Chemical speciation of L-glutamic acid complexes of some toxic metal ions in DMSO-water mixtures

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Abstract : Chemical speciation of L-glutamic acid complexes of some toxic metal ions has been investigated pH-metrically in DMSO-water mixtures (0-60% v/v) at 303 K and ionic strength of 0.16 mol L^{-1}. The predominant species detected for Pb^{II} and Cd^{II} are ML_2H_4, ML_2H_3, ML_2H_2, ML_2 and ML and for Hg^{II} are ML_2H_4, ML_2H_3, ML_2H_2 and ML. The trends in variation of stability constants of the complexes with dielectric constant of the medium are attributed to the electrostatic and non-electrostatic forces.

Keywords : Chemical speciation, glutamic acid, toxic metals, DMSO.

Introduction

DMSO is a polar solvent that dissolves most organics and inorganic salts. It is miscible with water in all proportions. Protonation equilibria of L-Glu and L-His in DMSO-water mixtures have already been studied in this laboratory[1]. Glutamic acid (Glu) plays a major role in brain development, effecting neuronal migration, neuronal differentiation, axon genesis, and neuronal survival[2-4]. It is also known as "Brain fuel"[5]. It is a major excitatory neurotransmitter in the brain and spinal cord[6]. In the mature nervous system, Glu is central to neuroplasticity, in which there are use-dependent alterations in synaptic efficacy as well as changes in synaptic structure. These latter actions are intimately implicated in memory and related cognitive functions. Finally, persistent or overwhelming activation of glutamate-gated ion channels can cause neuronal degeneration[7] depending on the circumstances, this occurs by means of necrosis or apoptosis[8].

Results and discussion

The results of the final best fit models that contain the stoichiometry of the complex species and their overall formation constants are given in Table 1. Very low standard deviation in overall stability constants (log β) signifies the precision of these constants.

Effect of solvent :
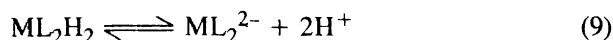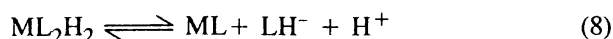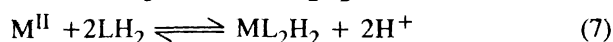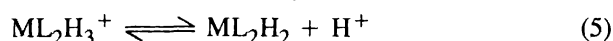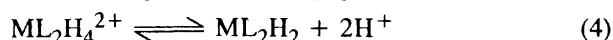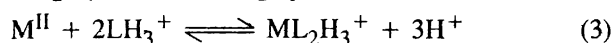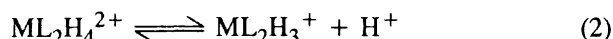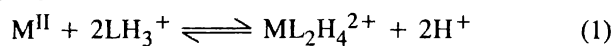
The magnitude of stability constants (log β) of Glu

Table 1. Parameters of best-fit chemical models of Glu complexes of Pb^{II}, Cd^{II} and Hg^{II} in DMSO-water mixtures

System (% v/v) DMSO	log β_{mlh} (SD)				
	110	120	122	123	124
Pb^{II}					
0.0	4.74(13)	8.88(9)	23.87(28)	28.97(18)	32.94(18)
10.0	5.04(39)	–	24.50(76)	29.69(55)	33.95(51)
20.0	5.30(17)	9.20(18)	24.81(34)	30.04(26)	33.88(39)
30.0	5.79(48)	9.08(51)	26.17(62)	31.83(56)	36.06(60)
40.0	6.19(50)	10.44(71)	26.63(63)	32.41(60)	36.97(62)
50.0	5.86(9)	9.42(17)	26.1(10)	31.49(11)	35.64(24)
60.0	5.32(26)	8.12(45)	25.50(70)	31.87(49)	36.71(89)
Cd^{II}					
0.0	4.22(13)	7.81(11)	24.27(20)	29.34(16)	33.44(14)
10.0	4.45(9)	–	25.09(10)	30.80(7)	35.03(8)
20.0	5.52(26)	9.34(26)	25.60(27)	30.33(28)	34.22(38)
30.0	4.46(18)	8.19(16)	24.54(72)	31.05(24)	35.43(25)
40.0	4.91(9)	8.43(10)	24.89(20)	30.74(12)	34.84(24)
50.0	5.67(6)	9.60(7)	26.17(6)	31.56(7)	36.04(9)
60.0	5.48(31)	9.00(33)	25.68(73)	32.84(39)	38.41(37)
Hg^{II}					
0.0	9.22(8)	–	26.03(9)	30.09(5)	32.69(9)
10.0	9.23(48)	–	26.43(50)	31.37(48)	34.63(50)
20.0	10.24(8)	–	27.65(9)	31.71(4)	33.96(16)
30.0	10.88(18)	–	28.23(27)	32.21(17)	35.45(12)
40.0	10.97(13)	–	30.10(9)	34.26(7)	37.28(6)
50.0	9.76(12)	–	29.37(9)	34.06(6)	37.15(6)
60.0	9.57(8)	–	29.87(5)	34.91(5)	38.82(2)

complexes with Pb^{II}, Cd^{II} and Hg^{II} vary linearly as a function of inverse of dielectric constant of DMSO-water mixtures. DMSO is a polar aprotic and coordinating solvent. It is a structure former and it enhances the water structure in DMSO-water mixtures; hence, it removes water from coordination sphere of metal ions, making them more reactive towards the ligands. As a result, the stability of the complexes is expected to increase. At the same time, it is a coordinating solvent and competes with the ligands for coordinating the metals. This decreases the stability of the complexes. Hence, the stability of the complexes is expected to either increase or decrease. The linear variation indicates that electrostatic forces dominate the equilibrium process under the present experimental conditions[9].

Distribution diagrams :

L-Glutamic acid has two dissociable protons and one amino group which can associate with a proton. It exists as LH_3^+ at low pH and gets deprotonated with the formation of LH_2, LH^- and L^{2-} successively with increase in pH, in the ranges 2.0-6.0, 3.0-11.0 and above 8.0, respectively. Hence, the plausible binary metal-ligand complexes can be predicted from these data. The present investigation reveals the existence of ML_2H_4, ML_2H_3, ML_2H_2, ML_2 and ML for Pb^{II} and Cd^{II} and Hg^{II} forms ML_2H_4, ML_2H_3, ML_2 and ML. The formation of various L-glutamic acid complex species is shown in the following equilibria.

$$M^{II} + 2LH_3^+ \rightleftharpoons ML_2H_4^{2+} + 2H^+ \tag{1}$$

$$ML_2H_4^{2+} \rightleftharpoons ML_2H_3^+ + H^+ \tag{2}$$

$$M^{II} + 2LH_3^+ \rightleftharpoons ML_2H_3^+ + 3H^+ \tag{3}$$

$$ML_2H_4^{2+} \rightleftharpoons ML_2H_2 + 2H^+ \tag{4}$$

$$ML_2H_3^+ \rightleftharpoons ML_2H_2 + H^+ \tag{5}$$

$$M^{II} + 2LH_3^+ \rightleftharpoons ML_2H_2 + 4H^+ \tag{6}$$

$$M^{II} + 2LH_2 \rightleftharpoons ML_2H_2 + 2H^+ \tag{7}$$

$$ML_2H_2 \rightleftharpoons ML + LH^- + H^+ \tag{8}$$

$$ML_2H_2 \rightleftharpoons ML_2^{2-} + 2H^+ \tag{9}$$

Typical distribution diagrams in DMSO-water mixtures are shown in Fig. 1. They indicate that the L-Glu complexes of Pb^{II}, Cd^{II} and Hg^{II} are formed in the pH range 2.0-10.0. $ML_2H_4^{2+}$ is the predominant species which is formed from M^{II} and LH_3^+ at a pH < 4.0 (Equilibrium 1). The species $ML_2H_3^{2+}$ may be formed from free metal

and LH_3^+ or by the deprotonation of $ML_2H_4^{2+}$ (Equilibria 2 and 3). ML_2H_2 species is formed by the interaction of free metal ion with either LH_3^+ or LH_2 (Equilibria 6 and 7) and by the deprotonation of $ML_2H_3^{2+}$ and $ML_2H_4^{2+}$ (Equilibria 4 and 5). As observed in Fig. 1, the concentration of ML_2H_2 is decreasing even before the formation of ML_2; simultaneously the concentrations of ML and LH are increasing. From this observation it is concluded that ML_2H_2 is dissociating to form ML and LH (Equilibrium 8), the only way of forming ML species. ML_2^{2-} species is formed from the deprotonation of ML_2H_2 (Equilibrium 9). The high magnitudes of stabi-

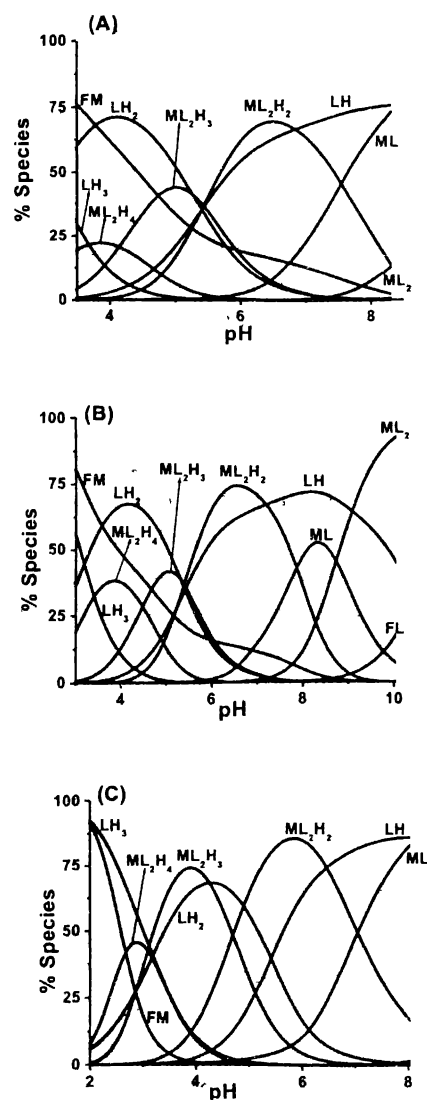Fig. 1. Distribution diagrams of binary complexes of Glu in 50% v/v DMSO-water mixture : (A) Pb^{II}, (B) Cd^{II} and (C) Hg^{II}

lity constants of binary complexes given in Table 1 indicate that metals are amenable for transportation in biological systems. Instead the metal complexes with small stabilities make the metals bioavailable.

Experimental

0.05 mol L^{-1} L-glutamic acid and 0.1 mol L^{-1} Pb^{II} and Cd^{II} and 0.05 mol L^{-1} Hg^{II} nitrate solutions were prepared by dissolving G.R. grade (E. Merck, Germany) salts in triple-distilled deionised water by maintaining 0.05 mol L^{-1} nitric acid concentration to increase the solubility of the ligand and to suppress the hydrolysis of metal salts. DMSO (Qualigens, India) was used as received. 0.2 mol L^{-1} nitric acid (Qualigens, India) was prepared. 2 mol L^{-1} sodium nitrate (Qualigens, India) was prepared to maintain the ionic strength in the titrand. Sodium hydroxide (Qualigens, India) of 0.4 mol L^{-1} was prepared. All the solutions were standardized by standard methods. To assess the errors that might have crept into the determination of the concentrations, the data were subjected to analysis of variance of one way classification[10]. The strengths of alkali and mineral acid were determined using the Gran plot method[11,12]. The titrimetric data were obtained by using calibrated Elico (Model LI-120) pH meter (readability 0.01) at 303.0 $\pm$ 0.1 K and 0.16 mol L^{-1} ionic strength. The equilibration of glass electrode in DMSO-water mixtures (0.0–60.0% v/v), calibration of the instrument and other experimental details are given elsewhere[9]. The computer programs SCPHD[13] and MINIQUAD75[14] were used to calculate the correction factor and the binary stability constants, respectively.

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