The values of $\bar{n}$ approach 2 for Gd^{3+}, Dy^{3+}, Er^{3+} and Tb^{3+} chelates with tyrosine indicating the formation of 1:1 and 1:2 complexes. The order of overall stability constants of these complexes is: $Yb^{3+} > Er^{3+} > Dy^{3+} > Gd^{3+}$ at 25°, 35° and 45° in accordance with their electronic configurations. The data show an increase in log K_1 and log K_2 values with increase in temperature which indicates that higher temperature is favourable for complex formation. A comparison of metal-ligand stability constants of tyrosine with those of serine reveals that hydroxy group is unionized and is not participating in complex formation[6,12]. The coordination appears to be through amino nitrogen and carboxylic oxygen only. The free energies of formation ($\Delta G°$) have more negative values at higher temperatures showing that complex formation is a spontaneous process. The formation of all the complexes is an endothermic reaction which explains the increase in the values of formation constants with increase in temperature. The $\Delta S°$ values are positive in all the cases indicating favourable entropy change for the formation of complexes.

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Stability Constants of Glutamic Acid Complexes with Some Metal Ions

H. L. GIRDHAR, (Miss) SHAMAH PARVEEN & M. K. PURI

Department of Chemistry, The University of Kashmir Srinagar

Stepwise stability constants of glutamic acid complexes with a number of metal ions have been determined by Bjerrum-Calvin pH titration method. The compositions of the complexes are 1:1 for Cr^{3+}, Fe^{3+}, La^{3+}, Nd^{3+}, Pr^{3+}, Zr^{4+}, Th^{4+} and both 1:1 and 1:2 for Ag^+, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, UO_2^{2+}.

IN spite of known chelating ability of glutamic acid[1-3], no systematic study on the complexes of this ligand with various metal ions has been carried out. Further in view of its importance from biochemical point of view, we thought it fit to study its complexes with a number of metal ions in solution employing Bjerrum-Calvin pH titration technique[4,5].

Glutamic acid (E. Merck, AR) was used to prepare $0.005M$ aqueous solution. Stock solutions ($0.005M$) of metal ions were prepared using analytical grade reagents and standardized by conventional methods[6]. The complex equilibria were studied at 25° and $\mu = 0.1M$. Potassium nitrate and nitric acid were used to maintain constant ionic strength. All pH measurements were made using Philips pH meter (PR 9405) which was calibrated at 4.0 and 9.2 pH values. The following solutions (total vol. 50 ml) were titrated separately against $0.1M$ KOH; (A) 5 ml of KNO_3 ($1M$) + 10 ml of HNO_3 ($0.01M$); (B) A — 10 ml of glutamic acid ($0.005M$); and (C) B + 2 ml of metal ion solution ($0.005M$).

From the titration curves of solutions (A) and (B), $\bar{n}$H values at different pH were calculated by the method of Irving and Rossotti[7]. The calculated values of $\bar{n}$H were plotted against pH and the protonation constants computed by interpolation at half $\bar{n}$H values. The values of K_1^H and K_2^H are 9.20 and 4.15 respectively. From the titration plots of solutions (B) and (C), $\bar{n}$ and pL values were calculated and the formation curves were obtained by plotting $\bar{n}$ values against pL values. For each metal ion the stepwise stability constants were evaluated by interpolation at half $\bar{n}$ values and are recorded in Table 1. Since the values of stability constants for the complexes of Ag^{1+} to UO_2^{2+} are less than 2 log units apart, therefore, the stability constants for these were also calculated by the method of least squares.

It has been found that the complexes of UO_2^{2+}, Cr^{3+}, Fe^{3+}, La^{3+}, Nd^{3+}, Pr^{3+}, Zr^{4+}, Th^{4+} get hydrolysed in the pH range 3.0 to 8.0. However, in other cases the complexes are stable towards hydrolysis because there is no precipitate formation even when the pH

TABLE 1 — STEPWISE STABILITY CONSTANTS OF GLUTAMIC ACID COMPLEXES

Cation	Log K_1^a	Log K_2^a	Log K_1^b	Log K_2^b	Log β_n	ΔF (kcal/mole)
Ag^{1+}	4.07	3.20	4.14	3.32	7.46[b]	−10.17
Mn^{2+}	4.07	3.50	4.10	3.55	7.65	−10.43
Co^{2+}	4.60	3.73	4.74	3.74	8.48	−11.57
Ni^{2+}	5.90	4.37	5.90	4.38	10.28	−14.09
Cu^{2+}	8.23	6.07	8.17	6.11	14.28	−19.48
Zn^{2+}	5.40	4.37	5.37	4.23	9.60	−13.09
UO_2^{2+}	8.30	6.37	8.23	6.64	14.87	−20.28
Cr^{3+}	9.70	—	—	—	9.70[a]	−13.23
Fe^{3+}	9.56	—	—	—	9.56	−13.04
La^{3+}	5.50	—	—	—	5.50	−7.50
Nd^{3+}	5.80	—	—	—	5.80	−7.71
Pr^{3+}	4.80	—	—	—	4.80	−6.54
Zr^{4+}	8.30	—	—	—	8.30	−11.32
Th^{4+}	9.10	—	—	—	9.10	−12.41

(a) Values calculated by half $\bar{n}$ method.
(b) Values calculated by least square method.

is raised to 10. The data in Table 1 show that the Cr^{3+}, Fe^{3+}, La^{3+}, Nd^{3+}, Pr^{3+}, Zr^{4+} and Th^{4+} form 1:1 complexes only and Ag^{1+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and UO_2^{2+} form both the 1:1 and 1:2 complexes. The order of stability of 1:1 and 1:2 complexes of bivalent metal ions is $UO_2^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+} > Mn^{2+}$ which is in agreement with the general order of stability given by Irving and Williams[8].

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Determination of Hydrazine, Methylhydrazine, Semicarbazide & Hexacyanoferrate(II) Using Periodate

R. L. KAUSHIK, O. P. VERMANI & RAJENDRA PROSAD

Department of Chemistry, Regional Engineering College Kurukshetra

Hydrazine, methylhydrazine, semicarbazide and hexacyanoferrate(II) have been oxidized with excess of metaperiodate under suitable conditions. The equivalent amount of iodate liberated is treated with potassium iodide in chloroacetic acid buffer and the iodine liberated by titrating with standard sodium thiosulphate after masking the excess metaperiodate with molybdate.

SINGH and coworkers have used metaperiodate as an oxidizing titrant for the determination of hydrazine and its derivatives under the conditions of Andrews and Lang[1,2]. In the presence of bicarbonate, reduction of metaperiodate with hydrazine, methylhydrazine and semicarbazide goes only up to iodate stage. Similarly, in the presence of boric acid, metaperiodate is reduced to iodate with hexacyanoferrate(II)[3]. Since the iodate formed in these reactions is stoichiometrically related to the amount of hydrazine, methylhydrazine, semicarbazide and hexacyanoferrate(II) taken, it would be better to determine organic compounds by titrating the iodate and hexacyanoferrate(II) by titrating the iodate and hexacyanoferrate(III) formed[3]. Under the conditions each organic molecule and hexacyanoferrate(II) ion would give rise to twelve and eight iodine atoms respectively. With this background, we describe in this note a sensitive

method for the estimation of hydrazine, methylhydrazine, semicarbazide and hexacyanoferrate(II) using periodate.

All the chemicals used were of AR (BDH or E. Merck) grade. Solutions of hydrazine sulphate, methylhydrazine sulphate, semicarbazide hydrochloride and potassium hexacyanoferrate(II) were prepared in distilled water and standardized by iodine.

Chloroacetic acid buffer was prepared by dissolving 25 g of the substance in 70 ml distilled water and its pH adjusted to 2·9 with strong sodium hydroxide solution.

$2M$ molybdate solution was obtained by dissolving ammonium molybdate in hot distilled water.

Determination of hydrazine, methylhydrazine and semicarbazide — A suitable aliquot of the substance to be determined was added to aq. sodium bicarbonate (10 ml, 1%) containing an excess of potassium metaperiodate (50-100 mg). The contents were shaken for 2-3 min and molybdate solution (10 ml, $2M$) followed by same volume of chloroacetic acid buffer and 1 g of potassium iodide were added. The contents of the flask were thoroughly mixed and the iodine liberated was titrated against $0·1N$ sodium thiosulphate. The results are recorded in Table 1.

Determination of hexacyanoferrate(II) — To an aliquot containing 40-90 mg of hexacyanoferrate(II) was added 0·5 g of boric acid and an excess of 1% sodium metaperiodate solution (5-10 ml). The reaction mixture was kept at room temperature for 2-3 min to complete the reaction and 10 ml of $2M$ ammonium molybdate followed by 10 ml of chloroacetic acid buffer were added. The reaction mixture was then treated with 1 g of potassium iodide and 10-15 ml of 3% zinc sulphate solution and set aside for 2 min. The liberated iodine was titrated with $0·1N$ sodium thiosulphate. The results are given in Table 1.

It has been reported[4] that periodate can be masked with molybdate whereas iodate remains

TABLE 1 — ESTIMATION OF HYDRAZINE, METHYLHYDRAZINE, SEMICARBAZIDE AND HEXACYANOFERRATE(II)

Hydrazine (mg)		Methylhydrazine (mg)	
Taken	Found	Taken	Found
2·33	2·23	2·85	2·86
2·72	2·61	3·32	3·34
3·11	2·97	3·80	3·80
3·50	3·49	4·27	4·27
3·89	3·84	4·74	4·75
4·28	4·24	5·22	5·19

Semicarbazide (mg)		Hexacyanoferrate(II) (mg)	
Taken	Found	Taken	Found
5·13	5·13	41·98	41·87
5·99	6·00	55·97	55·92
6·84	6·75	61·56	61·48
7·70	7·75	69·96	70·23
8·55	8·50	75·56	75·53
9·41	9·38	83·95	84·01