

Potentiometric and Thermodynamic Studies of 2-Acrylamidosulfacetamide and its Metal Complexes in Monomeric and Polymeric Forms

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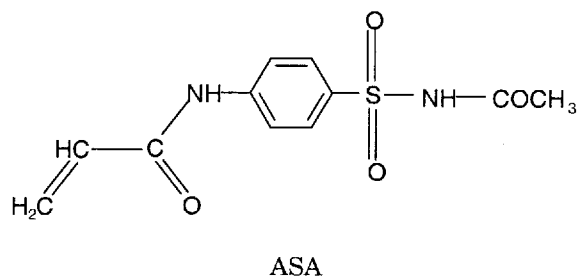
Proton—monomeric ligand dissociation and metal—monomeric ligand stability constants of 2-acrylamidosulfacetamide (ASA) with some metal ions were calculated potentiometrically in 0.1 M-KCl and 40 vol. % ethanol—water mixture. Also, in the presence of 2,2'-azobisisobutyronitrile as initiator the proton—polymeric ligand dissociation and metal—polymeric ligand stability constants were calculated. The effect of temperature on the dissociation of ASA and the stability of its formed complexes was studied in monomeric and polymeric forms. The corresponding thermodynamic functions were derived and discussed. The dissociation process is nonspontaneous, endothermic and entropically unfavourable. The formation of the metal complexes has been found to be spontaneous, endothermic and entropically favourable.

In solution, polymer—metal complexes form micro-heterogeneous regions occupied by polymer backbone in the bulk solution [1, 2]. Several significant criteria for facile metal ion removal from aqueous solution include 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 [3, 4].

In the present paper, we describe the dissociation constant of 2-acrylamidosulfacetamide (ASA) and the stability constants for its complexes with Mn^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} in monomeric and polymeric forms, which were obtained by potentiometric studies. Furthermore, the corresponding thermodynamic functions of dissociation and complexation are derived and discussed.

EXPERIMENTAL

ASA was prepared according to the method [4] by amidation of sulfacetamide (Aldrich) with acryloyl chloride (Aldrich) at 0 °C using dry benzene. The product was recrystallized from ethanol and then dried in a vacuum desiccator over anhydrous calcium chloride. Its purity was checked by elemental analysis (w_i (calc.): 29.24 % C, 4.51 % H, 10.40 % N); w_i (found): 48.98 % C, 4.45 % H, 10.40 % N).



The monomeric ligand solution (0.001 M) was prepared by dissolving the accurate mass of the solid in ethanol (AnalaR). Metal ion solutions (0.0002 M) were prepared from AnalaR metal chlorides (BDH) in doubly distilled water and standardized with EDTA [5]. Solution of 2,2'-azobisisobutyronitrile (AIBN) as initiator (0.001 M) was prepared by dissolving the accurate mass of the solid in ethanol (AnalaR). Solutions of 0.001 M-HCl and 1 M-KCl were prepared in doubly distilled water. A carbonate-free sodium hydroxide solution in 40 vol. % ethanol—water mixture was used as titrant and standardized against AnalaR oxalic acid.

The apparatus, general conditions, and methods of calculation were the same as in the previous works [3, 4]. The following mixtures were prepared and titrated potentiometrically against standard 0.002 M-NaOH in 40 vol. % ethanol—water mixture at 298 K, 308 K, and 318 K, respectively

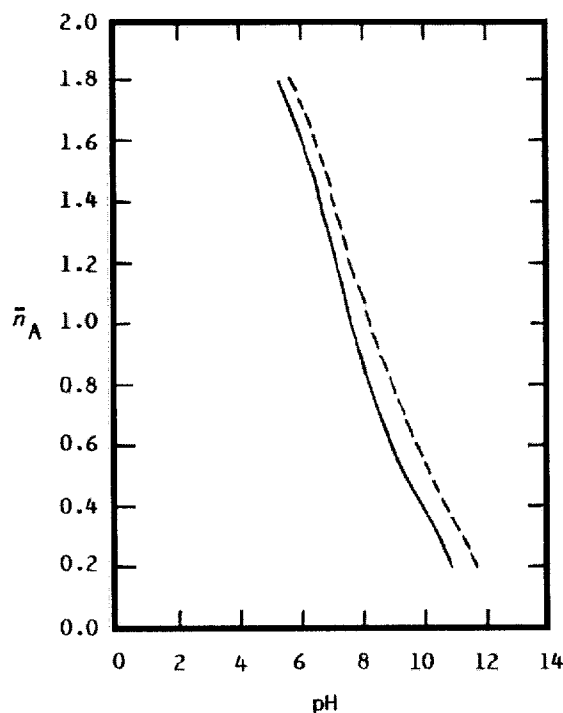


Fig. 1. Dissociation constant pK^H of ASA (—) and PASA (---) in 40 vol. % ethanol—water mixture at 298 K.

i) 5 cm^3 0.001 M-HCl + 5 cm^3 1 M-KCl + 20 cm^3 ethanol

ii) 5 cm^3 0.001 M-HCl + 5 cm^3 1 M-KCl + 15 cm^3 ethanol + 5 cm^3 0.001 M-ASA

iii) 5 cm^3 0.001 M-HCl + 5 cm^3 1 M-KCl + 15 cm^3 ethanol + 5 cm^3 0.001 M-ASA + 5 cm^3 0.0002 M-metal chloride

For each mixture, the volume was made up to 50 cm^3 with doubly distilled water before the titration. These titrations were repeated in the presence of 5 cm^3 of 0.001 M-AIBN as initiator for the polymerization [6]. A constant temperature was maintained to 0.05 K by using an ultrathermostat (Gallenkamp thermostirrer 85). The pH-meter readings in 40 vol. % ethanol—wa-

ter mixture are corrected according to the *Van Uitert* and *Hass* relation [7].

RESULTS AND DISCUSSION

The average number of the protons associated with the reagent molecule \bar{n}_A in monomeric (ASA) and polymeric (PASA) forms was determined at different pH values applying the following equation

$$\bar{n}_A = Y + \frac{(V_1 - V_2)(N^o + E^o)}{(V^o - V_1)TC_L^o} \quad (1)$$

where V_1 and V_2 are the volumes of alkali required to reach the same pH in the titration curves of hydrochloric acid and reagent, respectively. V^o is the initial volume (50 cm^3) of the mixtures, TC_L^o the total concentration of the reagent, N^o molarity of sodium hydroxide solution, and E^o the initial concentration of the free acid. Thus, the formation curves (\bar{n}_A vs. pH) for the proton—ligand systems were constructed and found to extend between 0 and 2 in the \bar{n}_A scale (Fig. 1). This means that ASA and PASA have two dissociable protons, the enolized hydrogen ion of the sulfonamide proton (SO_2NH , pK_1^H) and amidic proton (CONH , pK_2^H). Different computational methods [8] were applied to evaluate the dissociation constants. The number of replicates is three, and the average values obtained are listed in Table 1.

The PASA has a lower acidic character (higher pK_2^H values) than ASA. This is quite reasonable because the presence of the vinyl group ($\text{H}_2\text{C}=\text{CH}-$) in monomeric form will decrease the electron density, whereby weaker N—H bonds are formed [1–4]. The absence of vinyl group in polymeric form will lead to the opposite effect (*i.e.* retard the removal of the ligand proton and hence increase the basicity of PASA).

The formation curves for the metal complexes were obtained by plotting the average number of ligand in monomeric and polymeric forms, respectively, attached per metal ion (\bar{n}) vs. the free ligand exponent (pL), according to *Irving* and *Rossotti* [9]. These curves were analyzed and calculated using the equations

Table 1. Thermodynamic Functions for the Dissociation of ASA and PASA in 40 vol. % Ethanol—Water Mixture and 0.1 M-KCl

Compound	T/K	Dissociation constant		Gibbs 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	$-\Delta S_1$	$-\Delta S_2$
ASA	298	6.54 ± 0.06	9.33 ± 0.04	37.32	53.24	28.26	27.35	30.40	86.88
	308	6.40 ± 0.04	9.18 ± 0.06	37.74	54.14			30.78	86.98
	318	6.23 ± 0.05	9.03 ± 0.06	37.93	54.98			30.41	86.89
PASA	298	6.90 ± 0.05	10.20 ± 0.05	39.37	58.20	28.26	30.09	37.28	94.33
	308	6.75 ± 0.06	10.03 ± 0.04	39.81	59.15			37.50	94.35
	318	6.59 ± 0.05	9.87 ± 0.05	40.12	60.10			37.30	94.37

$$\bar{n} = \frac{(V_3 - V_2)(N^\circ + E^\circ)}{(V^\circ - V_2)\bar{n}_A TC_M^\circ} \quad (2)$$

and

$$pL = \log_{10} \frac{\sum_{n=0}^{n=J} \beta_n \left(\frac{1}{\text{anti log pH}} \right)^n}{TC_L^\circ - \bar{n} TC_M^\circ} \cdot \frac{V^\circ + V_3}{V^\circ} \quad (3)$$

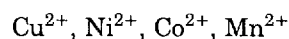
where TC_M° is the total concentration of the metal ions present in the solution, and β_n^H overall proton-reagent stability constant. V_1 , V_2 , and V_3 are the volumes of alkali required to reach the same pH in the titration curves of hydrochloric acid, organic ligand, and complex, respectively (Fig. 2). These curves were analyzed and the successive stability constants were determined using different computational methods [10, 11]. The values of the stability constants ($\log K_1$ and $\log K_2$) 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 [12].

ii) No precipitate was observed in the titration vessel, indicating that the possibility of formation of metal hydroxide can be excluded [13].

iii) For all complexes, the stability constants of PASA are higher than those of ASA. This is quite reasonable because the ligand in polymeric form is better complexing agent [3, 4].

iv) The decrease of the values of stability constants of the metal complexes of ASA and PASA was found to be in the order



The dissociation constant (pK^H) for ASA and PASA as well as the stability constants of their complexes with Mn^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} have been evaluated at 298 K, 308 K, and 318 K, and are given in Tables 1 and 3. The slope of the plot (pK^H or $\log K$ vs. $1/T$) was utilized to evaluate the enthalpy change ΔH for the dissociation or complexation process, respectively. From the Gibbs energy change ΔG and ΔH values one can deduce the entropy change ΔS using the well-known relationships

$$\Delta G = -2.303 RT \log K = 2.303 RT pK \quad (4)$$

$$\Delta S = (\Delta H - \Delta G)/T \quad (5)$$

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

i) The pK^H values decrease with increasing temperature revealing that their acidity increases with increasing temperature.

ii) A positive value of ΔH indicates that its dissociation is accompanied by adsorption of heat and the process is endothermic.

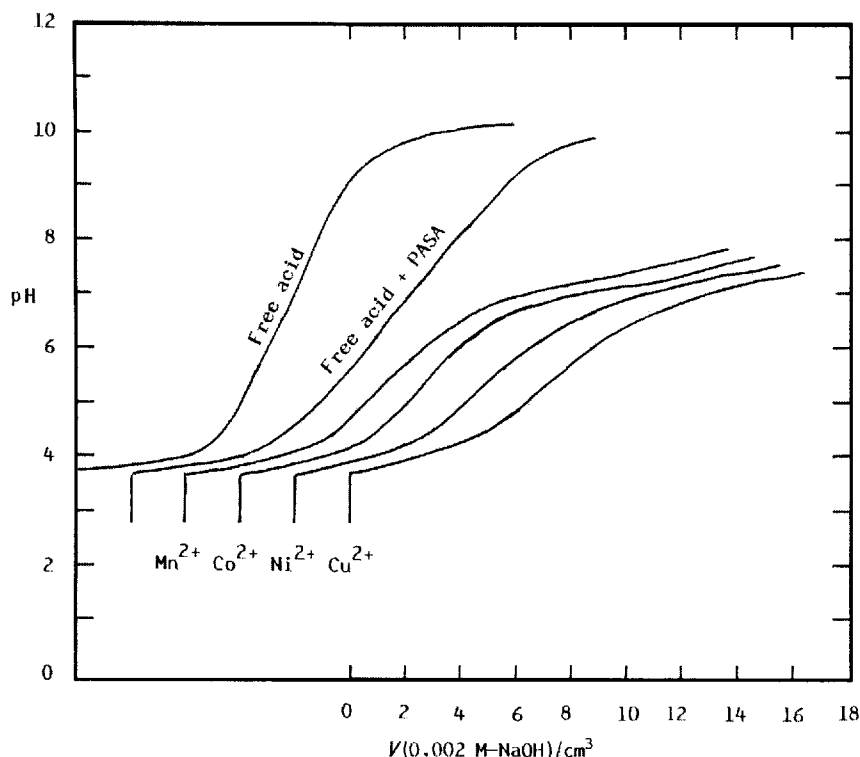


Fig. 2. Potentiometric titration curves of PASA and its metal complexes in 40 vol. % ethanol—water mixture at 298 K. The given scale (0, 2, 4, etc., cm^3) is just for Cu^{2+} complex and is shifted in parallel for the others.

Table 2. Stepwise Stability Constants for the Complexes ML and ML₂ of ASA and PASA in 40 vol. % Ethanol—Water Mixture and 0.1 M-KCl at Different Temperatures

Compound	M ⁿ⁺	298 K		308 K		318 K	
		log K ₁	log K ₂	log K ₁	log K ₂	log K ₁	log K ₂
ASA	Mn ²⁺	8.12 ± 0.06	6.22 ± 0.04	8.25 ± 0.04	6.35 ± 0.05	8.37 ± 0.04	6.48 ± 0.06
	Co ²⁺	8.21 ± 0.06	6.32 ± 0.04	8.34 ± 0.05	6.46 ± 0.05	8.48 ± 0.04	6.59 ± 0.05
	Ni ²⁺	8.28 ± 0.05	6.38 ± 0.04	8.42 ± 0.06	6.51 ± 0.05	8.55 ± 0.05	6.65 ± 0.05
	Cu ²⁺	8.57 ± 0.06	6.69 ± 0.06	8.72 ± 0.05	6.83 ± 0.04	8.88 ± 0.06	6.98 ± 0.05
PASA	Mn ²⁺	9.25 ± 0.05	7.12 ± 0.06	9.40 ± 0.04	7.26 ± 0.06	9.55 ± 0.06	7.40 ± 0.04
	Co ²⁺	9.36 ± 0.04	7.23 ± 0.05	9.50 ± 0.04	7.35 ± 0.05	9.64 ± 0.06	7.48 ± 0.06
	Ni ²⁺	9.45 ± 0.06	7.30 ± 0.05	9.61 ± 0.04	7.44 ± 0.06	9.76 ± 0.04	7.57 ± 0.06
	Cu ²⁺	9.79 ± 0.06	7.91 ± 0.05	9.95 ± 0.06	8.05 ± 0.04	10.11 ± 0.04	8.21 ± 0.04

iii) A large positive value of ΔG indicates that the dissociation process is not spontaneous.

iv) A negative value of ΔS is obtained due to the increased order as a result of solvation processes.

All the thermodynamic parameters of the stepwise stability constants of ASA and PASA complexes are recorded in Table 3. It is known that the divalent metal ions exist in solution as octahedrally hydrated species [11] and the obtained values of ΔH and ΔS can then be considered as a sum of two contributions: *a*) release of H₂O molecules, and *b*) metal—ligand bond formation.

It was suggested [14] that the ions in aqueous solution order the water molecules around them and during complex formation between oppositely charged ions (ligand L²⁻ and Mⁿ⁺) 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 K₁ and log K₂) for ASA and PASA complexes increase with increasing temperature in the case of Mn²⁺, Co²⁺, Ni²⁺, and Cu²⁺, *i.e.* the stability constants increase with increasing the temperature [15].

Table 3. Thermodynamic Functions for the Complexes ML and ML₂ of ASA and PASA in 40 vol. % Ethanol—Water Mixture and 0.1 M-KCl

Compound	M ⁿ⁺	T /K	Gibbs energy change/ (kJ mol ⁻¹)		Enthalpy change/ (kJ mol ⁻¹)		Entropy change/ (J mol ⁻¹ K ⁻¹)	
			-ΔG ₁	-ΔG ₂	ΔH ₁	ΔH ₂	ΔS ₁	ΔS ₂
ASA	Mn ²⁺	298	46.33	35.49	22.79	23.71	231.95	198.66
		308	48.65	37.45			231.95	198.57
		318	50.96	39.46			231.92	198.65
	Co ²⁺	298	46.84	36.06	24.62	24.62	239.80	203.62
		308	49.18	38.10			239.61	203.64
		318	51.63	40.12			239.78	203.58
	Ni ²⁺	298	47.24	36.40	24.62	24.62	241.14	204.77
		308	49.66	38.39			241.17	204.58
		318	52.06	40.49			241.13	204.75
Cu ²⁺	298	48.90	38.17	28.26	26.44	258.93	216.81	
	308	51.42	40.28			258.70	216.62	
	318	54.07	42.50			258.90	216.79	
PASA	Mn ²⁺	298	52.78	40.63	27.35	25.53	268.89	222.01
		308	55.43	42.81			268.77	221.88
		318	58.15	45.06			268.87	221.98
	Co ²⁺	298	53.41	41.25	25.53	22.79	264.90	214.90
		308	56.02	43.34			264.77	214.71
		318	58.70	45.54			264.87	214.87
	Ni ²⁺	298	53.92	41.65	28.26	24.62	275.77	222.38
		308	56.67	43.88			275.75	222.40
		318	59.43	46.09			275.75	222.36
	Cu ²⁺	298	55.86	45.13	29.18	27.35	285.37	243.22
		308	58.68	47.47			285.26	242.92
		318	61.56	49.99			285.35	243.21

ii) The negative values of ΔG for the complexation process of Mn^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} with ASA and PASA suggest a spontaneous nature of such process.

iii) The ΔH values are positive for the complexation process of ASA and PASA with Mn^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} . This means that these processes are endothermic and favourable at higher temperatures [16].

iv) The positive values of ΔS for the complexation process of ASA and PASA with Mn^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} confirm that the complex formation is entropically favourable.

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