J. Chemtracks 23(1&2) 207-208, 2021

Abstracted / Indexed in
A division of the American Chemical Society
Chemical Abstract U.S.A.

ISSN 0973-239X
CODEN:JCOHF7
IMPACT FACTOR : 4.950

Evaluation of protonation constants of binary complexes of diethylene triamine pentaacetic acid as ligands

Govind Krishna Mishra
Department of Chemistry, B.S.N.V.P.G. College, Station Road, Charbagh, Lucknow-226001

Manuscript received online 07 February 2021, accepted on 16 July 2021

Abstract: Potentiometric studies have been carried out on H_3ML and H_2ML complexes where 'M' represents Mn(II), Zn(II), Pb(II), Hg(II), La(III), Ce(III), Pr(III) and Nd(III)and'L'represents diethylene triamine pentaacetic acid (DTPA) using Bjerrum-Calvin pH- titration technique. The Protonation constants of these complexes in solution (aqueous) have been determined at an ionic strength x = 0.1M KNO_3 and temperatures 20°C and 40oC. The values of overall changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) accompanying complex formation have also been evaluated.

(**Keywords:** Potentiometry/protonation constants/ metal-DTPA complexes)

Introduction

In present study the evaluation of protonation constants of Mn(II), Zn(II), Pb(II), Hg(II), La(III), Ce(III), Pr(III) and Nd(III) metal complexes with DTPA have been done by using potentiometric method. These M-DTPA complexes may be used as ligands for the formation of homonuclear or hetero nuclear dimetallic complexes[1,2].

Experimenal

Materials and Method

Solutions of Mn(II), Zn(II), Pb(II), Hg(II), La(II), Ce(III), Pr(III) and Nu(III) metalions were prepared and standardised by EDTA titrations[3]. A 0.1M solution of diethylenetriamine pentaacetic acid (DTPA) was prepared by dissolving it into two equivalent of alkali (NaOH) which was prepared in double distilled water and had earlier been standardised against oxalic acid solution Solutions of carbonate free sodium hydroxide(E-Merck) and perchloric acid(A.R.) were standardised potentiometrically[4]. Metal : DTPA molar ratio was kept 2:1.

The values of protonation constants, ΔG, ΔH and ΔS have been evaluated by using the method described elsewhere[5].

Results and Discussion

The logarithemic values of ß1,$ß_2$ and $ß_3$ for metal-DTPA complexes have beendetermined by graphical method as referred by Rossotti and Rossotti[6]. The logarithmic values of ß1,$ß_2$ and $ß_3$obtained are 7.7, 12.4, 15.6 for H_3Mn(II) DTPA; 8.9, 13.5, 16.0for H_3Zn(II) DTPA; 9.3, 13.2, 16.2 for H_3Pb(II) DTPA and 5.7. 9.4, 12.1 for H_3Hg(II)DTPA; respectively and ß1,$ß_2$ values 2.8 5.1 for H_2La(III) DTPA: 2.5, 4.7 for H_2Ce(III)DTPA; 2.3,4.4 for H_2Pr(III) DTPA and 2.3,4.6 for H_2Nd(III) DTPA complexes respectively at 20°C. (relative error :± 0.1).

On the comparison of the values of K_1^H,$K_2^H$and K_3^H for simple DTPA (H_3L^{2-}) andcomplexed H_3ML ligand, it is very clear that the proton dissociation becomes more facile in the metal-DTPA complexes than simple ligand DTPA. However, due to formation of coordinate bonds between the metal and the various coordination sites of the ligand the complexed DTPA does not remain as flexible as uncomplexed DTPA. This leads to decrease in the values of protonation constants of H_3M(II) DTPA or H_2M(III) DTPA as compared to H_3L^{2-}. Due to the

factors discussed above the stability of the H_3M(II) DTPA or H_2M(III)DTPA complex affects the values of protonation constant to great extent. So far as the effect of metal ions is concerned K_1^H decreases for the M-DTPA complexes in the order: Pb > Zn > Mn > Hg > La > Ce > Pr >Nd. The values of ΔG, ΔH and ΔS have also been evaluated at only one ionic strength. They qualitatively reflect the change in the respective thermodynamic parameters and are given in Table 1.

Table -1
The values of ΔG, ΔH and ΔS for H_3M(II) DTPA and H_2M(III) DTPA complexes

System	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS ($JK^{-1}mol^{-1}$)
H_3Mn(II) DTPA	- 43.8	+ 2.5	+ 158.6
	(-46.8)		(+ 157.5)
H_3Zn(II) DTPA	-49.7	+4.3	+185.5
	(-52.9)		(+183.6)
H_3Pb(II) DTPA	-51.7	+19.2	+242.3
	(-53.7)		(+233.6)
H_3Hg(II) DTPA	-32.1	+13.1	+154.2
	(-33.1)		(+148.2)
H_2La(III) DTPA	-15.3	+6.3	+72.8
	(-15.9)		(+70.1)
H_2Ce(III) DTPA	-14.7	+1.9	+56.7
	(-15.7)		(+56.1)
H_2Pr(III) DTPA	-13.3	+1.4	+54.3
	(-14.1)		(+53.2)
H_2Nd(III) DTPA	-13.2	+7.1	+68.8
	(-13.6)		(+65.6)

Values given in bracket are at 40°C.
Relative error ± 0.20

References

1. F. P. Dwyer,D. P. Mellor,"Chelating agents and metal chelates", *Academic Press,* New York, p. **177**, (1964).
2. J. R. Behari and G. Gregoriadis, *Int. J. Pharmaceutics*, **79**, p.213, (1992).
3. F.J.Welcher,"The Analytical uses of ethelene diaminetetra acetic acid", D. *Van Nostarand Company, New York,* p. 164.(1957).
4. H. Irving, and H.S. Rossotti, *J. Chem. Soc.*, 3397, (1953).
5. G.K.Mishra, K. P. Dubey, & V. Krishna, *J. Indian Chem. Soc.,* **76**(3),151,(1999).
6. F. J. C. Rossotti, H. Rossotti, *"The determination of stability constants",* Mc Graw Hill Inc., New York, p. 92,(1961).