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Polymer Complexes XXXV. Potentiometric and Thermodynamic Studies of Monomeric and Polymeric Complexes Containing 2-Acrylamidosulphamethoxazole

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Summary

2-Acrylamidosulphamethoxazole (ASM) was synthesized and characterized by elemental analyses, IR and ^1H NMR spectra. Proton-monomeric ligand dissociation and metal-monomeric ligand stability constants of ASM with some metal ions were determined potentiometrically in 0.1 M KCl and 40 % (v/v) ethanol-water mixture. In the presence of 2,2'-azobisisobutyronitrile as initiator, the dissociation and stability constants of ASM were determined in polymeric form (PASM). The influence of temperature on the dissociation of ASM and the stability constants of their complexes in monomeric and polymeric forms were precisely studied. The pK_2^H value of PASM was found to be higher than ASM, this means that the vinyl group in the monomeric form decreases the electron density and hence reduces the N-H bond strength. The stability constants of the metal complexes in polymeric form are higher than those of the monomeric form. This reveals that the ligand in a polymeric form is considered as a better complexing agent.

Introduction

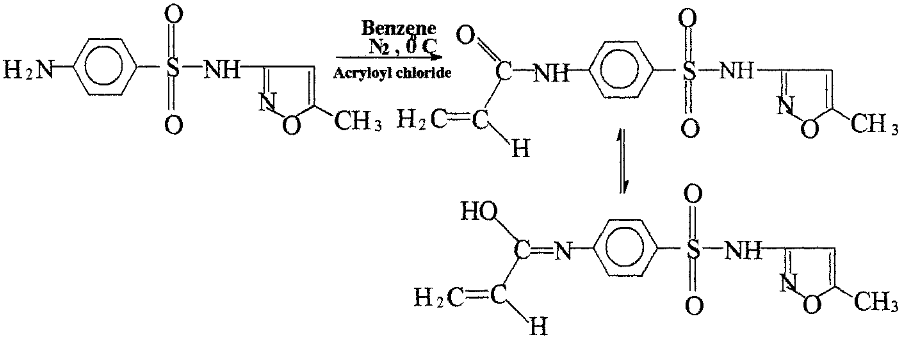
In recent years considerable interest has been focused on the aqueous chemistry of organometallic in the view of environmental and toxicological sides [1]. In solution, polymer-metal complexes form microheterogeneous regions occupied by polymer backbone in the bulk solution [2,3]. Several significant criteria for facile metal ion removal from aqueous solution includes the hydrophilicity of the organic ligand when it is anchored to a hydrophobic, pH stable polymer backbone such as modified, kinetics and thermodynamics of the pendant ligand reaction with the selected metal ion [4, 5].

In this paper we extend our previous investigation [6-8] and focus attention on the preparation of polymers as pendant. Here we describe the synthesis and characterization of 2-acrylamidosulphamethoxazole which possesses one polymerizable vinyl group. Our approach is to study the dissociation of ASM and determine the stability constants of its metal complexes with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, La^{3+}, UO_2^{2+} and Th^{4+} in monomeric and polymeric forms, using potentiometric measurements and thermodynamic calculations.

Experimental

Reagents: Sulphamethoxazole (Aldrich) was used without purification. acryloyl chloride (Aldrich) was freshly used. 2,2`-azobisisobutyronitrile (AIBN), was purified by fractional crystallization from ethanol. Other reagents (extra-pure grade) were used without purification.

Preparation of the Monomer: 2-acrylamidosulphamethoxazole (ASM) was prepared [8] by selective amidation of sulphamethoxazole with acryloyl chloride at 0°C using dry benzene (Scheme 1). To a solution of sulphamethoxazole (0.1 mol) in dry benzene (100 ml), a solution of (0.15 mol) of acryloyl chloride in 20 ml of benzene was added dropwise under N_2 atmosphere with magnetic stirring. After reacting for 5 h, the solvent was distilled off at reduced pressure, and the solid residue was washed twice with a water/ethanol solution. The isolated product was recrystallized twice from ethanol/water (2:1) and vacuum dried over phosphorus pentoxide. The yield was 70%.



Scheme 1

Characterization of the Monomer: The monomer (ASM) was characterized by infra-red (i.r.) and ^1H n.m.r. spectroscopy. I.r. spectra was recorded in KBr pellets on a Perkin-Elmer 1430 spectrometer at room temperature. N.m.r. spetra were recorded in deuterated dimethylsulfoxide (DMSO-d_6) solutions on a EM-390 90 MHz spectrometer in absence and presence D_2O.

The important bands in the infrared spectrum of the monomer are collected in Table 1. These spectroscopic data agree with the structure suggested. The IR spectrum of the monomer shows no characteristic absorption assignable to NH_2 function. It is noteworthy to point out that the sulphamethoxazole (Scheme 1) exhibits three bands in the frequency range 4000–3000 cm^{-1}, two of which are due to the stretching modes of NH_2 (v_{as} and v_s, respectively at 3395 and 3260 cm^{-1}) and one to v_{NH} (at 3120 cm^{-1}).

Only two bands are observed in this region for the monomer; one for the CONH group between 3430 and 3370 cm^{-1}, and the other due to the imine NH in the 3090 – 3040 cm^{-1}.

The ^1H n.m.r. spectrum of monomer (300 MHz, DMSO) at room temperature shows a singlet at 11.77 (1H) and 8.06, 8.03 (1H) ppm due to the NH protons (disappear by D_2O) and NH nearer to C=O, very deshielded as expected, while the signal of the proton of OH(1H) at 10.74 ppm. The hydrogen on the $C=N_{py}$ double bond is found at 8.74 (2H) ppm. The aromatic protons appear in the range 8.53 – 8.48 (4H) and 7.96 – 7.05 (3H) ppm.

Reagents and materials: Metal ion solutions (0.001 M) were prepared from metal salt samples (BDH) in bidistilled water and standardized with EDTA. The ligand solution (0.002 M) was prepared by dissolving the accurate weight of the monomer (ASM) in ethanol. Solutions of 1 M KCl were also prepared in bidistilled water. A carbonate-free sodium hydroxide solution in 40% (v/v) ethanol-water mixture was used as a titrant and standardized against AnalaR oxalic acid.

Potentiometric measurements: The apparatus, general conditions and methods of calculation were the same as given previously [6-9]. The following mixtures were prepared and titrated potentiometrically at 298 K against standard 0.004 M NaOH in 40% (v/v) ethanol-water mixture: **(1)** 5 ml 0.001 M HCl + 5 ml 1 M KCl + 20 ml ethanol; **(2)** 5 ml 0.001 M HCl + 5 ml 1 M KCl + 5 ml 0.001 M monomer (ASM) + 15 ml ethanol and **(3)** 5 ml 0.001 M HCl + 5 ml 1 M KCl + 5 ml 0.001 M monomer (ASM) + 15 ml ethanol + 1 ml 0.001 M metal salt.

For each solution mixture, the volume was made up to 50 ml with bidistilled water before the titration. These titrations were also carried out in the presence of 5 ml of AIBN (0.001 M) as initiator for the polymerization step. A constant temperature was maintained ±0.05 K using an ultrathermostat (Galenkamp thermostirrer 85). The pH-meter readings in 40% (v/v) ethanol-water mixture were corrected by Van Uitert and Hass relation [10].

Results and discussion

Potentiometric studies

Acid dissociation constants: The average acid dissociation constants of the ligand in monomeric (ASM) and in polymeric (PASM) form at different pH values, n_A, were calculated from the titration curves of the acid in the absence and presence of ligand. The formation curves ($\bar{n}_A$ vs. pH) for the acid systems were constructed and found to extend between (0 and 2) in the $\bar{n}_A$ scale for ASM (Fig. 1) and PASM (Fig. 2).

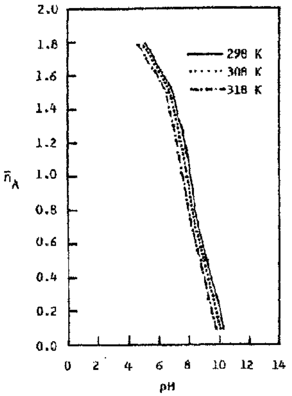


Fig. 1. Dissociation constant pK^H of ASM in 40% (v/v) ethanol-water mixture.

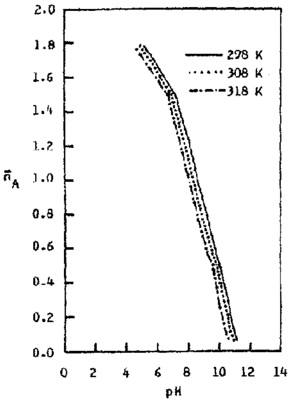


Fig. 2. Dissociation constant pK^H of PASM in 40% (v/v) ethanol-water mixture.

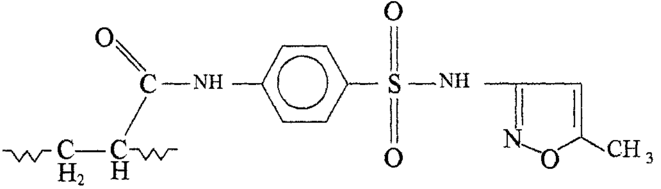
This means that, each of ASM and PASM has two dissociable protons (the enolized hydrogen ions of the amidic proton, CONH and sulphonamide proton SO_2NH). Different computational methods [11] were applied to evaluate the stepwise dissociation constants. The average values obtained are listed in Table 1.

Table 1. Thermodynamic functions for the dissociation of ASM and PASM in 40 % (v/v) ethanol-water mixture in the presence of 0.1 M 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	$-\Delta S_1$	$-\Delta S_2$
ASM	298	6.90	9.17	39.32	52.25	15.96	21.76	78.40	102.32
	308	6.78	9.00	39.93	53.07			77.84	101.66
	318	6.65	8.81	40.44	53.57			76.99	100.03
PASM	298	7.20	10.00	41.03	56.98	31.91	34.81	30.93	74.39
	308	7.00	9.82	41.23	57.84			30.25	74.77
	318	6.82	9.65	41.47	58.68			30.07	75.06

* The values given present an average of three measurements.

The values of PASM were found to be lower than that of ASM values. The vinyl group ($H_2C{=}CH$) in the monomeric form (ASM) decreases the electron density, and hence reduces the N-H bond strength [6, 12]. On the other hand, the absence of the vinyl group in the polymeric form (PASM) retards the removal of the ligand protons and decreases the acidity (higher pK_1^H values).



(PASM)

Complex stability constants: The formation curves for the metal complexes were obtained by plotting the average number of ligands, in the monomeric (ASM) and polymeric (PASM) forms, respectively attached per metal ion ($\bar{n}$) versus the free ligand exponent (pL), according to the method of Irving and Rossotti [13]. These curves were analyzed and the successive stability constants were determined using different computational methods [14].

The stability constants $\log K_1$ and $\log K_2$ are given in Tables 2 & 3. The following general remarks can be made; (i) the maximum $\bar{n}$ values in all cases were found to be ≅2, revealing that both ML and ML_2 types of complexes were formed in solution; (ii) no precipitate was observed in the titration vessel, indicating that the possibility of metal hydroxide formation is excluded; (iii) The stability constants of PASM in metal complexes are higher than the corresponding metal complexes of ASM. This denotes that the ligand in polymeric form is considered as a better complexing agent [3, 6] and (iv) the sequence of stability constants of the metal complexes of ASM and PASM is: $Th^{4+} > UO_2^{2+} > La^{3+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$. The sequence of stability ($Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$) of the complexes of ASM and PASM is in agreement with the Irving and Williams series [15, 16]. The order reflects the change in the heat of complex formation across the series and arises from combination of the influence of both polarizing ability of the metal ion and crystal-field stabilization energies. The greater stability of Cu^{2+} complexes is due to Jahn-Teller effect. The higher values of the stability constants of the Th^{4+} complexes is expected on the basis of the higher charge and ionization potential of the Th^{4+} ion in the octahedral field environment.

Table 2. Stepwise stability constants for ML and ML_2 complexes of ASM in 40 % (v/v) ethanol-water mixture in the presence of 0.1 M KCl at different temperatures*.

M^{n+}	298 K				308 K				318 K			
	$\log K_1$	$\log K_2$	$\log K_\beta$	$\log K_1/\log K_2$	$\log K_1$	$\log K_2$	$\log K_\beta$	$\log K_1/\log K_2$	$\log K_1$	$\log K_2$	$\log K_\beta$	$\log K_1/\log K_2$
Mn^{2+}	9.74	8.44	18.18	1.15	9.88	8.58	18.46	1.15	10.02	8.73	18.75	1.15
Co^{2+}	9.85	8.64	18.49	1.14	9.99	8.78	18.77	1.38	10.13	8.91	19.04	1.14
Ni^{2+}	9.96	8.84	18.80	1.13	10.10	8.98	19.08	1.12	10.24	9.12	19.36	1.12
Cu^{2+}	10.15	9.04	19.19	1.12	10.29	9.22	19.51	1.12	10.42	9.39	19.81	1.11
Zn^{2+}	10.00	8.90	18.90	1.12	10.14	9.11	19.25	1.11	10.27	9.32	19.59	1.10
La^{3+}	10.20	9.10	19.30	1.12	10.34	9.35	19.69	1.11	10.48	9.59	20.07	1.09
UO_2^{2+}	10.29	9.19	19.48	1.12	10.43	9.53	19.96	1.09	10.56	9.87	20.43	1.07
Th^{4+}	10.38	9.28	19.66	1.12	10.50	9.71	20.21	1.08	10.66	9.98	20.64	1.07

* The values given present an average of three measurements.

Table 3. Stepwise stability constants for ML and ML_2 complexes of PASM in 40 % (v/v) ethanol-water mixture in the presence of 0.1 M KCl at different temperatures*.

M^{n+}	298 K				308 K				318 K			
	$\log K_1$	$\log K_2$	$\log K_\beta$	$\log K_1/\log K_2$	$\log K_1$	$\log K_2$	$\log K_\beta$	$\log K_1/\log K_2$	$\log K_1$	$\log K_2$	$\log K_\beta$	$\log K_1/\log K_2$
Mn^{2+}	10.86	9.43	20.29	1.15	11.00	9.57	20.57	1.15	11.14	9.71	20.85	1.15
Co^{2+}	10.99	9.57	20.56	1.15	11.13	9.70	20.83	1.15	11.26	9.83	21.09	1.15
Ni^{2+}	11.10	9.70	20.80	1.14	11.25	9.80	21.05	1.15	11.38	9.95	21.33	1.14
Cu^{2+}	11.23	9.86	21.09	1.14	11.38	9.98	21.36	1.14	11.52	10.10	21.62	1.14
Zn^{2+}	11.13	9.80	20.93	1.14	11.29	9.90	21.19	1.14	11.46	9.99	21.45	1.15
La^{3+}	11.27	9.93	21.20	1.13	11.40	10.05	21.45	1.13	11.60	10.17	21.77	1.14
UO_2^{2+}	11.36	10.02	21.38	1.13	11.53	10.14	21.67	1.14	11.69	10.26	21.95	1.14
Th^{4+}	11.45	10.11	21.56	1.13	11.62	10.20	21.82	1.14	11.78	10.35	22.13	1.14

* The values given present an average of three measurements.

Effect of Temperature: The dissociation constants (pK^H) for ASM and PASM as well as the stability constants of their complexes with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, La^{3+}, UO_2^{2+} and Th^{4+} have been evaluated at 298, 308 and 318 K, and are given in

Tables 1, 2 and 3. The slope of the (pK^H or log K vs. $^1/_T$) plot was applied to evaluate the enthalpy change (ΔH) for the dissociation or complexation process, respectively. The thermodynamic parameters of the dissociation process of ASM and PASM are recorded in Table 1. It can be pointed out that: (i) a positive value of ΔH indicates that its dissociation is endothermic; (ii) a large positive value of ΔG points that the dissociation process is not spontaneous. (iii) a negative value of ΔS is obtained, due to increased order as a result of increased solvation of the ionic form.
The thermodynamic parameters of the stepwise stability constants of ASM and PASM complexes are given in Tables 4 and 5.

Table 4. Thermodynamic functions for ML and ML_2 complexes of ASM in 40 % (v/v) ethanol-water mixture in the presence of 0.1 M KCl.

M^{n+}	Temp. (K)	Free Energy Change (k J mol^{-1})			Enthalpy Change (k J 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	55.50	48.09	103.59	15.36	20.54	35.90	237.79	230.30	468.09
	308	58.19	50.53	108.72				238.79	230.75	469.54
	318	60.93	53.09	114.02				239.91	231.54	471.45
Co^{2+}	298	56.13	49.23	105.36	19.20	20.88	40.08	252.79	235.27	488.06
	308	58.84	51.71	110.55				253.38	235.68	489.06
	318	61.60	54.18	115.78				254.08	236.04	490.12
Ni^{2+}	298	56.76	50.37	107.13	22.98	21.29	44.27	267.58	240.47	508.05
	308	59.49	52.89	112.38				267.76	240.08	507.84
	318	62.27	55.46	117.73				268.08	241.35	509.43
Cu^{2+}	298	57.84	51.51	109.35	21.06	25.64	46.70	264.77	258.89	523.66
	308	60.60	54.30	114.90				265.13	259.55	524.68
	318	63.36	57.10	120.46				265.47	260.19	525.02
Zn^{2+}	298	56.98	50.72	107.70	22.98	31.25	54.23	268.32	275.07	543.39
	308	59.72	53.65	113.37				268.51	275.65	544.10
	318	62.15	56.67	119.12				268.65	276.48	545.13
La^{3+}	298	58.12	51.86	109.98	21.10	36.38	57.48	265.84	296.11	562.76
	308	60.90	55.07	115.97				266.23	296.92	563.15
	318	63.73	58.32	122.05				266.76	297.79	563.15
UO_2^{2+}	298	58.64	52.37	111.01	21.18	26.23	47.41	267.85	263.76	531.61
	308	61.43	56.13	117.56				268.21	267.40	535.61
	318	64.21	60.02	124.23				268.52	271.22	539.74
Th^{4+}	298	59.15	52.88	112.03	19.15	13.40	32.55	262.75	222.42	485.17
	308	61.84	57.19	119.03				262.95	229.19	492.14
	318	64.82	60.69	125.51				264.06	232.39	497.05

It is known that the divalent metal ions exist in solution as 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. Examination of these values shows that: (i) The stepwise stability constants log K_1 and log K_2 for ASM and PASM complexes increased with increasing temperature in the case of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, La^{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+}, Zn^{2+}, La^{3+}, UO_2^{2+} and Th^{4+} with ASM and PASM suggest a spontaneous nature of such process; (iii) The ΔH values are positive in the case of the complexes for the metal ions investigated. This means that these processes are endothermic and hence favoured at higher temperatures and (iv) The positive values of ΔS for the complexation process of ASM and PASM with the metal ion under study confirm that the complex formation is entropically favourable [17,18].

Table 5. Thermodynamic functions for ML and ML_2 complexes of PASM in 40 % (v/v) ethanol-water mixture in the presence of 0.1 M KCl.

M^{n+}	Temp. (K)	Free Energy Change (k J mol^{-1})			Enthalpy Change (k J 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	61.88	53.74	115.62	21.06	22.02	43.08	278.32	254.74	533.06
	308	64.79	56.36	121.15				278.73	254.48	533.21
	318	67.74	59.05	126.79				279.25	254.94	534.19
Co^{2+}	298	62.63	54.53	117.16	19.15	17.23	36.38	274.43	240.81	515.24
	308	65.55	57.13	122.68				275.00	241.48	516.43
	318	68.47	59.77	128.24				275.53	242.14	517.67
Ni^{2+}	298	63.25	55.27	118.52	22.02	19.14	41.16	286.14	249.69	535.83
	308	66.26	57.72	123.98				286.62	249.55	536.17
	318	69.20	60.50	129.70				286.86	250.44	537.30
Cu^{2+}	298	63.99	56.19	120.18	17.23	13.42	30.65	272.65	233.59	506.14
	308	67.02	58.78	125.8				273.54	234.42	507.96
	318	70.05	61.42	131.47				274.47	235.35	509.82
Zn^{2+}	298	63.42	55.84	119.26	22.89	19.20	42.09	289.63	251.81	541.44
	308	66.49	58.31	124.8				290.19	251.66	541.85
	318	69.69	60.75	130.44				291.13	251.42	542.55
La^{3+}	298	64.22	56.59	120.81	24.89	14.74	39.63	299.03	239.36	538.39
	308	67.14	59.19	126.33				298.79	240.03	538.82
	318	70.54	61.84	132.38				300.09	240.81	540.91
UO_2^{2+}	298	64.73	57.10	121.83	24.9	14.55	39.45	300.77	240.43	541.21
	308	67.91	59.72	127.63				301.33	241.14	542.47
	318	71.09	62.39	133.48				301.86	241.95	543.81
Th^{4+}	298	65.25	57.61	122.86	25.85	16.28	42.13	305.70	247.95	553.65
	308	68.44	60.07	128.51				306.14	247.89	554.03
	318	71.63	62.94	134.57				306.64	249.12	555.76

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