

TABLE 3 — ELECTRONIC SPECTRAL ASSIGNMENTS, SPECTRAL PARAMETERS AND MAGNETIC MOMENT VALUES

Complexes	Electronic transition (cm ⁻¹)			D _q	B'	β	μ _{eff} (B.M.)
	² A _{1g} → ² T _{1g} (P)	² A _{1g} → ² T _{1g} (F)	² A _{1g} → ² T _{2g} (F)				
[Ni(en) ₂][Hg(SeCN) ₄]	31250	18870	11470	1164	1013	0.95	2.92
[Ni(en) ₂][Cd(en)(NCSe) ₄]	31250	18870	11500	1164	1013	0.95	2.90
[Ni(en) ₂][Zn(en)(NCSe) ₄]	30300	18500	11430	1152	950	0.89	2.97
[Ni(trien) ₂][Zn(NCSe) ₄]	29410	18180	11330	1140	892	0.84	2.89

Di(selenocyanato)bis(ethylenediamine)-μ-bis(ethylenediamine)Co(II), Cd(II) or Zn(II) selenocyanate, [en > Co < en] M < (en) (NCSe)₂]²⁺ [NCSe₂]²⁻ (M = Zn or Cd)—The molar conductances of these complexes in DMF indicate that these are 1:2 electrolytes (Λ_M = 185-190 ohm⁻¹ cm² mole⁻¹). The positions and numbers of νCN, νCSe and δNCSe bands in infrared spectra indicate the presence of both nitrogen bonded and free selenocyanate^{9,10,12} groups. Ethylenediamine is coordinated through both of its nitrogens. The magnetic moment values and electronic spectral band positions again indicate that Co(II) has square-planar configuration in these complexes. Two ethylenediamine molecules act as bridges between Co(II) and Zn(II) or Cd(II). Such a bridging by ethylenediamine is quite common^{13,14}. The Cd(II) and Zn(II) complexes show magnetic moment values of 2.45 and 2.82 B.M. respectively. Their electronic spectra show two bands at 18050 and 17360 cm⁻¹ (²A_{1g} → ²E_g) and 7560 and 8030 cm⁻¹ (²A_{1g} → ²B_{2g}) for Cd(II) and Zn(II) complexes respectively.

Tris(ethylenediamine)Ni(II)tetrakis(selenocyanato)mercurate(II) and related complexes [Ni(en)₃][Hg(SeCN)₄], [Ni(en)₃][M(en)(NCSe)₄] (M = Zn(II), Cd(II)) and [Ni(trien)₂][Zn(NCSe)₄]—The position of electronic spectral bands, various spectral parameters and magnetic moment values (Table 3) very clearly show that Ni(II), in these complexes, is in octahedral configuration. The molar conductance data in DMF (Λ_M = 110-120 ohm⁻¹ cm² mole⁻¹) indicate them to be 1:1 electrolytes. The infrared spectra (Table 2) show that ethylenediamine is coordinated through both the nitrogen atoms. In the case of triethylenetetramine there is a free N—H band also. The positions of νC—N, νC—Se and δNCSe frequencies indicate that selenocyanate is bonded through the nitrogen atom to zinc or cadmium^{10,12} and through the selenium atom to mercury¹¹. On the basis of these results cationic-anionic type of structures have been suggested for these complexes (Table 1).

The authors gratefully acknowledge the financial support of UGC, New Delhi, through their COSIP grant and to the University of Montreal for instrumentation facilities.

References

- LEVER, A. B. P., LEWIS, J. & NYHOLM, R. S., *J. chem. Soc.*, (1963), 2552.
- FIGGIS, B. N. & NYHOLM, R. S., *J. chem. Soc.* (1954), 12.
- SHIKAWA, H. N. & YAMADA, S., *Bull. chem. Soc., Japan*, **37** (1964), 8.
- LEVER, A. B. P., *Inorganic electronic spectroscopy* (Elsevier, New York), 1968, 328.

- NISHIDA, Y. & KIDA, S., *Inorg. nucl. Chem. Lett.*, **7** (1971), 325.
- SINGH, P. P., SHUKLA, U. P., MAKHIJA, R. & RIVEST, R., *J. inorg. nucl. Chem.*, **37** (1975), 679.
- SINGH, P. P. & KHAN, S. A., *Inorg. chim. Acta*, **14** (1975), 143.
- SINGH, P. P., SRIVASTAVA, A. K. & RIVEST, R., *J. inorg. nucl. Chem.* (in press).
- MORGON, H. W., *J. inorg. nucl. Chem.*, **16** (1961), 367.
- BAILEY, R. A., KOZAK, S. L., MICHELSEN, T. W. & MILLS, W. N., *Coord. chem. Rev.*, **6** (1971), 407.
- TURCO, A., PECILE, C. & NICOLINI, M., *Proc. chem. Soc.*, (1961), 213; *J. chem. Soc.*, (1962), 3008.
- FORSTER, D. & GOODGAME, D. M. L., *Inorg. Chem.*, **4** (1965), 1712.
- KRISHNAN, K. & PLANE, R. A., *Inorg. Chem.*, **5** (1966), 852.
- NEWMAN, G. & POWELL, D. P., *J. chem. Soc.*, (1961), 477.

Polarographic Study of Cd(II) & Pb(II) Complexes of Tris-(hydroxymethyl)-aminomethane in Water & Aqueous Methanolic Solutions

P. C. RAWAT

Department of Chemistry, M.R. Engineering College, Jaipur and

C. M. GUPTA

Department of Chemistry, University of Rajasthan, Jaipur

Received 22 August 1975; accepted 2 February 1976

Cd(II) and Pb(II) form 1:2 complexes with tris-(hydroxymethyl)aminomethane (TRIS) in aqueous medium. The presence of methanol in the medium considerably affects the nature and composition of the complex species. The effect of change of temperature on the system has also been investigated and the thermodynamic parameters ΔG, ΔH and ΔS have been computed for the reaction equilibria.

THE importance of tris-(hydroxymethyl) aminomethane, (HOCH₂)₃C.NH₂ (herein as TRIS), has been widely recognized¹. Except for a few potentiometric investigations on certain metal-TRIS complexes², the chelating properties of this compound have not been extensively studied. No attempts seem to have been made to study the TRIS-metal complexes polarographically. It was, therefore, felt worthwhile to investigate the coordinating tendencies of TRIS towards metal ions by polarographic technique. The present note deals with studies on Cd-TRIS and Pb-TRIS systems in aq. and aq.-methanolic media.

All chemicals used were of AR grade. TRIS (Fluka, Switzerland) was used as such. The solu-

tions were prepared in air-free conductivity water. Polarograms were recorded with a manual polarograph in conjunction with SCE. Capillary had the following characteristics: $m = 2.35$ mg/sec and $t = 3.8$ sec measured in $1.0M$ KCl at 1.0 V versus SCE and at 55 cm mercury height.

Experiments were performed in solutions containing 0.5 mM of metal ions with [ligand] ranging from $0.0M$ to $0.3M$ at $\mu = 0.5M$ (KNO_3). Gelatine (0.004%) was used as maximum suppressor. The test solutions were deoxygenated by passing purified nitrogen for 15 min.

TRIS imparted a $pH \approx 11.0$ in its $1.0M$ aq. solution. Since any change in its pH while investing its complexing tendencies was considered undesirable, the metal-TRIS systems reported here were investigated at the original pH (10.5 ± 0.2) of the final solutions thus showing negligible variation. Studies on simple metal ions alone were performed in the original pH of the supporting electrolyte which was almost a neutral medium. The metal-TRIS systems were further studied in 10 , 30 and 50% methanolic media and the results compared with those in aq. medium. All the half wave potentials have been corrected for the iR drop.

Cd-Tris system — The polarographic reduction of Cd-TRIS system gave a well defined single wave in each case. The wave was found to be diffusion-controlled and reversible as inferred from the linearity of log plots having slopes of $31 \pm mV$, the linear dependence of wave height on mercury pressure and temperature coefficients of diffusion currents of different solutions (1.0 to 1.5%). The nature of electrode process remained the same at all conditions of investigations. The solutions containing TRIS $\geq 0.1M$ were perfectly clear and behaved as true solutions. These gave a cathodic shift in half-wave potential of Cd^{2+} coupled with decrease in magnitude of the diffusion current with increasing [TRIS]. This suggested complexation of the metal ion with TRIS. The plots of $-E_{1/2}$ versus $-\log C_x$ were linear. It was, therefore, reasonable to conclude that the complex being reduced was one single species. The slopes of the linear plots were 0.072 V (25°) and 0.068 V (35°) suggesting $1:2$ as the metal to ligand ratio. The values of overall stability constants: $\log \beta_2$, as calculated from Lingane³ method have been found to be 4.77 and 4.03 at 25° and 35° respectively. The values of change of free energy (ΔG), -6.55 and -5.68 kcal/mole at 25° and 35° respectively, enthalpy (ΔH), -31.1 kcal/mole at 35° and entropy (ΔS), -8.25 e.u. have been calculated from standard expression described earlier⁴.

The polarographic analysis of solutions, identical in their constituents to aqueous studies, in 10 , 30 and 50% water-methanol mixtures were also performed. Here too, as in aq. medium, the complexation of Cd^{2+} with TRIS molecules was noted, as observed from the cathodic shift in reduction (half-wave) potential of the metal ion, coupled with decreasing diffusion current with increasing ligand. Unlike studies in aq. medium, the plots of $-E_{1/2}$ versus $-\log C_x$ were linear but having higher slopes: 0.80 V, 0.090 V and 0.093 V in 10 , 30 and 50% aq.

methanolic solutions. With the present data it is difficult to explain the increase in the slope values.

Pb-Tris system — Preliminary polarographic examination of lead ions in TRIS solutions gave a single wave which was well defined, diffusion controlled and reversible involving two electrons. The nature of reduction step was unaltered at all experimental conditions at which the system has been investigated.

A set of solutions containing $Pb^{2+} = 0.5$ mM, $\mu = 0.5M$ (KNO_3), gelatine = 0.004% and [TRIS] = $0.0M$ to $0.5M$ were prepared for polarographic analysis. Here too, as in Cd-TRIS system, the solutions up to TRIS $\geq 0.14M$ were clear and with increase in depolarizer concentration there was a distinct negative shift in reduction potentials of lead coupled with decreasing wave height. Such a trend signifies complexation of the metal ions by TRIS molecules in solutions. The plots of $-E_{1/2}$ versus $-\log C_x$ were linear with slopes 63 mV and 64 mV at 25° and 35° respectively. This lead to the value of 2 for p at both these temperatures. The overall formation constants ($\log \beta_2$) for $1:2$ complex were estimated³ to be 6.29 and 6.06 at 25° and 35° respectively. The values of thermodynamic parameters for Pb-TRIS system calculated from $\log \beta_2$ values using standard expressions are: $\Delta G = -8.58$ and -8.54 kcal/mole at 25° and 35° respectively; $\Delta H = -9.9$ kcal/mole at 35° and $\Delta S = -4.5$ e.u.

The polarographic analysis of the Pb-TRIS complexation in 10 and 30% aq.-methanolic media, showed that the results upto [TRIS] = $0.14M$ (10%) and $0.20M$ (30%) may be ignored on account of initial turbidities. At higher concentration of the depolarizer the Pb-TRIS complex is reduced with a clear well defined two electron wave which is reversible and diffusion-controlled. The thermodynamic constants: p and $\log \beta_2$ for the system were calculated by the method of Lingane³. The number of ligand bound per metal ion comes to 2 and the overall formation constant $\log \beta_2$ (for $1:2$ species) was estimated to be 6.4 and 6.05 in 10 and 30% methanolic solutions respectively.

From the results it is inferred that (i) the ligand has displayed a moderate coordination tendency towards the metal ions, (ii) the metal ions have coordinated to give stability values in the order of $Pb > Cd$ and (iii) the stabilities of the complexes have shown an increasing trend, though, slightly, in aq. methanolic medium as compared to aq. medium. This is quite significant and in agreement with our earlier work⁴⁻⁶ as also with the observations of many other workers⁷⁻⁹. Such a behaviour is well understood in the light of solvating power and dielectric constant of the medium.

The coordinating capacity of the ligand molecule has been largely due to its base strength and a nitrogen donor atom of primary amine group in its molecule. The base strength of the TRIS is comparable to ammonia and other primary amines. This is evident from present stability values, which are almost similar to those of corresponding ammonia complexes⁷. Remarkably, the coordination number with Cd(II) or Pb(II) in their complexa-

tion with TRIS seems to have reached to a maximum of 2 instead of four or six for both.

We are thankful to Principal, Malaviya Regional Engineering College, for his encouragement.

References

1. WEBBER, P., *Z. analyt. Chem.*, **166** (1959), 186.
2. KEMULA, W., BRACHACZEK, W. & HULANICKI, A., *Theory and structures of complex compounds*, edited by B. Jezowska-Trzebiatowska (Pergamon Press, London), 1964.
3. LINGANE, J. J., *Chem. Rev.*, **29** (1941), 1.
4. RAWAT, P. C. & GUPTA, C. M., *Bull. chem. Soc. Japan*, **46** (1973), 3079.
5. RAWAT, P. C. & GUPTA, C. M., *J. inorg. nucl. Chem.*, **34** (1972), 951; 1621.
6. RAWAT, P. C. & GUPTA, C. M., *Talanta*, **19** (1972), 706.
7. CLARK, M. E. & BEAR, J. L., *J. inorg. nucl. Chem.*, **32** (1970), 3569.
8. MIGAL, P. K. & TSIPLYAHOYRA, V. A., *Russ. J. inorg. Chem.*, **9** (1964), 333.
9. MANAHARI, S. E. & IWAMOTA, R. T., *J. electroanal. Chem.*, **14** (1963), 213.

Potentiometric Study of Be(II) Salicylates

SHAHID ABBAS ABBASI, B. G. BHAT & R. S. SINGH
Department of Chemistry, Indian Institute of Technology
Powai, Bombay 400076

Received 25 August 1975; accepted 12 December 1975

Formation constants of the complexes of Be(II) with salicylic acid and substituted salicylic acids have been determined by potentiometric titrations in aqueous solutions containing 0.10M NaClO₄. The results have been discussed with reference to the effects of substitutions in the ligand.

THE complex formation of Be(II) with salicylic acid or substituted salicylic acid has been studied by several workers¹⁻⁸. In the present work, formation constants of complexes of Be(II) with a series of substituted salicylic acids have been determined potentiometrically.

The preparation of sulphocresotic acids and their stock solutions were described earlier⁹. Potentiometric titrations were carried out under CO₂-free nitrogen atmosphere with carbonate-free 0.1000M KOH on well-stirred, thermostated (30° ± 1°) solutions containing 0.10M NaClO₄, 0.01M HClO₄ and ligand or metal and ligand in ratios of 1:10 and 1:20. Universal pH meter (model OP-204, Hungary, accuracy ± 0.02 pH unit) was used.

The formation constants (Table 1) of the 1:1 and 1:2 complexes were calculated by interpolation of \bar{n} values to 0.5 and 1.5. More precise values were obtained by linear plot¹⁰.

In all the titrations with Be(II) and salicylic acid, buffer regions were observed at 0 < a ≤ 2 (a = equivalent of base per mole of ligand) and 2 < a ≤ 4 with inflexions at a ≈ 2 and a ≈ 4 indicating the stepwise formation of 1:1 and 1:2 complexes. In non-sulphonated ligands, precipitations occurred at a ≈ 4. The \bar{n} value steadily increased with pH to ≈ 2 indicating the formation of 1:2 complex as the highest complex in Be(II)-salicylic acid system. Absence of disproportionation and constancy of \bar{n} in the pH range 7-10 in Be(II) complexes of sulpho-

TABLE 1 — FORMATION CONSTANTS (LOG K₁ AND LOG K₂) OF Be(II)-SALICYLATES AT 35° IN Aq. 0.1M NaClO₄

Ligand	pK [*] COOH	pK [*] OH	log K ₁	log K ₂
<i>o</i> -Cresotic acid (oCA)	2.84	14.14	13.05	8.78
<i>p</i> -Cresotic acid (pCA)	2.87	13.74	12.94	9.97
<i>m</i> -Cresotic acid (mCA)	2.94	13.54	12.87	9.89
Sulpho- <i>p</i> -cresotic acid (SpCA)	2.52	13.47	12.75	9.00
Salicylic acid (SA)	2.82	13.24	12.69	9.65
Sulpho- <i>o</i> -cresotic acid (SoCA)	2.54	12.58	12.04	8.99
5-Chlorosalicylic acid (ClSA)	2.43	12.50	11.97	9.30
5-Bromosalicylic acid (BrSA)	2.40	12.41	11.84	9.28
Sulpho- <i>m</i> -cresotic acid (SmCA)	2.68	12.33	12.72	9.25
5-Sulphosalicylic acid (SSA)	2.44	11.90	11.61	8.95
5-Nitrososalicylic acid (NO ₂ SA)	1.90	9.89	9.71	7.86

*Ref. 10.

salicylic acids point towards their resistance to hydrolysis.

Plot of log K₁ vs pK_{COOH} + pK_{OH} is linear with slope ≈ 1. Deviations from the linear plot are observed in case of *o*-cresotic (oCA) and sulpho-*m*-cresotic acids (SmCA). The unusually high stability of Be-SmCA complex could not be explained. The low stability of Be-oCA complex is probably due to the steric hindrance of -CH₃ group which is *ortho* to the -OH group. There should have been similar steric hindrance in Be-3-sulpho-*p*-cresotic acid (SpCA) and Be-sulpho-*o*-cresotic acid (SoCA) systems also but it appears that the coulombic attraction between dipositive Be(II) ion and trinegative ligand anion overcomes the hindrance due to *ortho* -CH₃ or -SO₃ groups during chelate formation. This assumption gains support from the plot of log K₂ vs pK_{COOH} + pK_{OH}. In the linear plot of slope ≈ 0.6, deviations towards low stability are observed in cases of oCA as well as SoCA and SpCA. Since formation of 1:2 complex involves a neutral or mononegative 1:1 complex and negatively charged ligand anion, there is no coulombic attraction between them and the steric factors become operative. The slope values of the curves indicate that in 1:1 complexes, substitution affects the stabilities of the metal-ligand complexes to the same extent as that of the corresponding proton-ligand complexes but in 1:2 complexes the effect of substitution on stabilities is 60% of the effect on basicities.

One of the possible reasons for this, besides statistical and coulombic factors, is that 1:2 complexes form at relatively higher pH values than 1:1 complexes and there is a pronounced effect of the competition of hydroxyl ions with ligand anions for 1:1 complexes.

The higher stability of complexes of sulphocresotic acids give the corresponding ligands an edge over sulphosalicylic acid (SSA) as complexing agents for Be(II). It has been shown¹⁰ that if salicylic acid (SA) is regarded as reference substance, then in the case of metal complexes of substituted sali-