Polymer Complexes. XXXI. Potentiometric and Thermodynamic Studies of 2-Acrylamido-2-amino-3-hydroxy pyridine and Its Metal Complexes

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ABSTRACT: Proton ligand dissociation and metal ligand stability constants of 2-acrylamido-2-amino-3-hydroxy pyridine (AAHP) with some transition metal ions in 0.1 *M* KCl and 50% (v/v) ethanol–water mixture were calculated potentiometrically. In the presence of 2,2′-azobisisobutyronitrile as initiator the proton-polymeric ligand dissociation and metal polymeric ligand stability constants were also evaluated. The influence of temperature on the dissociation of AAHP and the stability of its metal complexes in the monomeric and polymeric forms were critically studied. On the basis of the thermodynamic functions, the dissociation process of AAHP was found nonspontaneous, endothermic, and entropically unfavorable, although the formed metal complexes showed spontaneous, endothermic, and entropically favorable behavior. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2552–2557, 2000

Key words: 2-acrylamido-2-amino-3-hydroxy pyridine; dissociation constants; stability constants; thermodynamic parameters

INTRODUCTION

In recent years considerable interest has been focused in the aqueous chemistry of organometallic in the view of environmental and toxicological sides.[1] In solution, polymer–metal complexes form microheterogeneous regions occupied by polymer backbone in the bulk solution.[2,3] Recently, some polymer–metal complexes in solid form were critically investigated by El-Sonbati and El-Bindary.[4–6] Therefore, the goal of the present work was focused on studying the dissociation constants of AAHP and the stability constants for its metal complexes with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, La^{3+}, Ce^{3+}, UO_2^{2+} and Th^{4+} in monomeric and polymeric forms, using potentiometric and thermodynamic measurements.

EXPERIMENTAL

Preparation of the Monomer

The monomer ligand (AAHP) was prepared by El-Sonbati and coworkers.[5,6]
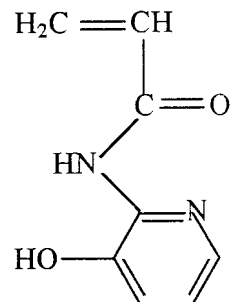
Reagents and Materials

The monomeric ligand solution (2×10^{-3} *M*) was prepared by dissolving an accurate weight of the

Table I   Thermodynamic Functions for the Dissociation of AAHP and PAAHP in 50% (v/v) Ethanol–Water Mixture in the Presence of 0.1M KCl at Different Temperatures

| Compound | Temp (K) | Dissociation Constant | | Free Energy Change (kJ mol^{-1}) | | Enthalpy Change (kJ mol^{-1}) | | Entropy Change (J mol^{-1} K^{-1}) | |
		pK_1^H	pK_2^H	ΔG_1	ΔG_2	ΔH_1	ΔH_2	$-\Delta S_1$	$-\Delta S_2$
AAHP	298	7.95	5.90	45.36	33.66			79.22	31.20
	308	7.82	5.75	46.12	33.91	21.75	24.36	79.12	31.01
	318	7.70	5.62	46.88	34.22			79.02	31.00
PAAHP	298	8.10	6.30	46.22	35.95			70.43	47.65
	308	7.96	6.18	46.94	36.45	25.23	21.75	70.48	47.72
	318	7.81	6.05	47.55	36.84			70.18	47.45

The values given present an average of three measurements.

solid in ethanol (AnalaR). Metal ion solutions (2 × 10^{-4} M) also were prepared from BDH Chemicals (Poole, UK) in doubly distilled water and standardized with EDTA.[7] The initiator, 2,2′-azobisisobutyronitrile (AIBN; 2 × 10^{-3} M), was prepared by dissolving an accurate weight of the solid in ethanol (AnalaR). Solutions of 1 × 10^{-3} M HCl and 1M KCl were prepared in doubly distilled water. A carbonate-free sodium hydroxide solution in 50% (v/v) ethanol–water mixture was used as titrant and standardized against standard oxalic acid.

Potentiometric Measurements

The apparatus and methods of calculation were the same as previously reported.[8–10] The mixtures: (i) 5 mL 1 × 10^{-3} M HCl + 5 mL 1 M KCl + 25 mL ethanol; (ii) 5 mL 1 × 10^{-3} M HCl + 5 mL 1 M KCl + 25 mL ethanol + 5 mL 2 × 10^{-3} M AAHP; and (iii) 5 mL 1 × 10^{-3} M HCl + 5 mL 1 M KCl + 25 mL ethanol + 5 mL 2 × 10^{-3} M AAHP + 5 mL 2 × 10^{-4} M metal salt were prepared and titrated potentiometrically with 4 × 10^{-3} M NaOH in 50% (v/v) ethanol–water mixture at 298, 308, and 318 K, respectively.

In each solution mixture, the volume was made up to 50 mL with doubly distilled water. The titrations also were carried out in the presence of 5 mL of AIBN (2 × 10^{-3} M) as initiator for the polymerization step. A constant temperature was maintained ±0.05 K using ultrathermostat (Gallenkamp thermo stirrer 85). The pH meter readings in 50% (v/v) ethanol–water mixture were corrected according to the Van Uitert and Hass relation.[11]

RESULTS AND DISCUSSION

Potentiometric Studies

Proton–Ligand Stability Constants

The average number of protons associated with the ligand in monomeric (AAHP) and in polymeric (PAAHP) form at different pH values, $\bar{n}_A$, were calculated from the titration curves. The formation curves ($\bar{n}_A$ vs. pH) for the proton–ligand systems were found in the range of 0 to 2 in the $\bar{n}_A$ scale. Thus, each of AAHP and PAAHP has two dissociable protons in the enolized hydrogen ion of the hydroxyl group in the pyridine ring and the amidic proton, CONH.
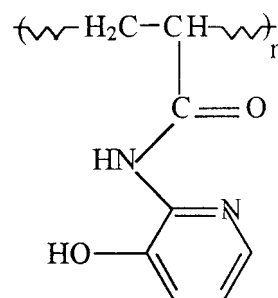
Different computational methods[12] also were used to evaluate the dissociation constants, and the data are summarized in Table I.

The values of the acidic character of PAAHP were found lower than that of AAHP values (Table I). The vinyl group (H$_2$C=CH) in the monomeric form (AAHP) decrease the electron density, and hence reduce the N–H and O–H bond strength.[8,13,14] On the other hand, the absence of

Table II   Stepwise Stability Constants for ML and ML$_2$ Complexes of AAHP in 50% (v/v) Ethanol–Water Mixture in Presence of 0.1M KCl at Different Temperatures

	298 K				308 K				318 K			
M^{n+}	$\log K_1$	$\log K_2$	$\log K_\beta$	$\log K_1/$ $\log K_2$	$\log K_1$	$\log K_2$	$\log K_\beta$	$\log K_1/$ $\log K_2$	$\log K_1$	$\log K_2$	$\log K_\beta$	$\log K_1/$ $\log K_2$
Mn^{2+}	5.20	3.55	8.75	1.46	5.35	3.78	9.13	1.42	5.51	4.01	9.52	1.37
Co^{2+}	5.30	3.73	9.03	1.42	5.48	3.94	9.42	1.39	5.66	4.16	9.82	1.36
Ni^{2+}	5.53	3.90	9.43	1.42	5.76	4.12	9.88	1.40	5.98	4.34	10.32	1.38
Cu^{2+}	5.70	4.14	9.84	1.38	5.92	4.33	10.25	1.37	6.13	4.35	10.66	1.35
La^{3+}	5.75	4.24	9.99	1.36	5.97	4.40	10.37	1.36	6.20	4.56	10.76	1.36
Ce^{3+}	5.83	4.30	10.13	1.36	6.04	4.49	10.53	1.35	6.25	4.68	10.93	1.34
UO_2^{2+}	5.90	4.45	10.35	1.33	6.24	4.71	10.95	1.32	6.58	4.97	11.55	1.32
Th^{4+}	6.20	4.63	10.83	1.34	6.44	4.90	11.34	1.31	6.68	5.19	11.87	1.29

The values given present an average of three measurements.

vinyl group in polymeric form (PAAHP) retard the removal of the ligand protons and increase the basicity (higher pK^H values).

Metal–Ligand Stability Constants

The formation curves of the metal complexes of AAHP and PAAHP, attached per metal ion ($\bar{n}$) versus the free ligand exponent (pL) were calculated by the Irving and Rossotti method.[15] The curves were analyzed, and the successive stability constants were determined using different computational methods.[16,17] The values of the stability constants ($\log K_1$, $\log K_2$, and $\log K_\beta$) and the ratio $\log K_1/\log K_2$ are summarized in Tables II and III. The following general remarks can be achieved:

(i) The maximum $\bar{n}$ values in all cases were found to be $\cong 2$, revealing that both ML and ML$_2$ types of complexes are formed in solution.[18]

(ii) No precipitate was observed in the titration vessel, indicating that the formation of metal hydroxide is excluded.[3]

(iii) The stability constants of PAAHP in metal complexes are higher than the corresponding metal complexes of AAHP. This is quite reasonable because the ligand in polymeric form is considered as a better complexing agent.[2,14]

(iv) The stability constants of the metal complexes of AAHP and PAAHP following the sequence:

$$Th^{4+} > UO_2^{2+} > Ce^{3+} > La^{3+}$$
$$> Cu^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+}$$
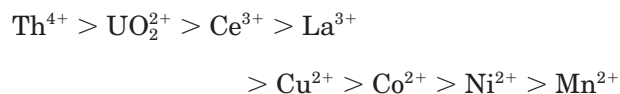
The higher values of the stability constants of the Th^{4+} complexes is expected on the basis of the

Table III   Stepwise Stability Constants for ML and ML$_2$ Complexes of PAAHP in 50% (v/v) Ethanol–Water Mixture in the Presence of 0.1M KCl at Different Temperatures

	298 K				308 K				318 K			
M^{n+}	$\log K_1$	$\log K_2$	$\log K_\beta$	$\log K_1/$ $\log K_2$	$\log K_1$	$\log K_2$	$\log K_\beta$	$\log K_1/$ $\log K_2$	$\log K_1$	$\log K_2$	$\log K_\beta$	$\log K_1/$ $\log K_2$
Mn^{2+}	7.00	5.31	12.31	1.32	7.22	5.50	12.72	1.31	7.43	5.70	13.13	1.30
Co^{2+}	7.11	5.55	12.66	1.28	7.31	5.77	13.08	1.27	7.50	5.96	13.46	1.26
Ni^{2+}	7.31	5.70	13.01	1.28	7.50	5.91	13.41	1.27	7.68	6.11	13.79	1.26
Cu^{2+}	7.49	5.95	13.44	1.26	7.72	6.18	13.90	1.25	7.94	6.41	14.35	1.24
La^{3+}	7.65	6.02	13.67	1.27	7.85	6.20	14.05	1.27	8.04	6.39	14.43	1.26
Ce^{3+}	7.70	6.07	13.77	1.27	7.91	6.29	14.20	1.26	8.10	6.50	14.60	1.25
UO_2^{2+}	7.80	6.19	13.99	1.26	8.04	6.41	14.45	1.25	8.28	6.62	14.90	1.25
Th^{4+}	7.98	6.35	14.33	1.26	8.19	6.52	14.71	1.26	8.39	6.69	15.08	1.25

The values given present an average of three measurements.

Table IV   Thermodynamic Functions for ML and ML$_2$ Complexes of AAHP in 50% (v/v) Ethanol–Water Mixture in the Presence of 0.1M KCl

M^{n+}	Temp (K)	Free Energy Change (kJ mol^{-1})			Enthalpy Change (kJ mol^{-1})			Entropy Change (J mol^{-1} K^{-1})		
		$-\Delta G_1$	$-\Delta G_2$	$-\Delta G_\beta$	ΔH_1	ΔH_2	ΔH_β	ΔS_1	ΔS_2	ΔS_β
Mn^{2+}	298	29.67	20.25	49.92				190.10	202.28	392.38
	308	31.55	22.29	53.84	26.98	40.03	67.01	190.03	202.33	392.36
	318	33.54	24.41	57.95				190.30	202.64	392.94
Co^{2+}	298	30.24	21.28	51.52				206.61	196.97	403.58
	308	32.31	23.23	55.54	31.33	37.42	68.75	206.62	196.91	403.53
	318	34.46	25.32	59.78				206.88	197.29	404.17
Ni^{2+}	298	31.55	22.25	53.80				237.28	203.15	440.43
	308	33.96	24.29	58.25	39.16	38.29	77.45	237.40	203.18	440.58
	318	36.41	26.42	62.83				237.64	203.49	441.13
Cu^{2+}	298	32.52	23.62	56.14				234.69	193.15	427.84
	308	34.91	25.53	60.44	37.42	33.94	71.36	234.83	193.08	427.91
	318	37.32	27.58	64.90				235.03	193.45	428.48
La^{3+}	298	32.80	24.19	56.99				241.47	174.63	416.10
	308	35.20	25.94	61.14	39.16	27.85	67.01	241.42	174.64	416.06
	318	37.75	27.76	65.51				241.85	174.87	416.72
Ce^{3+}	298	33.26	24.53	57.79				234.26	193.28	427.54
	308	35.61	26.47	62.08	36.55	33.07	69.62	234.28	193.31	427.59
	318	38.05	28.49	66.54				234.59	193.58	428.17
UO$_2^{2+}$	298	33.66	25.39	59.05				311.54	237.04	548.58
	308	36.79	27.77	64.56	59.18	45.25	104.43	311.59	237.07	548.66
	318	40.06	30.26	70.32				312.07	237.45	549.52
Th^{4+}	298	35.37	26.41	61.78				258.85	252.14	510.99
	308	37.97	28.89	66.86	41.77	48.73	90.49	258.89	252.01	510.90
	318	40.67	31.60	72.27				259.24	252.61	511.85

charge and ionization potential of the Th^{4+} ion in the octahedral field environment.

Effect of Temperature

The dissociation constants (pK^H) for AAHP and PAAHP as well as their stability constants of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, La^{3+}, Ce^{3+}, UO$_2^{2+}$ and Th^{4+} complexes have been evaluated at 298, 308 and 318 K (Tables I, IV, V). The enthalpy change (ΔH) for the dissociation and complexation process was calculated from the slope of the plot (pK^H or log K vs. 1/T). From the free energy change (ΔG) and (ΔH) values, one can deduce the entropy change (ΔS) using the well-known relationships (1) and (2):

$$\Delta G = -2.303 \, RT \log K = 2.303 \, RT \, pK \quad (1)$$

$$\Delta S = (\Delta H - \Delta G)/T \quad (2)$$

The thermodynamic parameters of the dissociation process of AAHP and PAAHP also are sum-

marized in Table I. The data reveal the following: (i) The values decrease with increasing temperature, confirming increasing of acidity with increasing temperature; (ii) Based on the positive values of ΔH, the dissociation process of AAHP and PAAHP is accompanied by adsorption of heat, and the process is endothermic; (iii) A large positive value of ΔG, indicating that the dissociation process is not spontaneous; and (iv) A negative value of ΔS is obtained as a result of solvation processes.

The thermodynamic parameters of the stepwise stability constants of AAHP and PAAHP complexes are also given in Tables IV and V. The divalent metal ions exist in solution in a hydrated octahedral form, where the ΔH and ΔS represent the sum of (i) release of H$_2$O molecules, and (ii) metal-ligand bond formation.

The metal ions in aqueous solution and the orientation of water molecules around them during complex formation process between the oppositely charged ions (ligand L^{-2} and metal M^{n+})

Table V   Thermodynamic Functions for ML and ML$_2$ Complexes of PAAHP in 50% (v/v) Ethanol–Water Mixture in the Presence of 0.1M KCl

M^{n+}	Temp (K)	Free Energy Change (kJ mol^{-1})			Enthalpy Change (kJ mol^{-1})			Entropy Change (J mol^{-1} K^{-1})		
		$-\Delta G_1$	$-\Delta G_2$	$-\Delta G_\beta$	ΔH_1	ΔH_2	ΔH_β	ΔS_1	ΔS_2	ΔS_β
Mn^{2+}	298	39.94	30.30	70.24				259.59	215.57	475.16
	308	42.57	32.43	75.00	37.42	33.94	71.36	259.70	215.49	475.19
	318	45.24	34.70	79.94				259.93	215.85	475.78
Co^{2+}	298	40.56	31.66	72.22				250.00	225.97	475.97
	308	43.10	33.61	76.71	33.94	35.68	69.62	250.12	224.97	475.09
	318	45.67	36.30	81.97				250.34	226.35	476.69
Ni^{2+}	298	41.70	32.52	74.22				247.99	228.86	476.85
	308	44.22	34.85	79.07	32.20	35.68	67.88	248.11	228.99	477.10
	318	46.76	37.20	83.96				248.30	229.18	477.48
Cu^{2+}	298	42.73	33.95	76.68				273.80	248.25	522.05
	308	45.52	36.44	81.96	39.16	40.03	79.19	274.93	248.27	523.20
	318	48.34	39.03	87.37				275.15	248.61	523.76
La^{3+}	298	43.64	34.35	77.99				260.33	223.32	483.65
	308	46.29	36.56	82.85	33.94	32.20	66.14	260.48	223.25	483.73
	318	48.95	38.91	87.86				260.66	223.61	787.27
Ce^{3+}	298	43.43	34.74	78.67				264.22	242.14	506.36
	308	46.64	37.09	83.73	34.81	37.42	72.23	264.44	241.91	506.35
	318	49.32	39.57	88.89				264.55	242.10	506.65
UO_2^{2+}	298	44.50	35.32	79.82				289.50	244.09	533.59
	308	47.41	37.80	85.21	41.77	37.42	79.19	289.54	244.22	533.76
	318	50.41	40.30	90.71				289.87	244.40	534.27
Th^{4+}	298	45.53	36.23	81.76				272.51	220.87	493.38
	308	48.29	38.45	86.74	35.68	29.59	65.27	272.62	220.90	493.52
	318	51.08	40.73	91.81				272.83	221.13	493.96

leads to the breakdown of metal–water arrangement, resulting in a positive entropy and enthalpy changes.[19] Thus, examination of the values of ΔG, ΔH, and ΔS for the formed metal complexes shows that (i) The stepwise stability constants log K_1 and log K_2 for AAHP and PAAHP complexes increased with increasing temperature in the case of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, La^{3+}, Ce^{3+}, UO_2^{2+}, and Th^{4+}; (ii) The negative values of ΔG for the complexation process of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, La^{3+}, Ce^{3+}, UO_2^{2+}, and Th^{4+} with AAHP and PAAHP suggests a spontaneous nature of such process; (iii) The ΔH values are positive for the complexation process of AAHP and PAAHP with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, La^{3+}, Ce^{3+}, UO_2^{2+} and Th^{4+}, suggesting an endothermic process that is favorable at higher temperatures; and (iv) The positive values of ΔS for the complexation process of AAHP and PAAHP with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, La^{3+}, Ce^{3+}, UO_2^{2+} and Th^{4+}, confirming that the complex formation process is entropically favorable.

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