DISCUSSION

Dithizone Method :

It was found that the percentage transmittance is linear between a concentration of 4–12 p.p.m. of mercury. After 12 p.p.m. the curve flattens. Extraction of mercury by dithizone is incomplete in the presence of high concentrations of sodium chloride in acid medium, as indicated by the formation of a precipitate when H_2S was bubbled through the extract. In the presence of excess chloride ion, mercury forms a complex of the type $(HgCl_4)^{2-}$ with which the dithizone is not able to reach quantitatively. This is also in agreement with a previous report[9]. The instability constants of the mercuric chloride complex and mercuric-dithizonate complex are almost of the same order, being 6×10^{-17} and $3{\cdot}0 \times 10^{-17}$ respectively. Moreover, the mercuric-dithizone complex also suffers photochemical decomposition, despite the addition of a little acetic acid as recommended by the other workers to stabilise the complex[-10]. The colour of the complex is more unstable in the presence of excess of sodium chloride.

It is our observation that the absorption due to the complex is influenced by the excess reagent, dithizone, which has not been mentioned in literature. Under these circumstances, the sulphide method which works better will be welcomed by the industrialists.

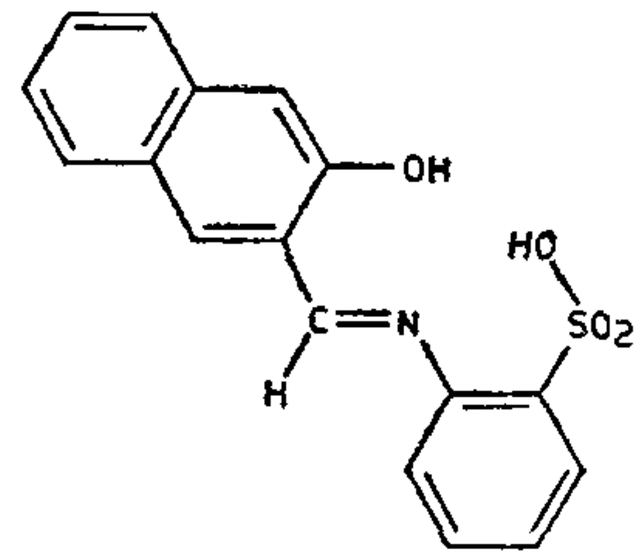
Department of Analytical and Inorganic Chemistry, University of Madras, A.C. College Campus, Madras 600 025, *December* 23, 1975.

P. B. JANARDHAN.
(Miss) S. RAJESWARI.

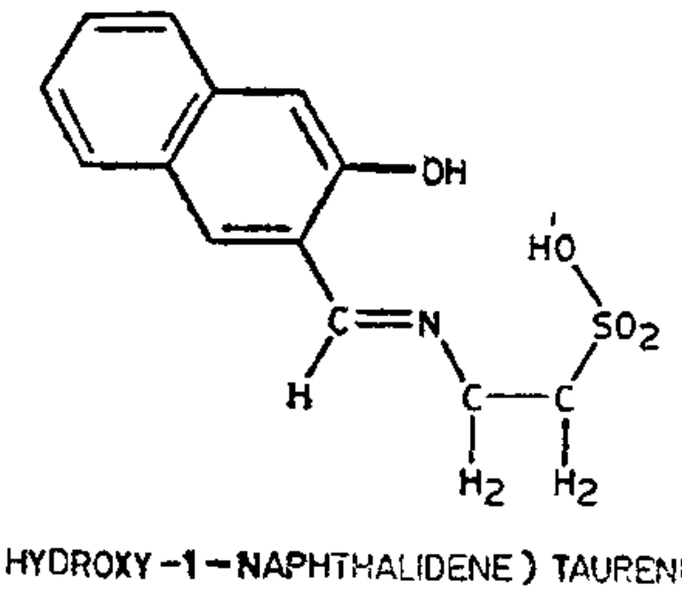
1. Coetzee, J. F., "Mercury," In : Kolthoff, I. M. and Elving, P. J., Eds., *Treatise on Analytical Chemistry,* Part II, Interscince Publishers, John Wiley and Sons, Inc., New York, 1961, 3, 231.
2. Kodama, K., *Methods of Quantitative Inorganic Analysis,* Interscience Publishers, John Wiley and Sons, Inc., New York, 1963, p. 150.
3. *Product Bulletin 400-A,* E I. du Pont de Nemours and Co., Inc., Wilmington, Del., 19898.
4. Doherty, P. E. and Dorsett, R. S.. *Anal. Chem.,* 1971, 43, 1887.
5. Lee, D. C. and Laufman, C. W., *Ibid.,* 1971, 43, 1127.
6. Schechter, M. M., *J. Ass. Offic. Anal. Chem.,* 1966, 49 (4), 778.
7. Ling, C., *Anal. Chem.,* 1968, 40, 1876.
8. Sandell, E. B., *Colorimetric Determination of Traces of Metals,* Interscience Publishers, Inc., New York, 1944, 3, 322.
9. Irving, H., Andrew, G. and Risdon, E. J., *J. Chem. Soc., London,* Part I, 1949, p. 541.
10. *Encyclopaedia of Industrial Chemical Analysis,* Edited by F. Snell and L. S. Ettre, Interscience, Publishers, John Wiley and Sons, Inc., New York, 1972, 16, 38.

STABILITIES OF SOME BIVALENT METAL-CHELATES OF TRIDENTATE LIGANDS DERIVED FROM 2-HYDROXY-1-NAPHTHALDEHYDE AND β-AMINO ACIDS

THE magnetic and spectral data on N-(2-hydroxy-1-naphthalidene) orthanilic acid (H_2NO) and N-(2-hydroxy-1-napthalidene) taurine (H_2NT) with Co (II), Ni (II), Cu (II), Zn (II), Cd (II) and UO_2 (II) complexes have been reported by us earlier[1]. H_2NO and H_2NT are biprotic tridentates containing sulphonic hydroxyl, phenolic hydroxyl and imino groups (Fig. 1). We have now determined the dissociation constants of these ligands and the stability constants of their metal complexes employing Calvin-Bjerrum pH-titration technique[2,3] in acqueous medium ($\mu = 0{\cdot}1$ M $NaClO_4$) at $30 \pm 0{\cdot}1°$ C.



N-(2-HYDROXY-1-NAPHTHALIDENE) ORTHANILIC ACID



N-(2-HYDROXY-1-NAPHTHALIDENE) TAURENE

FIG. 1

Precision pH-meter (Type OP–205, No. 837) with glass electrode assembly (accuracy ± ·05 pH) was used for pH-measurements. The ligands were synthesised by the method reported earlier[1]. H_2NO and H_2NT were titrated with 0·1 M sodium hydroxide in the absence and in the presence of metal-ions at 30° C.

TABLE I

Stability constants and free energy changes of H_2NO and H_2NT complexes

Metal		H_2NO Complexes				H_2NT Complexes log K_1
		A*	B	C*	D	
Co (II)	log K_1	5·32	5·27	5·31	5·84	2·82
	log K_2	2·97	2·89	2·97	2·45	..
	log β_2	8·29	8·16	8·28	8·29	..
Ni (II)	log K_1	6·10	5·84	6·09	6·52	2·98
	log K_2	3·45	3·48	3·45	3·03	..
	log β_2	9·55	9·32	9·54	9·55	..
Cu (II)	log K_1	7·55	7·52	7·55	8·27	6·85
	log K_2	4·03	4·29	4·03	3·31	..
	log β_2	11·58	11·81	11·58	11·58	..
UO_2 (II)	log K_1	8·23	8·20	8·22	8·68	7·25
	log K_2	5·62	5·55	5·62	5·17	..
	log β_2	13·85	13·75	13·84	13·85	..
Zn (II)	log K_1	..	..	..	..	2·80
Cd (II)	log K_1	..	..	..	..	2·65

where A = Interpolation at half $\bar{n}$ values; B = Interpolation at various $\bar{n}$ values:
C = Schroder method; and D = Correction term method.
* Most suitable methods in this case.

The dissociation constants (pK_1 and pK_2) of H_2NO and H_2NT, obtained by Algebraic and Interpolation at half $\bar{n}_A$ values, were 3·62, 8·07 and 3·37, 9·90, respectively.

The stability constants of the metal-ligand were calculated by using Calvin-Bjerrum pH-titration technique and from the formation curves, $\bar{n}$ *vs* $-\log [A^{-2}]$. The metal chelates of H_2NO with UO_2 (II), Cu (II), Ni (II) and Co (II) were found to form 1 : 2 complexes; Zn (II) and Cd (II) form 1 : 1 complexes only. The formation curves for all the metal –H_2NT systems attain maxima at $\bar{n} < 1·3$ which indicates the formation of 1 : 1 complex. The values of log K_1 and log K_2 in the metal –H_2NO systems were refined by different computational methods[4] and the values obtained are summarized in Table I along with those of the log K_1 values of H_2NT–chelates.

From the perusal of the values it is clear that H_2NO forms more stable complexes than H_2NT. The lower stability of H_2NT complexes may, perhaps, be due to steric factors and the presence of Zwitter-ion. The stability of these complexes follow the order[5]

UO_2 (II) > Cu (II) > Ni (II) > Co (II) > Zn (II) > Cd (II).

Department of Chemistry,
University of Jodhpur,
Jodhpur, *October* 9, 1975.

D. D. OZHA.
B. R. SINGHVI.
R. K. MEHTA.

1. Ozha, D. D., Kaul, K. N. and Mehta, R. K., *Indian J. Chem.* (In press).
2. Calvin, M. and Wilson, K. W., *J. Am. Chem. Soc.*, 1945, 67, 2003.
3. Bjerrum, J., *Metal Ammine Formation in Aqueous Solution* (P. Hasse and Son, Copenhagen). 1941.
4. Irving, H. and Rossotti, H. S., *J. Chem. Soc.*, 1953, p. 3397.
5. — and Williams, R. J. P., *Nature*, London, 1948 162, 746; *J. Chem. Soc.*, 1953, p. 3192.