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STABILITY CONSTANTS OF POLYMERIC COMPLEXES

تعيين ثوابت المتراكبات المتبلمرة

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خلاصة:

يحتوى هذا البحث على دراسة ثوابت الاتزان للعناصر Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} مع مركب أكريلونيتريل باستخدام طريقة معايرة الجهد. ووجد أن قيم هذه الثوابت أعلى في حالة البوليمر. وقد تم دراسة تعيين بعض ثوابت الديناميكا الحرارية لهذه المتراكبات ومناقشتها.

ABSTRACT

Proton-monomeric ligand dissociation and metal-monomeric ligand stability constants of Acrylonitrile (AN) with some transition metal ions were calculated potentiometrically in 0.1 M KCl and 50% (v/v) ethanol-water mixture. Also, in the presence of 2,2'-Azobisisobutyronitrile as initiator the proton-polymeric ligand dissociation and metal-polymeric ligand stability constants were calculated. The effect of temperature on the dissociation of (AN) and the stability of its formed complexes were studied in monomeric and polymeric forms. The corresponding thermodynamic functions were derived and discussed. The dissociation process is non-spontaneous, endothermic and entropically unfavorable. The formation of the metal complexes has been found to be spontaneous, endothermic and entropically favorable.

Keywords: Acrylonitrile, dissociation constant, stability constants and thermodynamic parameters.

INTRODUCTION

Polymer-metal complexes are composed of polymeric ligand and metal ions. Polymer-metal complexes show unique characteristic in absorption spectrum, coordination structure, stability, redox reactions, catalytic activities, electrochemical reactions and other areas compared

to those of corresponding low molecular metal complexes. Complexations of polymeric ligand with metal ions as well as ligand substitution reaction of polymer-metal complexes are utilized to separate metal ions and/or small molecules Diab et al [4], El-Bindary et al[5] and El-Sonbati et al [6] studied the polymer –metal complexes of vinyl derivative... The stability of these polymer-metal complexes was studied. The aim of this work was to assess the metal binding properties of AN towards some metal ions in aqueous solution. We report herein the dissociation constant of AN and the stability constants for its complexes with Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} in monomeric and polymeric forms, which was carried out by potentiometric studies. Furthermore, the corresponding thermodynamic functions of dissociation and Complexation are derived and discussed.

EXPERIMENTAL

Reagents and Materials

The monomeric ligand solution (2×10^{-3} M) was prepared by dissolving a known volume of the Acrylonitrile (Aldrich) in ethanol (AnalaR). Metal ion solutions (2×10^{-4} M) were also prepared from BDH chemicals in doubly distilled water and standardized with EDTA [9]. Solution of 2,2'-Azobisisobutyronitrile (AIBN) as initiator (2×10^{-3} M) was prepared by dissolving the accurate weight of the solid in ethanol (AnalaR). Solutions of 2×10^{-3} M HCl and 1 M KCl were also 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 AnalaR oxalic acid.

Potentiometric Measurements

The apparatus, general conditions and methods of calculation were the same as outlined by other authors [8,10,11]. The following

mixtures were prepared and titrated potentiometrically against standard 5×10^{-3} M NaOH in 50% (v/v) ethanol-water mixture at 308, 318 and 328 K, respectively.

- (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 + 20 ml ethanol + 5 ml 1×10^{-3} M AN;
- (iii) 5 ml 1×10^{-3} M HCl + 5 ml 1 M KCl + 20 ml ethanol + 5 ml 1×10^{-3} M AN + 5 ml 1×10^{-4} M metal salt.

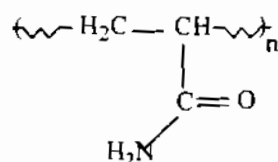
For each mixture, the volume was made up to 50 ml with doubly distilled water before titration. These titrations were repeated in the presence of 5 ml 1×10^{-3} M AIBN as initiator for the polymerization. A constant temperature was maintained to ± 0.05 K by using an ultrathermostat (Gallenkamp thermo stirrer 85). The pH-meter readings in 50% (v/v) ethanol-water mixture are corrected according to the Van Uiter and Hass relation [12].

RESULTS AND DISCUSSION

Potentiometric studies

Proton-ligand stability constants

The average number of protons associated with the ligand in monomeric (AN) and polymeric (PAN) form at different pH values, \bar{n}_A , were calculated from the titration curves, respectively. Thus, the formation curves (\bar{n}_A vs. pH) for the proton-ligand systems were constructed and found to extend between 0 to 1 in the \bar{n}_A scale. This means that AN and PAN has one dissociable proton (the enolized hydrogen ion of the amidic proton, CONH_2 [10] due to the hydrolysis of Acrylonitrile to acrylamide). Different computational methods [13] were applied to evaluate the dissociation constants. The number of replicates is three, and the average values obtained are listed in Table 1.



(PAN)

The PAN has a lower acidic character (higher pK_a values) than AN. This is quite reasonable because the presence of the vinyl group ($\text{H}_2\text{C}=\text{CH}$) in monomeric form (AN) will decrease the electron density, whereby weaker N-H bonds is formed [10,14,15]. The absence of the vinyl group in polymeric form (PAN) will lead to the opposite effect (i.e. retard the removal of the ligand proton and hence increase the basicity of PAN).

Metal-ligand stability constants

The formation curves for the metal complexes were obtained by plotting the average number of ligand in monomeric (AN) and polymeric (PAN) forms, respectively, attached per metal ion (\bar{n}) versus the free ligand exponent (PL), according to Irving and Rossotti [16]. These curves were analyzed, and the successive stability constants were determined using different computational methods [17,18]. The values of the stability constants ($\log K_1$, $\log K_2$ and $\log K_p$), as well as the ratio $\log K_1 / \log K_2$, are given in Table 2. The following general remarks can be made:

- (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 [19].

- (ii) No precipitate was observed in the titration vessel, indicating that the possibility of formation of metal hydroxide can be excluded [20].
- (iii) For all complexes, the stability constants of PAN are higher than AN. This is quite reasonable because the ligand in polymeric form is better complexing agent [3,15].
- (iv) The order of stability constants of the metal complexes of AN and PAN were found to be



Effect of Temperature

The dissociation constant (pK_d) for AN and PAN as well as the stability constants of its complexes with Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} have been evaluated at 308, 318 and 328 K, and are given in Tables 1 and 3. The slope of the plot (pK_d or $\log K$ vs. $1/T$) was utilized to evaluate the enthalpy change (ΔH) for the dissociation or Complexation process, respectively. From the free energy change (ΔG) and (ΔH) values one can deduce the entropy change (ΔS) using the well known relationships (1) and (2):

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

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

All thermodynamic parameters of the dissociation process of AN and PAN are recorded in Table 1. Inspection of these values reveals that:

- (i) The pK_d values decrease with increasing temperature revealing that its acidity increases with increasing temperature.
- (ii) A positive value of ΔH indicating that its dissociation is accompanied by adsorption of heat and the process is endothermic.

- (iii) A large positive value of ΔG indicating that the dissociation processes is not spontaneous.
- (iv) A negative value of ΔS is obtained, due to increased order as a result of solvating processes.

All the thermodynamic parameters of the stepwise stability constants of AN and PAN complexes are recorded in Table 3. It is known that the divalent metal ions exist in solution as octahedrally hydrated species and the obtained values of ΔH and ΔS can then be considered as sum of two contributions:

- (a) release of H_2O molecules, and
- (b) metal-ligand bond formation.

It was suggested [21] that the ions in aqueous solution, order the water molecules around them and during complex formation between oppositely charged ions (ligand L^- and M^{n+}) will lead to the breakdown of metal-water arrangement resulting in positive entropy and enthalpy changes. Examination of these values shows that:

- (i) The stepwise stability constants ($\log K_1$ and $\log K_2$) for APAT and PAPAT complexes increases with increasing temperature in the case of Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} i.e., the stability constants increase with increasing the temperature.
- (ii) The negative values of ΔG for the Complexation process of Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} with AN and PAN suggests a spontaneous nature of such process.

- (iii) The ΔH values are positive for the Complexation process of AN and PAN with Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} . This means that these processes are endothermic and favorable at higher temperatures.
- (iv) The positive values of ΔS for the Complexation process of AN and PAN with Mn^{2+} , Co^{2+} , Cu^{2+} and Zn^{2+} confirming that the complex formation is entropically favorable.

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Table (1) : Thermodynamic functions for the dissociation of AN and PAN in 50 % (v/v) ethanol-water mixture and 0.1 M KCl at different temperatures*.

Compound	Temp (K)	Dissociation Constant pK_a	Free Energy Change (k J mol ⁻¹) ΔG_1	Enthalpy Change (k J mol ⁻¹) ΔH_1	Entropy Change (J mol ⁻¹ K ⁻¹) $-\Delta S_1$
AN	308	10.30	60.74	38.29	72.89
	318	10.11	61.55		73.14
	328	9.91	62.24		73.02
PAN	308	9.35	55.14	33.51	70.23
	318	9.17	55.83		70.19
	328	9.00	56.52		70.15

* The given values are average of three measurements

Table (2) : Stepwise stability constants for M^{2+} and M^{3+} complexes of AN and PAN in 50% (v/v) ethanol-water mixture and 0.1 M KCl at different temperatures *

Compound	M^{n+}	308 K				318 K				328 K			
		$\log K_1$	$\log K_2$	$\log K_{\beta}$	$\log K_1 / \log K_2$	$\log K_1$	$\log K_2$	$\log K_{\beta}$	$\log K_1 / \log K_2$	$\log K_1$	$\log K_2$	$\log K_{\beta}$	$\log K_1 / \log K_2$
AN	Mn^{2+}	7.65	7.25	14.90	1.06	7.81	7.42	15.23	1.053	8.03	7.61	15.64	1.06
	Co^{2+}	7.83	7.40	15.23	1.06	7.98	7.60	15.58	1.05	8.20	7.78	15.98	1.05
	Ni^{2+}	7.85	7.45	15.30	1.05	8.02	7.62	15.64	1.05	8.21	7.80	16.01	1.05
	Cu^{2+}	8.23	7.85	16.17	1.06	8.51	8.02	16.53	1.061	8.72	8.18	16.90	1.07
	Zn^{2+}	8.02	7.58	15.60	1.06	8.21	7.76	15.97	1.06	8.41	7.95	16.36	1.06
	Mn^{3+}	5.35	4.92	10.27	1.087	5.51	5.07	10.58	1.087	5.70	5.24	10.94	1.09
PAN	Co^{2+}	5.49	4.95	10.44	1.11	5.64	5.10	10.74	1.106	5.80	5.26	11.06	1.11
	Ni^{3+}	5.50	5.09	10.40	1.12	5.71	5.23	10.79	1.12	5.90	5.38	11.16	1.12
	Cu^{3+}	6.00	5.60	11.60	1.07	6.18	5.78	11.96	1.07	6.35	5.95	12.30	1.07
	Zn^{2+}	5.68	5.28	10.96	1.076	5.81	5.42	11.23	1.072	5.95	5.57	11.52	1.07

* The given values are average of three measurements

Table (3) : Thermodynamic functions for M^{2+} and M^{1+} complexes of AN and PAN in 50 % (v/v) ethanol-water mixture and 0.1 M KCl at different temperatures *

Compound	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}
AN	Mn^{2+}	308	30.53	28.07	58.60	31.78	29.05	60.83	209.09	191.68	400.77
		318	32.49	29.90	62.39	31.78	29.05	60.83	208.67	191.40	400.07
		328	34.71	31.91	66.62	31.78	29.05	60.83	209.09	191.70	400.79
	Co^{2+}	308	31.23	28.24	59.56	28.13	28.11	56.24	199.50	189.09	388.59
		318	33.26	30.08	63.34	28.13	28.11	56.24	199.32	188.93	388.25
		328	35.31	32.03	67.34	28.13	28.11	56.24	199.50	189.12	388.62
	Ni^{2+}	308	31.38	29.04	60.42	36.25	26.31	62.56	226.95	185.74	412.69
		318	33.67	30.54	64.51	36.25	26.31	62.56	227.01	185.55	412.69
		328	35.92	32.76	68.68	36.25	26.31	62.56	226.95	185.75	412.70
	Cu^{2+}	308	34.23	31.95	66.18	31.73	31.73	63.46	221.34	213.69	435.03
		318	36.45	34.09	70.34	31.73	31.73	63.46	221.36	213.70	435.06
		328	38.66	36.023	74.89	31.73	31.73	63.46	221.35	213.71	435.06
Zn^{1+}	308	32.41	30.13	62.54	24.49	26.31	50.80	190.94	189.40	380.34	
	318	34.26	31.96	66.22	24.49	26.31	50.80	190.75	189.19	379.94	
	328	36.23	33.91	70.23	24.49	26.31	50.80	190.94	189.37	380.31	
PAN	Mn^{2+}	308	43.65	41.37	58.02	34.52	32.66	67.18	262.32	248.42	510.79
		318	46.06	43.76	62.82	34.52	32.66	67.18	261.62	248.12	509.74
		328	48.89	46.34	67.23	34.52	32.66	67.18	262.30	248.43	510.73
	Co^{2+}	308	44.68	42.22	86.90	33.64	34.43	68.07	262.82	257.21	520.03
		318	47.06	44.82	91.88	33.64	34.43	68.07	262.01	257.31	519.32
		328	49.93	47.37	97.30	33.64	34.43	68.07	262.80	257.23	520.03
Ni^{2+}	308	44.79	42.51	87.30	32.66	31.75	64.41	259.90	249.19	509.09	
	318	47.30	44.94	92.24	32.66	31.75	64.41	259.61	248.99	508.60	
	328	49.99	47.49	97.48	32.66	31.75	64.41	259.91	249.18	509.09	
Cu^{2+}	308	47.47	44.79	92.26	36.30	31.78	68.08	281.11	256.95	538.06	
	318	50.19	47.30	97.49	36.30	31.78	68.08	280.81	256.75	537.56	
	328	53.09	49.81	102.90	36.30	31.78	68.08	281.10	256.57	537.67	
Zn^{2+}	308	45.76	43.25	89.01	35.36	33.56	68.92	272.21	257.75	529.96	
	318	48.42	45.76	94.18	35.36	33.56	68.92	272.01	257.53	529.54	
		328	51.21	48.41	99.62	35.36	33.56	68.92	272.23	257.77	530.00

* The given values are average of three measurements