Potentiometric and Thermodynamic Studies of Acrylonitrile and Its Metal Complexes

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Proton ligand dissociation and metal ligand stability constants of acrylonitrile (AN) with some transition metal ions in 0.1 M KCl and 50% (v/v) methanol-water mixture were determined potentiometrically. In the presence of 2,2`-azobisisobutyronitrile as initiator of the proton-polymeric ligand dissociation of the metal polymeric ligand stability constants were also evaluated. The influences of temperature on the dissociation of AN and the stability of its metal complexes in the monomeric and polymeric forms were critically studied. Based on the thermodynamic functions, the dissociation process of AN was found non-spontaneous, endothermic and entropically unfavourable. The metal complexes formed exhibit spontaneous, endothermic and entropically favourable behavior.

Key words: acrylonitrile, dissociation constants, stability constants, thermodynamics .

Recently considerable interest has been focused on aqueous organometallic chemistry due to environmental and toxicological importance [1]. In solution, polymer-metal complexes form microheterogeneous regions occupied by polymer backbone [2,3]. Polymeric ligands are used to select a specific metal ion from a mixture, thus to isolate important metals from wastewater [4]. Therefore, the aim of the present work was focused on studying the dissociation constants of AN and the stability constants for its metal complexes with Pb^{2+} , Cd^{2+} , Hg^{2+} , UO_2^{2+} and Th^{4+} in monomeric and polymeric forms employing potentiometric and thermodynamic measurements.

EXPERIMENTAL

Reagents and Materials: The monomeric ligand solution $(2 \times 10^{-3} M)$ was prepared by dissolving a known volume of the acrylonitrile (Aldrich) in methanol (AnalaR). Metal ion solutions $(2 \times 10^{-4} M)$ were also prepared from BDH chemicals in doubly distilled water and standardized with EDTA[5]. The initiator 2,2`-azobisisobutyronitrile (AIBN) $(2 \times 10^{-3} M)$ was prepared by dissolving the solid in methanol (AnalaR). A carbonate-free sodium hydroxide solution in 50% (v/v) methanol-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 [6-8]. The mixtures: **(i)** 5 ml $1 \times 10^{-3} M$ HCl + 5 ml 1 M KCl + 25 ml methanol; **(ii)** 5 ml $1 \times 10^{-3} M$ HCl + 5 ml 1 M KCl + 20 ml methanol + 5 ml $2 \times 10^{-3} M$ AN and **(iii)** 5 ml $1 \times 10^{-3} M$ HCl + 5 ml 1 M KCl + 20 ml methanol + 5 ml $2 \times 10^{-3} M$ AN + 5 ml $2 \times 10^{-4} M$ metal salt were prepared and titrated potentiometrically with $4 \times 10^{-3} M$ NaOH in 50% (v/v) methanol-water mixture at 298, 308 and 318 K.
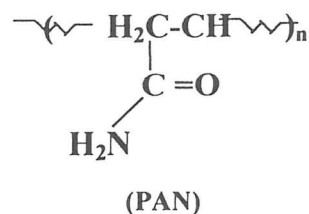
The titrations were carried out in the presence of 5 ml of AIBN $(2 \times 10^{-3} M)$ as initiator for the polymerization step. The pH-meter readings in 50% (v/v) methanol-water mixture were corrected according to the Van Uitert and Hass relation [9].

RESULTS AND DISCUSSION

Potentiometric Studies: *Acidity Constants:* The average number of protons associated with the ligand in monomeric (AN) and in polymeric (PAN) 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 from 0 to 1 in the $\bar{n}_A$ scale. Thus, each of AN and PAN has one dissociable proton (due to the hydrolysis of acrylonitrile to acrylamide). Different methods [10] were employed to evaluate the dissociation constants and the data are summarized in Table 1.

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

Compound	Temp. (K)	Dissociation Constant pK^H	Free Energy Change ΔG_1 (kJ mol^{-1})	Enthalpy Change ΔH_1 (kJ mol^{-1})	Entropy Charge $-\Delta S_1$ (J mol^{-1} K^{-1})
AN	298	9.3 ± 0.04	52.8		66.2
	308	9.1 ± 0.04	53.6	33.1	66.3
	318	8.9 ± 0.05	54.3		66.5
PAN	298	10.1 ± 0.05	57.9		78.5
	308	10.0 ± 0.04	59.0	34.5	79.6
	318	9.9 ± 0.04	60.2		80.8

$$\text{\textasciitilde} H_2C\text{-}CH \text{\textasciitilde}_n$$
$$|$$
$$C = O$$
$$H_2N /$$

(PAN)

The average values of the acidic character of PAN were found lower than that of AN values (Table 1). The vinyl group ($H_2C=CH$) in the monomeric form (AN) decreases the electron density, and hence reduces the N-H bond strength [8,11]. On the other hand, the absence of the vinyl group in the polymeric form (PAN) retards the removal of the ligand protons and increases the basicity (higher pK^H values).

Complex Stability Constants: The formation curves of the metal complexes of AN and PAN, attached per metal ion ($\bar{n}$) versus the free ligand exponent (pL) were calculated by Irving and Rossotti method [12]. The curves were analyzed and the successive stability constants were determined using different computational methods [13,14]. The average values of the stability constants ($log\ K_1$ and $log\ K_2$), are summarized in Table 2. The analysis of these data lead to the following general remarks: **(i)** The maximal $\bar{n}$ values in all cases were found to be $\cong 2$, revealing that both ML and ML_2 complexes are formed [15]; **(ii)** No precipitate was observed in the titration vessel, indicating that the formation of metal hydroxide is excluded [3]; **(iii)** The stability constants of PAN in metal complexes are higher than the corresponding metal complexes of AN. This is quite reasonable because the polymeric form ligand is considered as a better complexing agent [2,11] and **(iv)** The stability constants of the metal complexes of AN and PAN follow the sequence : $Th^{4+} > UO_2^{2+} > Hg^{2+} >$

$Cd^{2+} > Pb^{2+}$. Higher stability constants of the Th^{4+} complexes are expected, due to the charge and ionization potential of Th^{4+} ion in octahedral field environment.

Effect of Temperature: The average dissociation constants (pK^H) of AN and PAN as well as their stability constants of Pb^{2+}, Cd^{2+}, Hg^{2+}, UO_2^{2+} and Th^{4+} complexes have been evaluated at 298, 308 and 318 K (Tables 1 and 3). The enthalpy change (ΔH) for the dissociation and complexation processes were calculated from the slope of the plot pK^H or $\log K$ vs. $1/_T$ (Figs. 1 and 2). From the free energy change (ΔG) and (ΔH) values one can deduce the entropy change (ΔS) The thermodynamic parameters of the dissociation process of AN and PAN are summarized in Table 1. The data reveal that: **(i)** The pK^H value decreases with increasing temperature, confirming the increasing acidity with rising temperature; **(ii)** As ΔH, shows the dissociation process of AN and PAN is endothermic; **(iii)** Positive ΔG indicates that the dissociation process is not spontaneous and **(iv)** Negative ΔS is obtained. The thermodynamic parameters of the stepwise stability constants of AN and PAN complexes are also given in Table 3. 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_2O molecules, and **(ii)** metal-ligand bond formation. The metal ions in aqueous solution and the orientation of water molecules during complex formation between the oppositely charged ions (ligand L and metal M^{n-}) leads to the breakdown of metal-water arrangement, resulting in positive entropy and enthalpy changes

Table 2. Stepwise stability constants for ML and ML$_2$ complexes of AN and PAN in 50% (v/v) methanol-water mixture in the presence of 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$_2$
AN	Pb^{2+}	6.6± 0.04	6.3± 0.04	6.8± 0.04	6.5± 0.05	7.0± 0.04	6.7± 0.05
	Cd^{2+}	7.0± 0.06	6.7± 0.05	7.2± 0.04	6.8± 0.04	7.4± 0.04	7.0± 0.06
	Hg^{2+}	7.3± 0.06	7.0± 0.06	7.5± 0.06	7.2± 0.06	7.7± 0.06	7.4± 0.06
	UO$_2$$^{2+}$	7.3± 0.04	7.1± 0.04	7.5± 0.05	7.3± 0.06	7.7± 0.06	7.4± 0.05
	Th^{4+}	7.4± 0.05	7.2± 0.04	7.6± 0.04	7.4± 0.04	7.8± 0.04	7.6± 0.06
PAN	Pb^{2+}	8.6± 0.06	8.3± 0.06	8.8± 0.06	8.4± 0.05	8.9± 0.06	8.6± 0.04
	Cd^{2+}	9.1± 0.04	8.7± 0.04	9.2± 0.06	8.9± 0.05	9.5± 0.05	9.1± 0.05
	Hg^{2+}	9.4± 0.06	9.0± 0.05	9.5± 0.04	9.2± 0.04	9.7± 0.06	9.3± 0.04
	UO$_2$$^{2+}$	9.4± 0.05	9.1± 0.05	9.6± 0.06	9.3± 0.06	9.8± 0.04	9.5± 0.04
	Th^{4+}	9.6± 0.04	9.2± 0.04	9.8± 0.05	9.5± 0.04	10± 0.04	9.7± 0.06

Table 3. Thermodynamic functions for ML and ML$_2$ complexes of AN and PAN in 50% (v/v) methanol-water mixture in the presence 0.1M KCl.

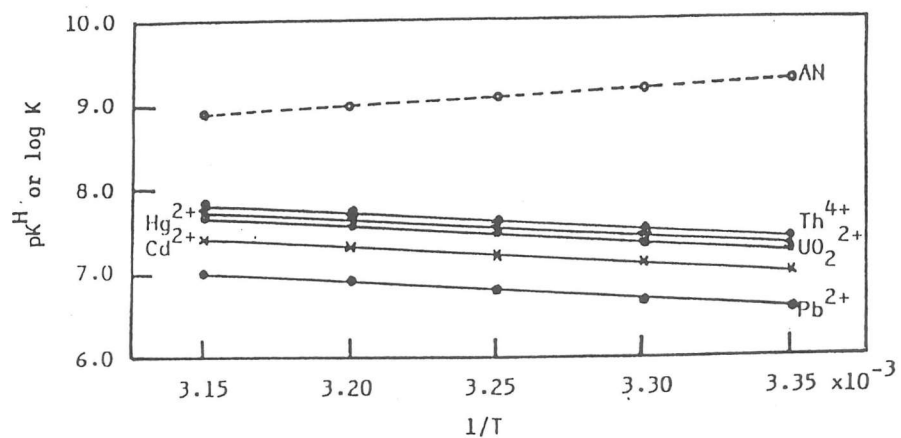| Compound	M^{n+}	Temp. (K)	Free Energy Change (k J mol^{-1})		Enthalpy Change (k J mol^{-1})		Entropy Change (J mol^{-1} K^{-1})	
			-ΔG$_1$	-ΔG$_2$	ΔH$_1$	ΔH$_2$	ΔS$_1$	ΔS$_2$
AN	Pb^{2+}	298	37.7	36.0	33.6	31.8	239.0	227.2
		308	40.0	38.2			238.9	227.0
		318	42.4	40.5			239.0	227.2
	Cd^{2+}	298	40.0	37.9	33.6	32.7	247.0	236.9
		308	42.5	40.2			247.0	236.6
		318	44.9	42.4			247.0	235.9
	Hg^{2+}	298	41.7	39.7	33.8	33.2	253.2	244.3
		308	44.1	42.4			252.9	245.3
		318	46.6	44.8			252.9	245.2
	UO$_2$$^{2+}$	298	41.8	40.2	37.2	37.1	264.9	259.5
		308	44.4	42.9			264.7	259.8
		318	46.9	45.3			264.3	259.1
	Th^{4+}	298	42.2	41.1	36.3	35.3	263.6	256.3
		308	44.7	43.5			263.1	255.9
		318	47.5	46.0			263.6	255.7
PAN	Pb^{2+}	298	48.8	47.1	35.3	33.6	282.3	250.8
		308	51.7	49.8			282.4	270.6
		318	54.4	52.6			282.3	270.8
	Cd^{2+}	298	51.6	49.6	39.1	38.5	304.4	295.9
		308	54.4	52.4			303.6	295.2
		318	57.7	55.2			304.4	294.7
	Hg^{2+}	298	53.4	51.1	34.5	35.3	294.7	289.9
		308	56.2	54.0			294.4	290.1
		318	59.2	56.9			294.7	289.9
	UO$_2$$^{2+}$	298	53.6	51.5	37.2	38.1	304.7	300.6
		308	56.6	54.6			304.5	300.7
		318	59.7	57.5			304.8	300.6
	Th^{4+}	298	54.7	52.5	39.8	41.7	317.1	315.9
		308	57.9	55.7			317.4	316.2
		318	61.0	58.8			317.1	316.0

Fig. 1. pK^H of AN and log K of metal-AN complexes vs. 1/T.
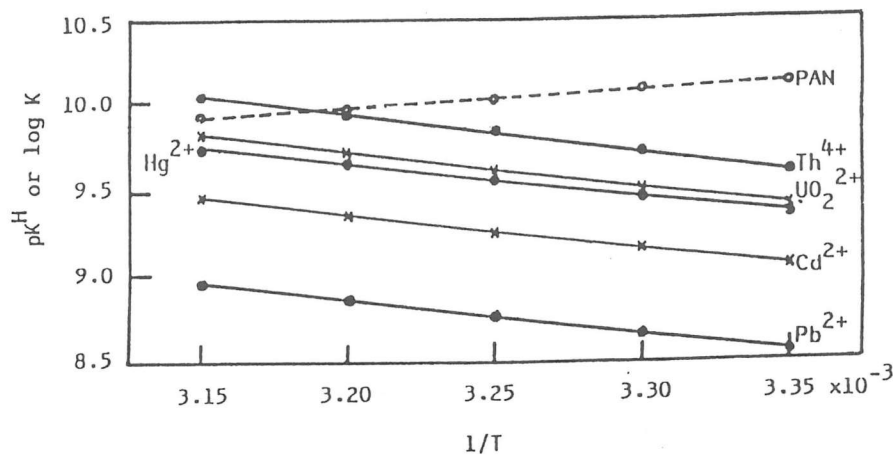
Fig. 2. pK^H of PAN and log K of metal-PAN complexes vs. 1/T.

[16]. Thus, examination 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 AN and PAN complexes increase with temperature in the case of Pb^{2+}, Cd^{2+}, Hg^{2+}, UO_2^{2+} and Th^{4+}; **(ii)** The negative values of ΔG for the complex formation of Pb^{2+}, Cd^{2+}, Hg^{2+}, UO_2^{2+} and Th^{4+} with AN and PAN suggest a spontaneous nature of such process; **(iii)** ΔH are positive for the complexation process of AN and PAN with Pb^{2+}, Cd^{2+}, Hg^{2+}, UO_2^{2+} and Th^{4+} and **(iv)** Positive ΔS for the complexation process of AN and PAN with Pb^{2+}, Cd^{2+}, Hg^{2+}, UO_2^{2+} and Th^{4+} confirm that the complex formation process is entropically favourable.

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EFFECT OF 1-BENZOYL-4-PHENYL-3-THIOSEMICARBAZIDE DERIVATIVES ON THE CORROSION INHIBITION OF COPPER IN NITRIC ACID

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ABSTRACT

The effect of 1-benzoyl-4-phenyl-3-thiosemicarbazide derivatives as inhibitors for the corrosion of copper in 3M HNO_3 acid has been studied using weight loss, galvanostatic polarization and C.V. techniques. The inhibition efficiency calculated from the three measurements are in good agreement and depends on the type and concentration of inhibitor. Application of Hammett equation supported the obtained results. The effect of temperature was studied over a temperature range 30-60°C using weight loss technique. The inhibitors appear to function through general adsorption following the Langmuir adsorption isotherm. Quantum calculations were performed to give a more general picture of the nature of corrosion inhibition.

Keywords: Copper, acid corrosion, Galvanostatic polarization, weight loss, 1-Benzoyl-4-Phenyl-3-thiosemicarbazide.

A large volume of literature exists on the use of organic compounds containing nitrogen, oxygen and/or sulphur functional groups, acting as inhibitors for the aqueous corrosion of metals such as aluminium, iron and copper[1-5]. The protection of metals against corrosion can be achieved either with inhibitors or with passivating agents[6]. The use of 2,4 dinitrophenylhydrazine as inhibitor for the corrosion of copper in sulphuric acid was studied by Siddagappo et al.[7] using weight loss and corrosion potential techniques. The inhibition effect of 3-benzamidorhodanine p- and o- substituted phenyl derivatives for copper corrosion in 3M HNO_3 acid solution was studied[8] by weight loss and galvanostatic polarization techniques. The rates of anodic dissolution of copper as well as hydrogen evolution in H_2SO_4 containing benzotriazoles were also examined[9] Inhibition effect of 1,5-diphenylcarbazide on the corrosion of copper in chloroacetic acids was also studied[10].