

Miceller effect on metal-ligand equilibria of magnesium(II) and calcium(II) with L-arginine

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Speciation of L-arginine complexes of Ca^{II} and Mg^{II} is investigated pH-metrically in 0–2.5% anionic, cationic and neutral micellar media. The stability constants are calculated using the computer program MINQUAD75. The best-fit chemical models are arrived at based on statistical parameters. The effects of micelles, dielectric constant of the medium and the electrostatic interactions between the complex species on the stability of the complexes are discussed.

L-Arginine has biological and medicinal applications¹. It behaves as bidentate ligand employing carboxylate and amino groups, forming a five-membered ring with the metal ion². The review of the literature reveals that not much data are reported³ in the complexation with calcium and magnesium with L-arginine. Hence, the complexation equilibria of L-arginine with Ca^{II} and Mg^{II} in micellar media has been studied.

Results and discussion

The formation constants of the complexes of L-arginine with Ca^{II} and Mg^{II} were calculated using the computer program MINQUAD75⁴. The best-fit models contained the species, ML_2H_4 , ML_2H_3 and ML_2H_2 (or ML_2H). The best-fit models are chosen based on the statistical parameters and the simulations.

The titration curves are simulated by assuming various number of species and the curves are superimposed on the experimental titration curves. The simulated titration curve coincided only when the curve is simulated assuming the species, ML_2H_4 , ML_2H_3 and ML_2H_2 . The parameters of the best-fit models are given in Tables 1 and 2 in CTAB, SDS and Triton X-100 media.

Effect of micelles :

The effect of micelles on the speciation is due to the compartmentalization. In sodium dodesyl sulfate (SDS) medium, the magnitude of stability constants of the arginine complexes of Ca^{II} and Mg^{II} passes through minimum. The stabilities of most of these complexes have decreased in cetyltrimethylammonium bromide (CTAB) medium and that of most of the species have varied randomly in nonionic surfactant (Triton X-100) medium. These variations are explained below.

The effect of micelles on the equilibria depends upon the incorporation of the species into the micellar pseudophase. The hydrophilic arginine will distribute between the micelle surface and bulk water leaving less of it available for reaction. Hence, the log K value may decrease. The variation of log K in SDS medium is due to the polarity of the medium and the electrostatic interactions between the complex species and the charged micelle surface. The CTAB micelle has positively charged Stern layer, which can repel the positively charged species, destabilizing it. The trend in Triton X-100 medium is due to the destabilization of the charged species. The dielectric constant of the solution⁵ is

Table 1. Best-fit chemical models of calcium(II)-arginine

Surfactant % (w/w)	log β_{min} (SD)			NP	U_{corr}	χ^2	R	Skew- ness	Kurol- sis
CTAB :	124	123	122						
0.0	46.26 (0.05)	37.26 (0.15)	28.58 (0.06)	78	4.73	29.79	0.006	1.00	4.86
0.5	45.96 (0.63)	36.99 (0.61)	27.32 (0.62)	92	144.94	28.41	0.039	1.24	4.12
1.0	45.84 (0.28)	37.34 (0.29)	27.66 (0.31)	82	66.58	68.41	0.028	1.08	4.81

Table 1 (contd.)

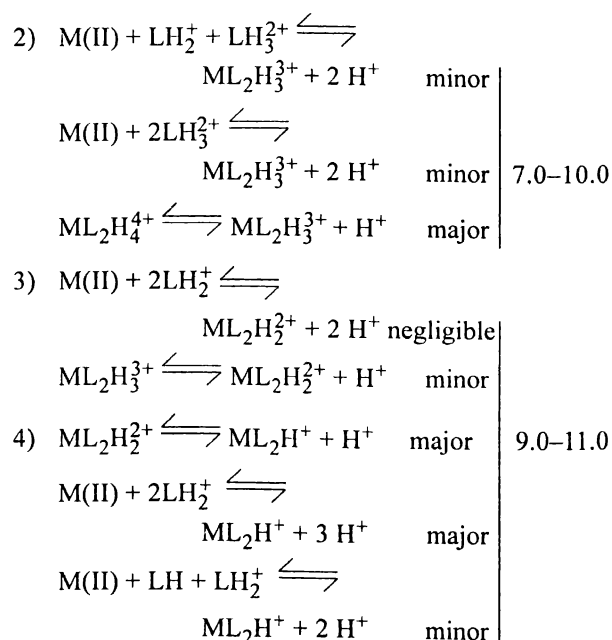
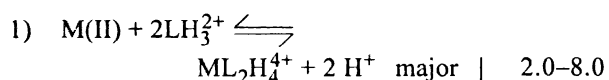
1.5	45.37 (0.30)	36.78 (0.31)	27.48 (0.30)	77	43.91	76.15	0.024	1.22	5.49
2.0	43.91 (0.11)	—	26.20 (0.12)	91	8.29	173.8	0.009	−1.10	19.27
2.5	43.80 (0.19)	35.51 (0.21)	26.42 (0.15)	92	29.66	139.7	0.018	0.35	5.10
% (w/w) SDS :									
0.5	39.77 (0.15)	32.74 (0.25)	—	102	92.14	79.52	0.026	0.91	6.70
1.0	38.60 (0.15)	31.58 (0.19)	—	103	63.36	54.78	0.021	1.19	6.83
1.5	41.19 (0.07)	33.05 (0.16)	24.91 (0.08)	107	14.13	81.12	0.009	0.94	5.01
2.0	43.94 (0.05)	34.97 (0.18)	26.08 (0.08)	83	4.98	161.06	0.005	−2.71	15.02
2.5	44.68 (0.08)	35.54 (0.17)	26.63 (0.10)	103	11.74	132.09	0.009	2.43	11.23
% (v/v) TX-100 :									
1.0	43.70 (0.08)	35.24 (0.19)	26.24 (0.10)	64	1.65	79.08	0.003	1.11	5.77
2.0	44.14 (0.12)	35.17 (0.37)	26.38 (0.13)	91	10.59	140.68	0.010	−0.35	12.17
3.0	44.90 (0.29)	36.68 (0.18)	26.49 (0.61)	82	50.12	154.91	0.19	0.47	5.86
4.0	45.22 (0.24)	36.33 (0.43)	26.86 (0.39)	77	22.83	101.85	0.015	1.38	6.89
5.0	43.26 (0.15)	34.71 (0.31)	26.02 (0.12)	85	21.46	113.53	0.015	−0.40	7.76

64 in SDS/CTAB/Triton X-100 at premicellar concentrations; it is 25, 75 and 10 at CMC, and 5, 10 and 10, respectively, above micellar concentrations.

Arginine exists either as charged species or as zwitterions and so the probability of inserting them into the inner core is minimal. Since there is alkyl chain between the polar groups of arginine, it may not completely go into the bulk water. Thus the stability depends on the charge on amino acid and the nature of the complex species. Therefore, at lower concentrations of SDS, dielectric constant of the solution is less than that of aqueous solutions and it destabilizes the charged species. Since all the complex species have positive charge, their stabilities are decreased.

Distribution diagrams :

The forms of L-arginine are LH_3^{2+} , LH_2^{2+} and LH in the pH regions 1.5–3.5, 2.5–9.0 and 8.0–11.5, respectively⁶. The plausible complex species can be predicted from these data in the pH range (2–11) of the present study as follows :



The distribution diagrams show that $\text{ML}_2\text{H}_4^{4+}$ and $\text{ML}_2\text{H}_3^{3+}$

Table 2. Best-fit chemical models of magnesium(II)–arginine

Surfactant % (w/w)	log β_{\min} (SD)				NP	U_{corr}	x^2	R	Skew- ness	Kurtosis
CTAB :	124	123	122	121						
0.0	46.49 (0.15)	37.96 (0.23)	28.53 (0.20)	18.07 (0.20)	90	32.20	181.32	0.018	0.52	7.30
0.5	43.31 (0.30)	34.41 (0.29)	–	–	84	146.34	51.37	0.037	1.62	5.59
1.0	–	34.34 (0.23)	24.48 (0.47)	–	92	86.66	171.25	0.035	2.75	17.32
1.5	42.51 (0.21)	34.41 (0.20)	24.88 (0.26)	–	86	59.03	173.75	0.029	2.51	17.71
2.0	43.81 (0.06)	–	26.23 (0.08)	–	62	1.40	40.75	0.003	–0.73	3.88
2.5	42.59 (0.16)	–	–	15.42	80	6.28	90.60	0.008	–0.10	7.51
% (w/w) SDS :										
0.5	39.60 (0.17)	36.81 (0.15)	28.67 (0.20)	–	104	57.15	90.46	0.020	1.82	8.65
1.0	38.96 (0.10)	31.69 (0.17)	23.70 (0.14)	–	108	26.85	59.51	0.014	0.92	7.00
1.5	40.12 (0.10)	32.36 (0.09)	–	–	99	8.94	171.93	0.007	0.76	8.23
2.0	43.97 (0.04)	35.38 (0.11)	26.34 (0.07)	–	86	4.13	94.25	0.004	–1.81	8.28
2.5	44.88 (0.06)	35.98 (0.12)	27.00 (0.08)	–	101	6.98	85.30	0.007	1.44	6.01
% (v/v) TX-100 :										
1.0	43.38 (0.14)	–	25.85 (0.14)	16.05 (0.07)	81	2.18	88.36	0.004	0.09	8.97
2.0	43.82 (0.10)	–	26.22 (0.11)	16.48 (0.06)	81	3.29	89.54	0.005	0.85	6.12
3.0	45.61 (0.05)	37.22 (0.08)	28.32 (0.05)	18.15 (0.06)	73	2.01	113.09	0.004	0.77	5.88
4.0	45.69 (0.17)	–	27.90 (0.16)	–	70	22.94	84.86	0.015	1.09	5.17
5.0	42.90 (0.52)	–	25.60 (0.59)	15.72 (0.45)	83	125.00	62.55	0.036	0.54	4.01

concentrations decrease in higher percentage of surfactant in CTAB and Triton X-100, whereas it passes through minimum in SDS. In all these systems, $\text{ML}_2\text{H}_4^{4+}$ is the predominant species. The existence of considerable amount of free metal indicates the weak interaction between the metal ion and the amino acid.

Experimental

Solutions of L-arginine, calcium(II) chloride and magnesium(II) chloride (Merck) were prepared in triple-distilled water. SDS ($\text{R}_{12}\text{SO}_4\text{Na}$) was purified by crystallizing from ethanol. CTAB ($\text{R}_{16}\text{N}(\text{CH}_3)_3\text{Br}$) and Triton X-100 (polyoxyethylene diisobutylphenol, $\text{R}_8\text{C}_6\text{H}_4[\text{OCH}_2\text{CH}_2]_{9.5}$

OH) were used as such, and their purity was checked by determining CMC conductometrically. CMC values of SDS, CTAB and TX-100 were 8.1×10^{-3} , 9.2×10^{-4} mol dm $^{-3}$ and 0.54 vol%, respectively, at 303 K.

The alkalimetric titrations were carried out using a Systronics 335 pH meter maintaining an ionic strength of 0.16 mol dm $^{-3}$ with NaCl at 303.0 ± 0.1 K. the surfactant concentration was varied in the range 0.0–2.5% w/w (or v/v). In order to obtain steady and reproducible results in surfactant medium the electrode was pre-equilibrated with the respective media⁷. The titrand, in each titration, contained approximately 1 mmol HCl, 0.4–0.8 mmol of

L-arginine, 0.2 mmol of metal and the requisite amounts of NaCl and surfactant in a total volume of 50 cm³. The titrand was titrated with 0.4 mol dm⁻³ NaOH. Three titrations were carried out for each metal-ligand system (metal-to-ligand ratios being in the range 1 : 2 to 1 : 4) in each percentage of the surfactant. In all these titrations, metal ion was the last component added to the titrand.

Some Ca^{II}-arginine systems were studied in 0–2.5% (w/w) SDS spectrophotometrically to provide corroborative evidence for the electrometric studies. The solutions were prepared keeping the amounts of the metal (Ca or Mg), arginine and electrolyte as in the case of electrometric studies. The required concentration of surfactant was maintained. The ratio of the concentrations of metal-to-ligand and other experimental conditions were maintained same as in pH-metric studies. A Milton Roy Spectronic 1201 spectrophotometer, with 1 cm quartz cells of was used.

The stability constants were evaluated using the computer program MINIQUAD75, following some heuristics⁸. The details of modeling are given elsewhere⁷.

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