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Stability studies on solution equilibria of Zn(II) pyrimidine nucleus bases

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pH-metric titrations were carried out to determine the activity and stability of metal chelates of a substituted pyrimidine nucleus base namely 5-Fluorouracil(5-FU: A) and some essential peptide constituents *ie.*, amino acids *viz.* glycine(gly; B), L-alanine(ala; B), L-valine(val; B), L-phenylalanine(phe; B). From the titration data, we have obtained satisfactory stability constant values for the metal chelates and the stability decreased with increasing temperature. At different temperatures (300, 310, 320 and 330 ± 0.1 K), the thermodynamic parameters *(*$\Delta^{\ddagger}G$, $\Delta^{\ddagger}H$ and $\Delta^{\ddagger}S$) of the formed species were calculated from the stability constants.

Keywords: pH-Metric titrations, Metal chelates, Stability constant, Thermodynamic parameters.

INTRODUCTION

The transition metal(II) ions play a vital role in complexation with nucleus bases and peptides since metal(II) ions which act as cofactors in the enzymatic regulation reactions [1] and as models for transition metal–based chemical nucleases in Nucleic acid and Medicinal chemistry [2, 3]. The chelates derived from nitrogen and oxygen donor atoms with transition metal (II) ions take a crucial place in biological, analytical, industrial and therapeutic applications [4]. The interactions of substituted pyrimidine nucleus bases and peptides with transition metal (II) ions are of considerable biological interest since such mixed chelation in biological fluids of living systems shows a sturdy relation between chelation therapy and pH-metry [5]. Thus, classical coordination and bioinorganic chemistry reaches to modern organometallic and bioorganometallic chemistry [6]. The interaction of a substituted pyrimidine nucleus base (A) with Zn(II) metal ion can be interpreted satisfactorily in terms of the equilibria for the 1:5 stoichiometry;

$$Zn^{2+} + A^{-} \rightleftharpoons ZnA^{+}, \quad ZnA^{+} + A^{-} \rightleftharpoons ZnA_2$$

where A = Primary Ligand

The Zn(II)–amino acids (1:5) systems indicate the following equilibria, for which the constants have been measured.

$$Zn^{2+} + B \rightleftharpoons ZnB^{2+}, \quad ZnB^{2+} \rightleftharpoons ZnB^{+} + H^{+}, \quad ZnB^{2+} + B \rightleftharpoons ZnB_2^{2+}$$

$$Zn^{2+} + B^{*-} \rightleftharpoons ZnB^{2+}, \quad ZnB^{2+} \rightleftharpoons ZnB^{+} + H^{+}, \quad Zn^{2+} + B^{-} \rightleftharpoons ZnB^{+}$$

$$ZnB^{+} \rightleftharpoons ZnB + H^{+} \quad \text{where B = Secondary Ligand}$$

The metal transport is possible in biofluids due to the extra stability of the formed mixed chelates [5]. The strong affinity of the metal (II) ions to ligands with nitrogen donor atoms makes peptides interesting targets for chelate formation research [7–9]. In view of this, the present work explores the stability constant and thermodynamic parameters *(*$\Delta^{\ddagger}G$, $\Delta^{\ddagger}H$ and $\Delta^{\ddagger}S$) at 300, 310, 320 and 330 K studies on Zn(II)–5-FU(A)–gly/ala/val/phe(B) metal chelates.

EXPERIMENTAL

Materials

All the chemicals were of extra pure Sigma Aldrich and Fluka (Puriss) products. The solvents used for the physical measurements are of AR grade and are purified by standard methods [10]. Carbonate free sodium hydroxide (NaOH) solution (0.3 M) was prepared from a Titrisol solution (ClNa) (Merck) and its concentration was standardized against standard potassium hydrogen phthalate ($KC_8H_5O_4$) solution [11]. Zinc (II) perchlorate: $Zn(ClO_4)_2$ solution was prepared and estimated. Doubly distilled CO_2 free water (H_2O) with a specific conductance equal to (1.81 ± 0.1 Λ^{-1} cm^{-1}) was used for the preparation of the solution.

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pH-metric and mixed equilibria studies

Multiple pH-metric titrations were carried out for each system as per the previously reported procedure [12–14] and the measurements were restricted within the pH range 2.5–9.0. Above these pH values, the systems undergo hydroxylation to form a precipitate of [$Zn(OH)_2$] which interferes with the measurements. The pH-metric titration curves are shown in Fig. (1).

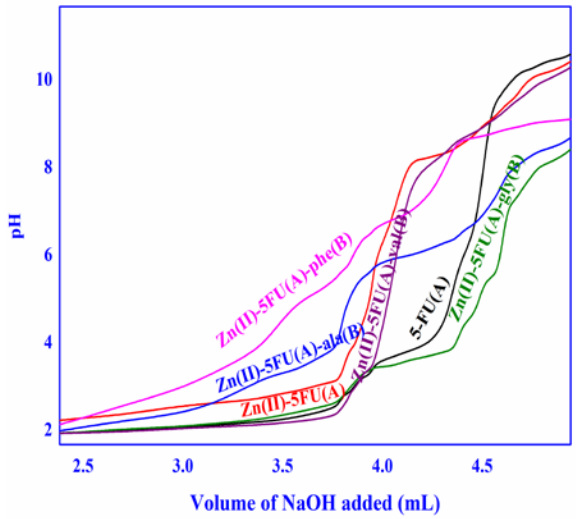

Fig. 1. pH-metric titration curves of 5-FU (0.15 M), Zn(II)–5-FU(A) (1:5), Zn(II)–5- FU(A)amino acids(B) (1:1:1) systems at 310 K and I = 0.15 M (where I = Ionic strength).

These pH-metric data were analysed with the aid of SCOGS (Stability Constants of Generalized Species) computer program [11–14]. The present experimental pH readings were corrected by the Van Uitert and Hass relation [15]. The concentration distribution curves of various metal speciations in solution were analysed by HySS (Hyperquad Simulation and Speciation) program using the calculated stability constant values [16].

RESULTS AND DISCUSSION

pH-metric and mixed equilibria studies

The binary chelate formation of Zn(II) with 5-FU(A) in 1:5 stoichiometry and calculated stability constant values for the binary systems have been reported [12, 13]. In addition to various binary species HA(5-FU–H), ZnA_2(Zn–5-FU_2), HB(gly/ala/val/phe–H), H_2B(H–gly/ala/val/phe–H), ZnB (Zn–gly/ala/val/phe) and ZnB_2(Zn–gly_2/ala_2/val_2/phe_2), the formation of metal chelates of stoichiometry MAB(Zn–5-FU–gly/ala/val/phe) and MAB_2 (Zn–5-FU–gly_2/ala_2/val_2/phe_2) have also been detected pH-metrically. Above pH > 9.0, the systems undergo hydroxylation, forming hydroxo species [$Zn(OH)_2$].

The $\log K^{Zn}_{ZnAB}$ / $\log K^{Zn}_{ZnAB_2}$ values obtained at different temperatures in Zn(II)–5-FU(A)–gly/ala/val/phe(B) systems are given in Table (1) and are compared favourably with $\log K^{Zn}_{ZnA}$ value in Zn(II)–5-FU(A) binary systems. This shows that, the ligand 5-FU(A) in mixed ligand system binds with a Zn(II) ion in a manner similar to its binding in their binary ZnA system *i.e.*, the ligand 5-FU(A) acts as bidentate and binds through deprotonated N_3 and C_4 carbonyl oxygen atoms. Again, $\log K^{Zn}_{ZnB}$ / $\log K^{Zn}_{ZnB_2}$ values in ZnAB/$ZnAB_2$ systems compare favourably with $\log K^{Zn}_{ZnB}$ / $\log K^{Zn}_{ZnB_2}$ values in Zn(II)–amino acid systems and this shows that the binding mode of secondary amino acid ligands(B) in mixed chelate ZnAB/$ZnAB_2$ species is similar to its bidentate binding mode in the corresponding binary systems. Thus, the four coordinating positions in Zn (II)–5-FU(A)–gly/ala/val/phe(B) systems would be occupied by the bidentate binding of 5-FU(A) and amino acids(B) respectively. The remaining positions in ZnAB systems would be occupied by two water molecules to form a stable hexa coordinated environment Fig. (2).

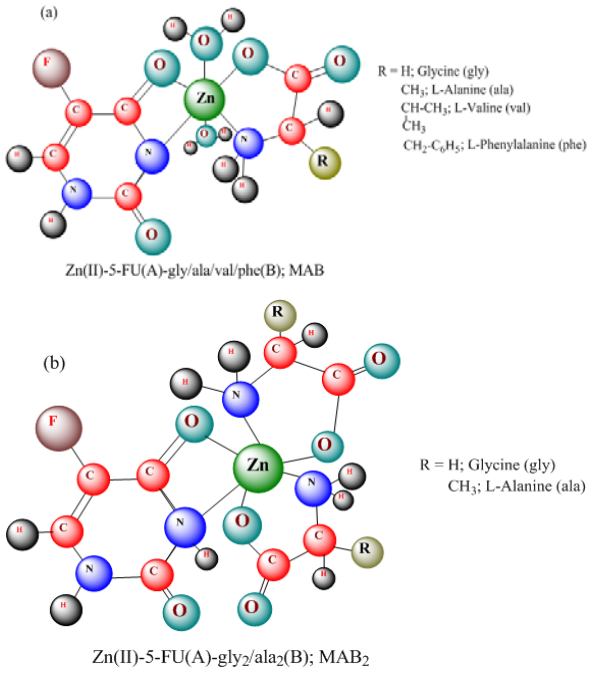

Fig. 2. The proposed structures of (a) MAB and (b) MAB_2 species as solution states.

The binding of amino acid(B) ligands in ZnAB species in the presence of 5-FU(A) ligand involves a stable chelate ring. This is also confirmed from the plot of $\log K^{Zn}_{ZnA}$ / $\log K^{ZnB}_{ZnAB}$ *vs. pKa* values of 5-FU(A) from which it is evident that all the points due to the binary species fit on a straight line [17]. Also, the points corresponding to the ZnAB metal chelates form a straight line parallel to those of the binary species which is shown in Fig. (3).

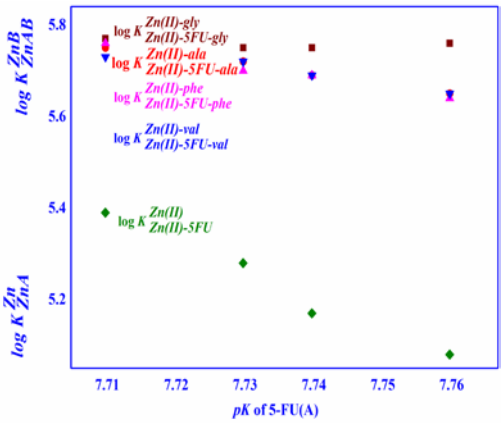

Fig. 3. The plot between $\log K^{M}_{MA}$ / $\log K^{MB}_{MAB}$ *vs. pK* values of primary ligand 5-FU(A) at different temperatures

From Table (1), the overall stability of ZnAB metal chelates follows the stability order as: Zn (II)–5-FU–gly > Zn(II)– 5-FU–ala > Zn(II)–5-FU–val > Zn(II)–5-FU–phe. From Table (1), the calculated $\Delta \log K_{ZnAB}$ values for all these systems are more positive compared to the statistically expected value [18] which indicates that the marked stabilities of metal chelates as compared to their binary analogues.

The calculated disproportionation parameter ($\log X$) values for all the species are higher than 2.28 (statistically expected value = + 0.6) which suggest that the preference for the formation of ZnAB metal chelates when compared to the formation of corresponding binary ZnA_2/ZnB_2 species *i.e.*, the inter–ligand and electronic interactions are present in the metal chelates [19].

The $\log X$ values can only indicate the coordination tendency of the secondary ligand towards binary ZnA species, but it fails to explain the stabilizing order of metal–ligand bonds after the species formation. Hence, a new parameter $\log X'$ is considered and the observed $\log X'$ values are greater than 0.3. It suggests that ZnA and ZnB bonds in mixed chelate systems are stronger than those of binary systems. Also, the percentage relative stabilization *% R.S.* parameter indicates a noticeable stabilization is present in the ZnAB metal chelates than the corresponding binary species [20].

Stability and structure of MAB_2 species

The $ZnAB_2$ species for the Zn(II)–5-FU(A)–gly/ala(B) systems, the solvent water molecules of ZnAB species would be replaced by a second molecule of glycine/alanine ligands(B). The obtained $\log K^{ZnB_2}_{ZnAB_2}$ / $\log K^{ZnA}_{ZnAB_2}$ values in Zn(II)–5-FU–gly/ala systems are comparable with $\log K^{Zn}_{ZnA}$ and $\log K^{ZnA}_{ZnB_2}$ values in the binary systems. The $ZnAB_2$ species in the Zn(II)–5-FU(A)–gly/ala(B) systems would be six coordinated due to the bidentate binding nature of one molecule of 5-FU(A) and two molecules of gly/ala(B) ligands respectively. The calculated $\Delta \log K_{ZnAB_2}$ values are more positive while compared to the statistically expected values indicating the enhanced stabilities for $ZnAB_2$ systems [19, 20].

Species distribution diagram

The speciation diagram for Zn(II) metal chelate systems, taken as a representative pyrimidine amino acid, is given in Fig. (4). The deprotonated Zn(II)–5-FU(A)–gly(B) species (M:A:B = 1:1:1) attains a maximum concentration of 61 % at pH 6.3. The log β value of this species is 10.50 at 310 K with a *% R.S.* value of 9.89. The species Zn(II)–5-FU(A)–ala(B) starts to form at pH ~3.4 and with increasing pH, its concentration increases reaching the maximum of 66% at a pH ~ 6.4. The MAB species of Zn(II)–5-FU(A)–val(B) and Zn(II)–5-FU(A)–phe(B) metal chelate systems were found with maximums of 63 % and 64 % at pH 7.1 and 6.4 respectively.

In addition, the $ZnAB_2$ species is formed with gly/ala(B) and the formation starts above a pH of 7.2. It has been found that their percentage of formation increases with the pH in the range 7.2–8.4 and reaches saturation values at only *ca.* 17.12–18.31 % of the total of Zn(II) ions.

Effect of temperature and thermodynamic parameters

Determination of the thermodynamic parameters ($\Delta^{\ddagger}G$, $\Delta^{\ddagger}H$ and $\Delta^{\ddagger}S$) relative to the formation of metal chelates for binary Zn(II) systems are given in Table (2) and are shown in Fig. (5).

Table 1. Stability constant and stabilization effects of the metal chelates for Zn(II)–5-FU(A)–gly, ala, val and phe(B) systems in an aqueous medium at different temperatures in I = 0.15 M ($NaClO_4$)

Parameters	Stability constant values at different temperature															
	300 K				310 K				320 K				330 K			
	gly	ala	val	phe	gly	ala	val	phe	gly	ala	val	phe	gly	ala	val	phe
$\log\beta_{ZnAB}$	10.63(4)	10.46(3)	10.16(7)	10.02(7)	10.50(3)	10.36(3)	10.06(3)	9.93(6)	10.38(4)	10.27(5)	9.97(7)	9.84(8)	10.29(6)	10.19(7)	9.87(4)	9.75(5)
$\log\beta_{ZnAB_2}$	14.91(5)	14.65(7)	--	--	14.71(6)	14.54(7)	--	--	14.56(5)	14.44(6)	--	--	14.40(6)	14.34(5)	--	--
$\log K^{ZnA}_{ZnAB}$	5.24	5.07	4.77	4.63	5.22	5.08	4.78	4.65	5.21	5.10	4.80	4.67	5.21	5.11	4.79	4.67
$\log K^{ZnB}_{ZnAB}$	5.76	5.65	5.64	5.65	5.75	5.69	5.69	5.69	5.75	5.72	5.70	5.72	5.77	5.75	5.76	5.73
$\log K^{ZnA}_{ZnAB_2}$	9.52	9.26	--	--	9.43	9.26	--	--	9.39	9.27	--	--	9.32	9.26	--	--
$\log K^{ZnB_2}_{ZnAB_2}$	5.93	5.82	--	--	5.85	5.80	--	--	5.84	5.78	--	--	5.80	5.75	--	--
$\log K^{ZnAB}_{ZnAB_2}$	4.28	4.19	--	--	4.21	4.18	--	--	4.18	4.17	--	--	4.11	4.15	--	--
$\Delta\log K_{ZnAB}$	0.37	0.26	0.25	0.26	0.47	0.41	0.41	0.41	0.58	0.55	0.53	0.55	0.69	0.67	0.68	0.65
$\Delta\log K_{ZnAB_2}$	0.54	0.43	--	--	0.57	0.52	--	--	0.67	0.61	--	--	0.72	0.67	--	--
$\log X_{Zn}$	2.59	2.40	2.32	2.28	2.60	2.44	2.41	2.38	2.63	2.47	2.48	2.44	2.70	2.51	2.54	2.49
$\log X'_{Zn}$	1.46	1.35	1.34	1.35	1.49	1.43	1.43	1.43	1.51	1.48	1.46	1.48	1.57	1.55	1.56	1.53
$\%RS$	7.60	5.41	5.53	5.95	9.89	8.71	9.38	9.67	12.53	12.09	12.41	13.35	15.27	15.09	16.55	16.17

Standard deviations are given in parentheses [Error limit: ± (0.02 – 0.08)

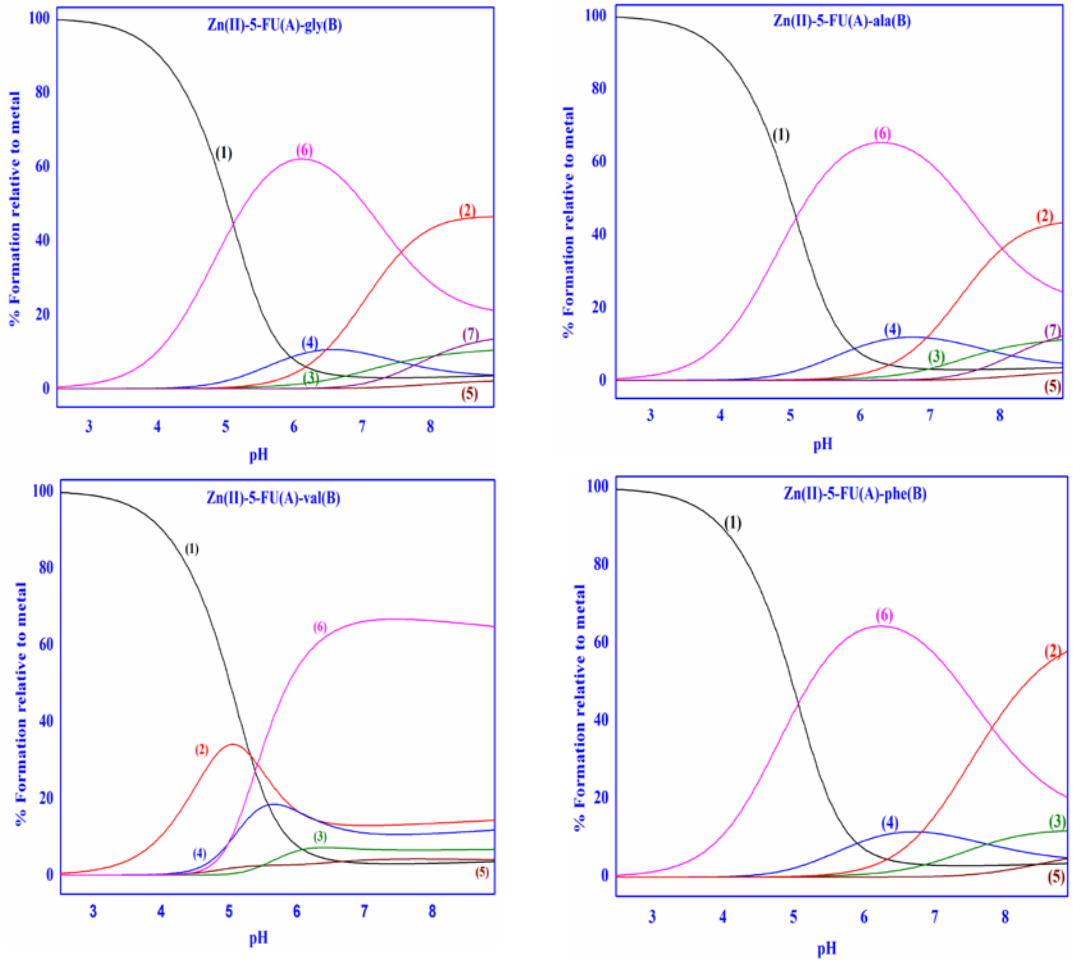

Fig. 4. Species distribution diagrams of Zn(II)–5-FU(A)–gly/ala/val/phe(B) chelates(1:1:1) at 300 K in aqueous medium (1) free Zn(II) ion, (2) Zn(II)–A, (3) Zn(II)–A_2, (4) Zn(II)–B, (5) Zn(II)–B_2, (6) Zn(II)–AB and (7) Zn(II)–AB_2 species.

Table 2. Thermodynamic parameters for binary systems of Zn(II)–5-FU(A) and Zn(II)–gly/ala/val/phe(B) and Zn(II)–5-FU(A)– gly/ala/val/phe(B) metal chelates.

System	Species	$-\Delta^{\ddagger}G$ (kJ mol^{-1}) Temperature (K)				$-\Delta^{\ddagger}H$ (kJ mol^{-1})	$\Delta^{\ddagger}S$ (J K^{-1} mol^{-1}) Temperature (K)			
		300	310	320	330		300	310	320	330
Zn(II)–5-FU(A)	HA	44.58	45.94	47.36	48.72	38.16	21.38	25.10	28.76	31.99
	H_2A	–	–	–	–	–	–	–	–	–
	ZnA	30.96	31.34	31.68	32.10	19.72	37.46	37.48	37.36	37.51
	ZnA_2	55.66	56.63	57.66	58.64	25.77	99.63	99.53	99.64	99.51
Zn(II)–gly(B)	HB	56.12	56.86	56.86	56.68	50.82	17.68	19.51	18.88	17.76
	H_2B	69.22	69.68	70.83	70.83	52.71	55.02	54.75	55.08	54.91
	ZnB	27.97	28.19	28.37	28.56	22.17	19.34	19.43	19.36	19.36
	ZnB_2	51.58	52.59	53.43	54.34	24.24	91.14	91.45	91.21	91.21
Zn(II)–ala(B)	HB	57.67	57.69	58.12	58.83	48.51	30.53	29.62	30.10	31.25
	H_2B	71.11	72.12	73.04	73.80	44.13	89.95	90.29	90.33	89.92
	ZnB	27.63	27.72	27.88	28.05	23.32	14.36	14.11	14.24	14.34
	ZnB_2	50.72	51.88	53.06	54.28	15.18	118.46	118.37	118.37	118.46
Zn(II)–val(B)	HB	58.07	58.41	59.13	59.58	42.86	50.70	50.14	50.82	50.67
	H_2B	72.72	73.90	74.57	75.57	45.09	92.12	92.94	92.13	92.38
	ZnB	25.76	25.94	26.16	25.97	25.77	0.64	0.54	1.22	0.60
	ZnB_2	47.73	48.49	49.32	50.04	24.45	77.61	77.56	77.72	77.55
Zn(II)–phe(B)	HB	54.51	54.73	54.90	55.48	45.38	30.42	30.14	29.73	30.58
	H_2B	68.70	69.27	70.34	71.21	42.51	87.30	86.32	86.97	86.97
	ZnB	25.10	25.17	25.24	25.40	22.19	9.70	9.60	9.54	9.72
	ZnB_2	46.36	47.13	47.98	48.84	19.51	89.48	89.09	88.95	88.88
Zn(II)–5-FU(A)–gly(B)	ZnAB	61.06	60.08	58.56	57.56	21.64	131.41	143.35	133.92	135.03
	$ZnAB_2$	85.65	84.15	83.11	75.07	31.86	179.28	245.47	169.11	174.74
Zn(II)–5-FU(A)–ala(B)	ZnAB	62.32	61.49	59.71	58.94	17.08	131.25	143.27	133.96	135.14
	$ZnAB_2$	87.31	86.30	87.73	82.01	19.51	178.88	215.46	173.11	162.11
Zn(II)–5-FU(A)–val(B)	ZnAB	63.60	62.93	61.08	60.29	18.19	131.13	243.27	134.87	135.02
Zn(II)–5-FU(A)–phe(B)	ZnAB	89.21	88.48	82.36	72.60	17.05	179.22	215.51	178.90	188.44

The calculated $\Delta^{\ddagger}H$ and $\Delta^{\ddagger}S$ values can be considered as the sum of two contributions such as the release of solvent (H_2O) molecules and metal–ligand bond formation. From Table (2), the abnormal high positive $\Delta^{\ddagger}S$ values of the binary systems are consistent with the hypothesis that a large number of water molecules are released upon complexation [19, 20].

The thermodynamic parameters for all the mixed ligand ZnAB and $ZnAB_2$ systems are given in Table (2). A negative $\Delta^{\ddagger}G$ values for all these complexes suggest the complexation process is spontaneous [17–20]. The negative $\Delta^{\ddagger}H$ values show that the chelation process is exothermic and the complexation process favorable at very low temperature. All the species show positive $\Delta^{\ddagger}S$ values which suggest that the complexation of the 5-FU(A) ligand with a Zn(II) ion in the presence of amino acid(B) ligands is entropically favorable.

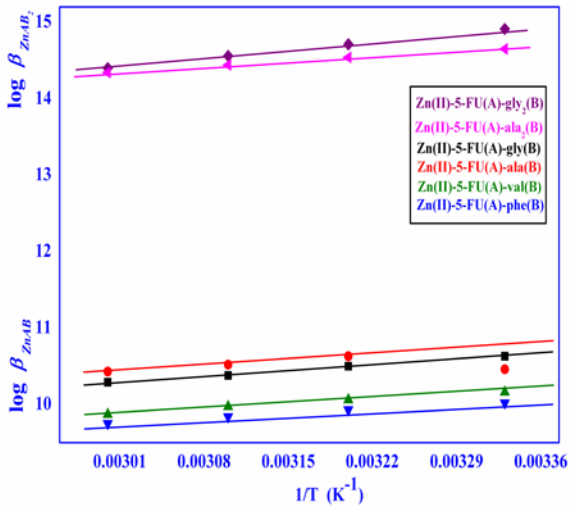

Fig. 5. The Van't Hoff plot of $\log \beta_{MAB}$ values of Zn(II)–5-FU–gly/ala/val/phe(B) and $\log \beta_{MAB_2}$ values of Zn(II)–5-FU(A)–gly_2/ala_2 systems *vs*. 1/T for MAB and MAB_2 mixed chelates.

Electronic absorption spectra

The diamagnetic nature of the Zn(II) ion does not show any d–d transition in the visible region. However, the Zn(II)–5-FU(A)–gly, ala, val and phe(B) metal chelates show only one band at 26381 (379 nm), 26246 (381 nm), 26455 (378 nm) and 26372 cm^{-1} (379 nm) respectively in the UV region due to L→M charge transfer (LMCT) transition, which corresponds to a six–coordinated distorted octahedral environment around the Zn(II) ion with two water molecules present in the z–axes of the cartesian coordinate [21].

CONCLUSION

The solution equilibria studies of Zn(II)–5-FU(A)–gly/ala/val/phe(B) metal chelates in an aqueous medium at different temperatures (300, 310, 320 and 330 ± 0.1 K) have been studied at a constant ionic strength (I = 0.15 M). The percentage distribution of various binary and metal chelate species in the solution state on the basis of various equilibrium data have shown that ZnAB metal chelates have a higher stability than other species formed. Moreover, the amino acids gly(B) and ala(B) have found to form moderately stable $ZnAB_2$ species in addition to the most stable ZnAB species. The thermodynamic factors such as $\Delta^{\ddagger}G$, $\Delta^{\ddagger}H$ *and* $\Delta^{\ddagger}S$, and the binding nature of ligands in terms of $\Delta \log K$ have also been determined along with the $\log X$ statistical parameter.

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ИЗСЛЕДВАНИЯ НА СТАБИЛНОСТТА НА РАВНОВЕСИЕТО В РАЗТВОРИ НА Zn(II)-КОМПЛЕКСИ С ПИРИМИДИНОВИ БАЗИ

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(Резюме)

Използвано е pH-метрично титруване за определяне на активността и стабилността на метални хелати на заместени пиримидинови бази т.е. 5-флуороацил(5-FU: A) и някои есенциални пептидни компоненти, т.е. аминокиселини*:* глицин (gly; B), L-аланин (ala; B), L-валин (val; B), L-фенилаланин (phe; B). От данните от титруването ние получихме задоволителни стойности за стабилитетните константи на метални хелати, като стабилността намаляваше с повишаването на температурата. От тези стабилитетни константи са изчислени термодинамичните параметри на изследваните съединения *($\Delta^{\ddagger}G$, $\Delta^{\ddagger}H$* и $\Delta^{\ddagger}S$) при различни температури (300, 310, 320 и 330 ± 0.1 K).