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Stability and Related Thermodynamics of Chelation of Zn(II) with Thiodiacetic Acid (TDAA), Thiodipropionic Acid (TDPA), Iminodiacetic Acid (IDAA), Dithiodiacetic Acid (DTDAA) and Diglycollic Acid (DGA)

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The chelation of Zn(II) with TDAA, TDPA, IDAA, DTDAA and DGA has been studied potentiometrically in aqueous medium at different ionic concentrations (0.1, 0.2 and 0.3 M $NaClO_4$) and different temperatures (25, 35 and 45°) using Calvin-Bjerrum pH titration technique as modified by Irving and Rossotti. The thermodynamic stability constants and thermodynamic functions (ΔG, ΔH and ΔS) have been reported.

It appears from a survey of literature[1-4] that no effort has been made to determine the thermodynamic stability constants of the complexes formed by Zn^{2+} ions with TDAA, TDPA, IDAA, DTDAA and DGA. It was therefore considered of interest to study these systems potentiometrically. The thermodynamic stability constants of Zn(II) complexes were obtained by extrapolating the determined stability constants at various ionic strengths (0.1, 0.2 and 0.3 M; 25°) to zero ionic strength. The thermodynamic functions (ΔG, ΔH and ΔS) were also calculated at 0.1 M. The titration technique was that of Calvin and Wilson as modified by Irving and Rossotti[5-7].

Experimental

Materials: The solutions of TDAA, TDPA and DTDAA (Evan's Chematics), IDAA (Sigma Chem), DGA (John Backer Inc.) and zinc sulphate ($ZnSO_4 \cdot 7H_2O$) were prepared in double distilled water. Perchloric acid (0.04 M) solution was prepared from the stock solution by dilution with double distilled water and standardized against standard NaOH solution. Other chemicals used were of A. R. grade. The stock solution of zinc sulphate was standardized gravimetrically as $ZnNH_4PO_4$.

Apparatus: A Philips pH meter (PR 9405 M) with glass and calomel electrodes assembly was used to measure the pH. The instrument was calibrated at pH 4.0 and 9.2 using buffer tablets.

Procedure: The experimental procedure used was the same as reported earlier[8]. The three solutions (total volume 50 ml in each case) were prepared as follows:

(i) 4×10^{-3} M perchloric acid,
(ii) 4×10^{-3} M perchloric acid$+3\times10^{-3}$ M ligand, and
(iii) 4×10^{-3} M perchloric acid$+3\times10^{-3}$ M ligand$+5\times10^{-4}$ M zinc ion solutions.

The concentration of the common ingradients in the solutions were identical in all the cases. An appropriate quantity of sodium perchlorate (2.0 M) was added to maintain the desired ionic concentrations of 0.1, 0.2 or 0.3 M. These solutions were titrated against a solution of 0.4 M caustic soda.

Results and Discussion

The pH range investigated for different systems were as follows:

System	pH range
Zn(II)-TDAA	2.9-5.4
Zn(II)-TDPA	4.1-5.0
Zn(II)-IDAA	5.3-7.8
Zn(II)-DTDAA	3.7-4.7
Zn(II)-DGA	2.4-3.5

The proton-ligand stability constants of TDAA, TDPA, IDAA, DTDAA and DGA and the stepwise formation constants of their chelates with Zn(II) were determined at 25±0.5°, 35±0.5° and 45±0.5° (Table 1) using Irving-Rossotti technique, and the values were further refined using the computational techniques[9,10], (i) curve fitting method and (ii) pointwise calculation method.

In Zn(II)-TDPA, Zn(II)-DTDAA and Zn(II)-DGA systems, the $\bar{n}$ values vary between 0.1 and 0.9, thereby indicating the formation of only 1 : 1 complex. In Zn(II)-TDAA and Zn(II)-IDAA, values of $\bar{n}$ vary between 0.2 and 1.9, indicating the formation of 1 : 1 as well as 1 : 2 complexes. The data in Table 1 reveal that stability constants decrease with increase in temperature and thus, lower temperature is favourable for complex formation. Metal-ligand stability constants increase with an increase in the ionic strength of the media. The thermodynamic stability constants (log $K_1^{\mu \to 0}$ and log $K_2^{\mu \to 0}$) have been evaluated at the standard state of infinite dilution and the values are given in Table 1.

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TABLE 1—PROTON-LIGAND STABILITY CONSTANTS OF TDAA, TDPA, IDAA, DTDAA AND DGA AND FORMATION CONSTANTS OF THEIR CHELATES WITH Zn(II)

Systems	Stability Constants	Temperature 25°C μ=0.1	25°C μ=0.2	25°C μ=0.3	35°C μ=0.1	45°C μ=0.1	25°C μ=0.0
TDAA	Log K_1^H	4.33	4.25	4.18	4.22	4.17	4.40
	Log K_2^H	3.14	3.11	2.95	3.09	2.87	3.23
TDPA	Log K_1^H	4.80	4.88	4.86	4.61	4.51	4.77
	Log K_2^H	3.63	3.66	3.74	3.54	3.58	3.58
IDAA	Log K_1^H	9.36	9.25	9.05	8.88	8.79	9.51
	Log K_2^H	2.74	2.56	2.58	2.40	2.32	2.82
DTDAA	Log K_1^H	3.96	3.82	3.66	3.98	4.15	4.11
	Log K_2^H	2.82	2.66	2.62	2.83	2.88	2.92
DGA	Log K_1^H	4.05	3.94	3.84	4.06	4.18	4.15
	Log K_2^H	2.63	2.49	2.42	2.64	2.85	2.73
Zn(II)-TDAA	Log K_1	3.20	3.30	3.38	3.12	3.08	3.14
	Log K_2	2.67	2.70	2.76	2.66	2.65	2.62
Zn(II)-TDPA	Log K_1	3.01	3.11	3.20	2.97	2.94	2.91
Zn(II)-IDAA	Log K_1	5.95	6.82	7.70	5.92	5.89	5.08
	Log K_2	4.42	4.92	5.42	4.42	4.41	3.96
Zn(II)-DTDAA	Log K_1	2.73	2.93	3.15	2.72	2.70	2.52
Zn(II)-DGA	Log K_1	3.79	3.87	3.94	3.75	3.72	3.71

TABLE 2—THERMODYNAMIC PARAMETERS OF Zn(II) COMPLEXES (μ=0.1 M)

Ligand	Temp. °C	$-\Delta G$(Kcal.mole^{-1}) $-\Delta G_1$	$-\Delta G_2$	$-\Delta H$(Kcal.mole^{-1}) $-\Delta H_1$	$-\Delta H_2$	ΔS(Cal.mole^{-1}.deg^{-1}) ΔS_1	ΔS_2
	25	4.36	3.64				
TDAA	35	4.40	3.75	2.77	0.80	5.16	9.22
	45	4.48	3.86				
	25	4.11	—				
TDPA	35	4.19	—	1.47	—	8.57	—
	45	4.28	—				
	25	8.12	6.03				
IDAA	35	8.35	6.23	1.88	1.01	21.87	16.29
	45	8.57	6.42				
	25	3.72	—				
DTDAA	35	3.83	—	0.86	—	9.28	—
	45	3.93	—				
	25	5.17	—				
DGA	35	5.29	—	1.66	—	11.39	—
	45	5.42	—				

The thermodynamic functions ΔG, ΔH and ΔS were calculated at different temperatures using the standard equations[11] and are given in Table 2. ΔH values were calculated by plotting the values of log K_n at different temperatures as a function of (1/T) and equating the gradient of this plot with $-\Delta H/4.57$. Chelates of Zn(II) with TDAA, TDPA, IDAA, DTDAA and DGA are formed spontaneously as evinced by the negative values of ΔG. The overall changes in the values of ΔH and ΔS indicate that the complexes are both enthalphy and entropy stabilized. The negative values of ΔH ensure that the reactions are exothermic. The relatively smaller values of ΔH as compared to ΔS indicate that entropy is the principal driving force for the complex formation in aqueous solution, i.e. increase in randomness in the systems will increase the stability of complex because entropy is a solvent property.

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