic acids. The validity of log K = apk + b relation is examined for these complexes.

SHERRY *et al.*[1] have investigated lanthanide complexes with carboxylic acids. Ramamoorthy and Manning[2] studied exhaustively the mixed ligand chelates of meso-dl-tartaric acid with divalent and trivalent metals. Recently, Darnall and Birnhaum[3-4] showed that lanthanide ions could substitute for calcium ion and produce an active enzyme system. Considering the biological significance of lanthanide ions, the present work is aimed at investigating the complexing ability of substituted sulphonic acids with lanthanide ions.

Experimental

The purity of the substituted sulphonic acids (Schuchardt, Germany) were checked by their melting points. Lanthanide perchlorates were prepared by the standard procedure. All the solutions were prepared in double-distilled water. The details of the *p*H measurements and other chemicals are given in an earlier paper[5].

Results and Discussion

The dissociation constants of the sulphonic acids and stability constants of the simple complexes were evaluated by the method of Irving and Rossotti[6] (Tables 1-4). It could be seen from Tables 2-4 that La^{III}, Ce^{III}, Pr^{III} and Gd^{III} form 1 : 2 complexes with most of the sulphonic acids while Nd^{III} and Sm^{III} form only 1 : 1 complexes with all ligands (sulphonic acids).

The stability constants for the 1 : 1 complexes for various rare earth ions have been plotted against e^2/r. For the calculation of e^2/r values of crystal radii of rare earth ions have been taken from the literature[7]. The plots of $\log K_1$ *vs* e^2/r show a linearity except in the case of 8A-1N-5, 7-DSA chelates.

Validity of log K=apk + b relation: This relation was tested for lanthanide complexes of sulphonates of 8-amino-1-naphthols. These complexes generally obey the linear relationship. In this particular case pK_2 and not (pK_1+ pK_2) is taken on Y axis. This is because of the fact that the lanthanide complexes of 8A-1N

TABLE 1—PROTON-LIGAND STABILITY CONSTANTS (*p*K) OF SUBSTITUTED SULPHONIC ACIDS

Sl. no.	Ligand	pK_1	pK_2
1.	1,2-DHB-3,5-DSA	7.86±0.04	12.60
2.	6,7-DHN-2SA	8.10±0.03	12.15
3.	8A-1N-5,7-DSA	2.90±0.05	8.60±0.05
4.	8A-1N-3,6-DSA	3.91±0.06	9.37±0.07
5.	8A-1N-3,5-DSA	3.08±0.06	8.64±0.04
6.	8A-1N-5SA	3.15±0.04	9.12±0.05
7.	7A-1N-3SA	3.68±0.06	9.52±0.04
8.	2A-BSA	2.88±0.02	–
9.	2A-4M-5Cl-BSA	2.60±0.01	–

TABLE 2—METAL-LIGAND STABILITY CONSTANTS

Sl. no.	Ligand	La		Gd	
		$\log k_1$	$\log k_2$	$\log k_1$	$\log k_2$
1.	1,2-DHB-3,5-DSA	13.21	11.40	13.34	8.90
2.	6,7-DHN-2SA	–	–	10.03	7.23
3.	8A-1N-5,7-DSA	4.42	3.13	4.22	3.00
4.	8A-1N-3,6-DSA	6.19	5.19	5.69	5.29
5.	8A-1N-3,5-DSA	4.70	3.20	8.04	5.61
6.	8A-1N-5SA	5.98	5.74	5.48	4.85
7.	7A-1N-3SA	5.48	3.90	5.88	–
8.	2A-BSA	6.90	5.13	2.00	–
9.	2A-4M-5Cl-BSA	7.80	6.03	7.23	–

TABLE 3—METAL-LIGAND STABILITY CONSTANTS

Sl. no.	Ligand	Pr^{III} log k_1	Pr^{III} log k_2	Ce^{III} log k_1	Ce^{III} log k_2
1.	1,2-DHB-3,5-DSA	5.00	4.15	8.10	4.02
2.	6,7-DHN-2SA	5.12	4.51	5.12	4.01
3.	8A-1N-5,7-DSA	4.60	3.06	4.92	3.62
4.	8A-1N-3,6-DSA	6.29	5.49	–	–
7.	7A-1N-3SA	–	–	9.12	7.10
8.	2A-BSA	1.79	1.07	2.20	1.52

TABLE 4—METAL-LIGAND STABILITY CONSTANTS

Sl. no.	Ligand	Sm^{III} log K_1	Nd^{III} log K_1
1.	1,2-DHB-3,5-DSA	13.44	6.04
2.	6,7-DHN-2SA	10.93	10.43
3.	8A-1N-5,7-DSA	4.02	4.62
4.	8A-1N-3,6-DSA	5.89	5.99
5.	8A-1N 3,5-DSA	4.50	4.80
6.	8A-1N-5SA	6.00	6.11
7	7A-1N-3SA	5.68	5.98
8.	2A-BSA	2.01	2.20
9.	2A-4M-5Cl-BSA	7.30	7.10

sulphonates are generally formed around pH 6.0 at which the NH_3^+ group is completely dissociated.

The slope values from the various plots of pK_2 *vs* log K_1 of 1 : 1 complexes are given below.

Metal ion complexes—	La^{III}	Nd^{III}	Sm^{III}	Gd^{III}
Slope values —	1.66	1.75	1.87	1.68

Jones *et al.*[8] suggested on the basis of purely electrostatic model that the slope will increase with increasing cationic charge and decreasing the distance of separation. In the case of substituted 8A-1N complexes of rare earths, the observed slope values are higher than those for the transition metal complexes. This is expected to give a higher value for the slope. The observed values are, therefore, justifiable in the light of Jones *et al.* suggestion.

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References

1. A. D. SHERRY, C. YOSHIDA, E. R. BIRNBAUM and D. W. DARNALL, *J. Am. Chem. Soc.*, 1973, **95**, 3011.
2. S. RAMAMOORTHY and P. G. MANNING, *J. Inorg. Nucl. Chem.*, 1972, **34**, 1977, 1988, 1997.
3. D. W. DARNALL and E. R. BIRNBAUM, *J. Biol. Chem.*, 1970, **245**, 6484.
4. D. W. DARNALL and E. R. BIRNBAUM, *Bio-chemistry*, 1973, **12**, 489.
5. M. L. NARWADE and D. V. JAHAGIRDAR, *J. Indian Chem. Soc.*, 1974, **51**, 1008.
6. T. T. MOELLER, D. F. MARTIN, L. C. TOMPSON R. FERRUS, G. R. GEISTEL and W. J. RANDALL, *Ch.m. Rev.*, 1965, **1**, 65.
7. F. A. COTTON, "Advanced Inorganic Chemistry", Interscience, New York, 1967, p. 1052.
8. J. G. JONES, J. B. POOLE, J. C. TOMKINSON and R. J. P. WILLIAMS, *J. Chem. Soc.*, 1958, 2001.