POLAROGRAPHIC STUDY OF UO_2^{2+} COMPLEXES WITH NORVALINE AND ISOLEUCINE

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Much of the stability constant data on uranyl-aminoacid complexes are not consistent with respect to ionic medium, anion associated with the uranyl ion and the pH at which the constants have been calculated [1,2]. Chelation of uranyl ion by amino acids itself appears to be uncertain. Many workers have reported that amino acids are bidentate chelating ligands for the uranyl ion, the chelation being effected through the carboxyl oxygen and amino nitrogen [3-5].

Li et al [6] and Feldman et al [7] have however reported that the amino nitrogen is not involved in coordination. A survey of literature reveals that the reduction of UO_2^{+2} at dropping mercury electrode has been studied in various complexing and non-complexing media by various investigators. However, complexation studies of UO_2^{+2} with norvaline and isoleucine have not been made. The present study was undertaken to investigate the composition and stability of the chelates of the said metal-ligand systems.

EXPERIMENTAL

All current potential curves were recorded on a manual set up using dme and SCE. The capillary had following characteristics, m = 1.72 mg/sec and t = 4 sec in 0.5 M potassium chloride in open circuit. All measurements were carried out at 30 ± 0.1 C. The ionic strength was maintained at 0.5 M with KCl. Gelatin (0.002%) was used as maximum suppressor. The pH of the solution was measured with an expanded scale pH-meter (ECIL Hyderabad, Model PH 821 B). The pH of the solution was maintained by using CO_2^- free sodium hydroxide or dilute perchloric acid solution.

A water soluble salt, uranyl acetate (BDH,AR) was used for stock solution. DL-Norvaline (Renal AR) and L-isoleucine (Fluka) were used without further purification. All other chemicals were of AR grade. The concentration of the ligand ion was calculated from the pH of the solution and pK of the ligands determined separately as pK_1 = 2.26, pK_2 = 9.53 for norvaline and pK_1 = 2.40, pK_2 = 9.58 for isoleucine by the pH-titration technique of Irving and Rossotti [8].

RESULTS AND DISCUSSIONS

Uranyl ion gave a well-defined reversible wave in 0.5 M potassium chloride medium with the half-wave potential at -0.185 V vs SCE. The reduction remained reversible in the presence of norvaline and isoleuucine but the wave shifted to more negative potentials indicating complexation (Table 1).

A plot of the half-wave potential ($E^{1/2}$) vs pA resulted in a straight line indicating the presence of only one complex, which is also confirmed by coordination number. The data were,therefore analysed by the method of Lingane [9].

TABLE 1

EFFECT OF LIGAND CONCENTRATION $[UO_2^{+2}]$ = 0.6 mM
μ = 0.5M (KCl). TEMP. = 30°C

$m^{2/3}\ t^{1/6}$ = 1.80 $mg^{2/3}\ sec.^{-1/2}$ pK = 2.26

[HA] M	pH	pA	$E_{1/2}$ −V vs SCE	i_d µA
		Uranyl - Norvaline		
0.00	-	-	0.185	1.70
0.12	2.08	1.32	0.187	1.60
0.16	1.95	1.28	0.189	1.59
0.16	2.07	1.20	0.195	1.56
0.28	1.83	1.12	0.200	1.53
0.28	2.17	0.90	0.212	1.52
0.32	2.19	0.83	0.215	1.51
0.32	2.48	0.70	0.223	1.51
0.32	2.63	0.65	0.228	1.50
0.32	3.48	0.52	0.234	1.48
		log β_1 = 1.35		
		Uranyl - Isoleucine		
0.10	2.19	1.42	0.189	1.64
0.125	2.22	1.30	0.194	1.62
0.125	2.43	1.19	0.200	1.59
0.125	2.61	1.11	0.205	1.57
0.125	3.00	1.00	0.216	1.58
0.175	2.81	0.90	0.219	1.55
0.175	3.02	0.85	0.222	1.53
0.20	3.15	0.77	0.225	1.51
0.24	3.23	0.68	0.230	1.49
		log β_1 = 1.45		

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According to Lingane's method

$$E_{1/2}^{(c)} - E_{1/2}^{(s)} = \frac{0.060}{n} \log K_c - p \frac{0.060}{n} \log C_x$$

The values of the stability constant obtained is log β_1 = 1.35 for norvaline and log β_1 = 1.45 for isoleucine.

The stabilities were found to be almost same for DL-norvaline and L-isoleucine. This may be because of pK of these amino acids are nearly same.

It was observed that the stability constants of amino acid complexes are very low. This may be due to the fact that `N' of amino acid is usually protonated in acidic solution and forms positive ion. The positive charge on the nitrogen of an amino group repulses the positively charged uranyl cation, resulting in lower values of stability constants.

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