Article

Preparation, Characterization and Potentiometric Studies on N-P-Tolylacrylamide (TAA)

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Abstract: N-P-Tolylacrylamide (PTAA) was prepared and characterized using different spectroscopic techniques. Four different compositions of copolymers of N-P-Tolylacrylamide (TAA) with methyl methacrylate (MMA) covering the entire composition range were prepared and characterized. The reactivity ratios of copolymerization were determined using ¹H-NMR techniques. The proton-ligand dissociation constants of N-P-Tolylacrylamide (PTAA) and its metal stability constants with (Mn²⁺, Co²⁺, Ni²⁺ and Cu²⁺) have been determined potentiometrically in monomeric and polymeric forms using 2,2'-azobisisobutyronitrile as initiator. The potentiometric studies were carried out in 0.1 mol.dm⁻³ (KCl) and 10 % (by volume) methanol-water mixture. The effect of temperature was studied at (298, 308 and 318 K) and the corresponding thermodynamic parameters (ΔG , ΔH and ΔS) 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: N-p-tolylacrylamide, Polymer, Stability constants, Thermodynamic.

1. Introduction

Potentiometric titrations were carried out, first to precisely measure the acid-base properties of the polymer,

and secondly to determine the stability constants of the complex species formed [1]. Potentiometric titration has been widely used to assess these interactions and changes, especially for linear polyelectrolytes in solution with their own counterions and also with those coming from a simple 1:1 salt added to the aqueous system [2-4]. For example, Mandel [4] has studied simultaneously the influence of the degree of dissociation (ca. $0.05 < \alpha < 0.85$) and the NaCl concentration (in the range from 0 to 0.1 mol 1⁻¹) on the apparent dissociation constant (pK_a) of poly(acrylic acid) by potentiometry and found that the value of pKa increased steadily with α and decreases with increasing salt concentration. Potentiometric analysis of polymeric solutions containing counterions of different valences has, on the other hand, received much less attention [5-7]. Ishikawa [5], for instance, has measured the change in pK of poly(acrylic acid) in the presence of Na and the divalent counterion quaternized ethylenediamine. Zhang and Nilsson [6] have studied the pH dependence of the conformational transition of poly(glutamic acid). Both of these contributions used the solution of the Poisson-Boltzmann equation in the cylindrical coordinates to interpret their results, assuming only electrostatic interactions between the polyelectrolyte and the low molecular ions in the solution. Marinski and Reddy [7] have studied the potentiometric titration of poly(acrylic acid) and poly(methacrylic acid) in the presence of an excess amount of 1:1 salt and trace concentrations of cobalt and zinc ions. Potentiometric titrations used (synthetic) polyelectrolyte poly-(acrylic acid), in solutions with different concentrations of added 2:1 simple salt cadmium nitrate, were performed with potassium hydroxide as the titrating solution. If binding of the divalent counterions occurs, it should modify the system in two important ways: (i) changing, i.e. lowering, the effective charge density of the polyelectrolytic chain and, (ii) decreasing the ionic strength of the bulk solution by the elimination of the divalent ions due to the binding process. In order to interpret the experimental results, we make use of the assumption that complete charge compensation of the polyion occurs due to chemical binding of the divalent counterions to the (ionized) polyion binding sites as was proposed for the Cu/poly(methacrylic acid) system [8].

As a part of our continuous work reporting on the determination of dissociation and stability constants of some organic compounds and their metal complexes by potentiometric techniques [9-12], we report here the proton-ligand dissociation constants of N-P-Tolylacrylamide (PTAA) and its metal stability constants with (Mn²⁺, Co²⁺, Ni²⁺ and Cu²⁺) in monomeric and polymeric forms. Furthermore, the corresponding thermodynamic functions are evaluated and discussed.

2. Experimental

2.1. Materials

All the compounds and solvents used were purchased from Aldrich or Sigma and used as received without further purification. Acryloyl chloride was used without further purification. It was stored below -18 °C in a tightly glass-stoppered flask. 2,2'-Azobisisobutyronitrile (AIBN) was used as initiator for all polymerizations. It was purified by dissolving it in hot ethanol and left to cool. The pure material was being collected by filtration and then dried [13].

2.2. Preparation of the monomer N-P-Tolylacrylamide

N-P-Tolylacrylamide (PTAA) (Fig. 1) was prepared by the reaction of equimolar amounts of AC and P-toludinein ice bath and dry benzene (50/50 V/V) until the evolution of hydrogen chloride ceased forming a powder of TAA monomer, which was collected by filtration.



Fig. 1. Proposed structure of the ligand TAA.

2.3. Potentiometeric Studies

N-P-Tolylacrylamide solution (0.001 mol.dm⁻³) was prepared by dissolving an accurate weight of the solid in ethanol (AnalaR). Metal ion solutions (0.0001 mol.dm⁻³) were prepared from AnalaR metal chlorides in bidistilled water and standardized with EDTA [14]. Solutions of 0.001 mol.dm⁻³ (HCl) and 1 mol.dm⁻³ (KCl) were also prepared in bidistilled water. A carbonate-free sodium hydroxide solution in a 10 % (by volume) ethanol-water mixture was used as titrant and standardized against oxalic acid (AnalaR).

The apparatus, general conditions and methods of calculation were the same as previously reported [9-12]. The following mixtures (i)-(iii) were prepared and titrated potentiometrically at 298 K ,308, and 318 K, respectively against standard 0.002 mol.dm⁻³ (NaOH) in a 10 % (by volume) ethanol-water mixture:

- i) $5 \text{ cm}^3 0.001 \text{ mol.dm}^{-3} (\text{HCl}) + 5 \text{ cm}^3 1 \text{ mol.dm}^{-3} (\text{KCl}) + 5 \text{ cm}^3 \text{ ethanol.}$
- ii) $5 \text{ cm}^3 0.001 \text{ mol.dm}^{-3} (\text{HCl}) + 5 \text{ cm}^3 1 \text{ mol.dm}^{-3} (\text{KCl}) + 5 \text{ cm}^3 0.001 \text{ mol.dm}^{-3} \text{ ligand.}$
- iii) 5 cm³ 0.001 mol.dm⁻³ (HCl) + 5 cm³ 1 mol.dm⁻³ (KCl) + 5 cm³ 0.001 mol.dm⁻³ ligand + 10 cm³ 0.0001 mol.dm⁻³ metal chloride.

For each mixture, the volume was made up to 50 cm³ with bidistilled water before the titration. The titrations also were carried out in the presence of 5 ml of AIBN (0.001 M) as initiator for the polymerization step. These titrations were repeated for temperatures of 308 and 318 K. All titrations have been carried out between pH 3.0 and 11.0.

2.4. Measurements

Spectroscopic data were obtained using the following instruments: FT-IR spectra (KBr discs, 4000-400 cm-1) by Jasco-4100 spectrophotometer; the ¹H NMR spectra by Bruker WP 300 MHz using DMSO-d⁶ as a solvent containing TMS as the internal standard. The pH measurements were carried out using VWR Scientific Instruments Model 8000 pH-meter accurate to \pm 0.01 units. The pH–meter readings in the non–aqueous medium were corrected [15]. The electrode system was calibrated according to the method of Irving et al. [16]. Titrations were performed in a double walled glass cell in an inert atmosphere (nitrogen) at ionic strength of 0.1 M KCl. Potentiometric measurements were carried out at different temperature. The temperature was controlled to within \pm 0.05 K by circulating thermostated water (Neslab 2 RTE 220) through the outer jacket of the vessel.

3. Results and Discussion

3.1. Characterization of Ligand

3.1.1. IR spectra

The IR spectrum of TAA monomer exhibits a band at ~ 1664 cm⁻¹ is assigned to the antisymmetric stretching vibration of amidic carbonyl group. The bands at 1606, 1508 and 1411cm⁻¹ are assigned to the v(C-H), v(C=C) and v(C-C) bands, respectively [17]. The bands in the region 1249-1070 cm⁻¹ are due to the C-H in plane deformation, while the out-of-plane deformation vibration between 985-750 cm⁻¹.

3.1.2. ¹H NMR spectra

¹H-NMR spectrum of monomer exhibits a peak at 7.94 ppm is due to NH proton, bands at 2.23 and 2.729 ppm are due to CH₂ and CH protons and a peak at 7.06 ppm is due to phenyl protons.

3.2. Proton-ligand stability constants

The average number of the protons associated with the reagent molecule, n_A , was determined at different pH values applying the following eq 1:

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

where *Y* is the number of available protons in TAA (Y=1) and V_1 and V_2 are the volumes of alkali required to reach the same pH on the titration curve of hydrochloric acid and reagent, respectively, V° is the initial volume (50 cm³) of the mixture, TC°_L is the total concentration of the reagent, N° is the normality of the sodium hydroxide solution and E° is the initial concentration of the free acid. The titration curves (\bar{n}_A vs pH) for the proton-ligand systems were constructed and found to extend between 0 and 1 on the \bar{n}_A scale. This means that TAA has one dissociable protons (the hydrogen ion of the -NH, pK^H, Different computional methods [18] were applied to evaluate the dissociation constants. Three replicate titrations were performed; the average values obtained are listed in Table 1.

The PTAA has a lower acidic character (higher pK values) than TAA. the vinyl group (H₂C=CH) in monomeric form will decrease the electron density, and hence reduce the N–H and O–H bond On the other hand, the absence of vinyl group in polymeric form (PTAA) retard the removal of the ligand protons and increase thebasicity (higher pK^{H} values).

| Compound | Temp. K | Dissociation constant pK ^H | Free energy change kJ mol ⁻¹ Δ G | Enthalpy change kJ mol ⁻¹ Δ H | Entropy change J mol ⁻¹ K ⁻¹ - Δ S |
|----------|------------|---|---|--|--|
| ТАА | 298 | 5.82 | 33.21 | 19.05 | 47.51 |
| | 308 | 5.74 | 33.85 | | 48.05 |
| | 318 | 5.61 | 34.16 | | 47.51 |
| РТАА | 298 | 6.17 | 35.21 | 29.06 | 54.21 |
| | 308 | 5.99 | 35.32 | | 52.84 |
| | 318 | 5.85 | 35.62 | | 52.11 |

Table 1. Thermodynamic functions for the dissociation of TAA and PTAA in 10 % (by volume) ethanolwater mixture in the presence of 0.1 mol.dm⁻³ KCl at different temperatures.

3.3. Metal-ligand Stability Constants

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ions (\overline{n}) versus the free ligand exponent (pL), according to Irving and

Rossotti [19]. The average number of the reagent molecules attached per metal ion, n, and free ligand exponent, pL, can be calculated using the eqs 2 and 3:

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

and

$$pL = \log_{10} \frac{\sum_{n=0}^{n=J} \beta_n^H \left(\frac{1}{[H^+]} \right)^n}{TC_L^o - \bar{n}.TC_M^o} \cdot \frac{V^o + V_3}{V^o}$$
(3)

where TC°_{M} is the total concentration of the metal ion present in the solution, $\beta^{H_{n}}$ is the overall protonreagent stability constant. V_{1} , V_{2} and V_{3} are the volumes of alkali required to reach the same pH on the titration curves of hydrochloric acid, organic ligand and complex, respectively. These curves were analyzed and the successive stability constants were determined using different computional methods [20, 21]. The values of the stability constants (log K₁ and log K₂) are given in Table 2. The following general remarks can be achieved:

- i) The maximum value of \overline{n} was ~ 1 indicating the formation of 1:1 (metal:ligand) complexes only [22].
- ii) The metal ion solution used in the present study was very dilute (2 x 10⁻⁵ mol.dm⁻³), hence there was no possibility of formation of polynuclear complexes [23,24].
- iii)The metal titration curves were displaced to the right-hand side of the ligand titration curves along the volume axis, indicating proton release upon complex formation of the metal ion with the ligand. The large decrease in pH for the metal titration curves relative to ligand titration curves point to the formation of strong metal complexes [25,26].
- iv) For all the complexes, the stability constants of PAAS are higher than AAS. This is quite reasonable because the ligand in polymeric forms are better complexing agent [12].
- v) For the same ligand at constant temperature, the stability of the chelates increases in the order Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺ [27-29]. This order largely reflects that the stability of Cu²⁺ complexes are considerably larger as compared to other metals of the 3d series. Under the influence of both the polarizing ability of the metal ion [30] and the ligand field [31], Cu²⁺ will receive some extra stabilization due to tetragonal distortion of octahedral symmetry in its complexes. The greater stability of Cu²⁺ complexes is produced by the well-known Jahn–Teller effect [32].

| | n+ | log K ₁ | | | log K ₂ | | |
|-------|--------------------|--------------------|-------|-------|--------------------|-------|-------|
| Comp. | М — | 298 K | 308 K | 318 K | 298 K | 308 K | 318 K |
| TAA | Mn^{2+} | 4.99 | 5.25 | 5.39 | 4.07 | 4.3 | 4.58 |
| | Co^{2+} | 5.1 | 5.31 | 5.43 | 4.13 | 4.43 | 4.46 |
| | Ni ²⁺ | 5.22 | 5.43 | 5.57 | 4.28 | 4.5 | 4.76 |
| | Cu^{2+} | 5.31 | 5.52 | 5.63 | 4.36 | 4.65 | 4.82 |
| PTAA | Mn^{2+} | 5.56 | 5.87 | 6.01 | 5.03 | 5.71 | 5.93 |
| | Co^{2+} | 5.69 | 6.00 | 6.24 | 5.28 | 5.84 | 6.12 |
| | Ni ²⁺ | 6.05 | 6.19 | 6.39 | 5.31 | 5.99 | 6.30 |
| | Cu^{2+} | 6.18 | 6.32 | 6.46 | 5.46 | 6.04 | 6.52 |

Table 2. Stepwise stability constants for ML complexe of TAA and PTAA in 10 % (by volume) ethanolwater mixture in the presence of 0.1 mol.dm⁻³ KCl at different temperatures.

3.4. Effect of Temperature

The dissociation constant (pK^{H}) for TAA and PTAA as well as their stability constants of Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} complexes have been evaluated at (298, 308 and 318) K, and are given in Tables 1 and 2. The enthalpy change (ΔH) for the dissociation and complexation process was calculated from the slope of the plot pK^{H} or log K vs. $^{1}/_{T}$ using the graphical representation of the van't Hoff eqs 4 and 5:

$$\Delta G = -2.303 RT \log K = \Delta H - T \Delta S$$
(4)

or

$$\log K = (-\Delta H/2.303R)(1/T) + (\Delta S/2.303R)$$
(5)

From the ΔG and ΔH values one can deduce the ΔS using the well-known relationships 4 and 6:

$$\Delta S = \left(\Delta H \cdot \Delta G\right) / T \tag{6}$$

where $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ is the gas constant, K is the dissociation constant for the ligand or the stability constant of the complex, and T is absolute temperature.

All thermodynamic parameters of the dissociation process of N-P-Tolylacrylamide (PTAA) are recorded in Table 1. From these results the following conclusions can be made:

i) The pK^H values decrease with increasing temperature, i.e., the acidity of the ligand increase.

- ii) A positive value of ΔH indicates that the process is endothermic.
- 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 the solvation process.

All the thermodynamic parameters of the stepwise stability constants of complexes are recorded in Table 1 & Table 3.

| | | | Gibbs energy | | Enthalpy | | Entropy | |
|-------|----------------------------|-----|------------------------|--------------------------|------------------------|--------------|---------------------------------------|--------------|
| Comp. | $\mathbf{M}^{\mathrm{n+}}$ | T/K | / kJ mol ⁻¹ | | / kJ mol ⁻¹ | | / J mol ⁻¹ K ⁻¹ | |
| | | | - <i>ΔG</i> 1 | - <i>ΔG</i> ₂ | ΔH_1 | ΔH_2 | ΔS_{l} | ΔS_2 |
| | Mn ²⁺ | 298 | 28.47 | 23.23 | 36.20 | 46.20 | 217.02 | 265.16 |
| | | 308 | 30.96 | 25.36 | | | 218.05 | 150.00 |
| | | 318 | 32.82 | 27.89 | | | 217.04 | 145.28 |
| | Co^{2+} | 298 | 29.09 | 23.56 | 2987 | 30.00 | 197.88 | 179.74 |
| | | 308 | 31.31 | 26.13 | | | 198.65 | 182.22 |
| TAA | | 318 | 33.06 | 27.16 | | | 197.90 | 179.73 |
| | Ni ²⁺ | 298 | 29.78 | 24.421 | 31.81 | 43.49 | 206.69 | 227.88 |
| | | 308 | 32.02 | 26.54 | | | 207.24 | 227.36 |
| | | 318 | 33.91 | 28.98 | | | 206.68 | 227.90 |
| | Cu^{2+} | 298 | 30.30 | 24.88 | 29.12 | 41.84 | 199.38 | 223.88 |
| | | 308 | 32.55 | 27.42 | | | 200.23 | 224.87 |
| | | 318 | 34.28 | 29.35 | | | 199.37 | 223.86 |
| | 2. | | | | | | | |
| | Mn^{2+} | 298 | 31.73 | 28.70 | 40.86 | 81.97 | 243.57 | 371.38 |
| | | 308 | 34.62 | 33.67 | | | 245.06 | 375.47 |
| | | 318 | 36.59 | 36.11 | | | 243.56 | 371.31 |
| | Co^{2+} | 298 | 32.46 | 30.13 | 49.95 | 76.37 | 276.56 | 357.37 |
| PTAA | | 308 | 35.38 | 34.44 | | | 277.06 | 359.77 |
| | | 318 | 37.99 | 37.26 | | | 276.55 | 357.34 |
| | Ni ²⁺ | 298 | 34.52 | 30.29 | 30.78 | 89.81 | 219.13 | 403.05 |
| | | 308 | 36.50 | 35.32 | | | 218.45 | 406.28 |
| | | 318 | 38.91 | 38.36 | | | 219.14 | 403.05 |
| | Cu^{2+} | 298 | 35.26 | 31.15 | 25.39 | 96.23 | 203.53 | 136.83 |
| | | 308 | 37.27 | 35.62 | | | 203.45 | 146.88 |
| | | 318 | 39.34 | 39.69 | | | 203.53 | 155.09 |

Table 3. Thermodynamic functions for ML complexe of TAA and PTAA in 10 % (by volume) ethanol-water mixture and 0.1 mol.dm⁻³ KCl.

It is known that the divalent metal ions exist in solution as octahedrally hydrated species [21] and the obtained values of ΔH and ΔS can then be considered as the sum of two contributions: (a) release of H₂O molecules, and (b) metal-ligand bond formation. Examination of these values shows that:

- i) The stability constants (log K₁ and log K₂) for ligand complexes increases with increasing temperature,
 i.e., the stability constants increase with increasing temperature [33].
- ii) The negative value of ΔG for the complexation process suggests the spontaneous nature of such processes [34].
- iii) The ΔH values are positive, meaning that these processes are endothermic and favourable at higher

temperature.

iv) The ΔS values for the ligand complexes are positive, confirming that the complex formation is entropically favourable [10].

4. Conclusion

N-P-Tolylacrylamide (PTAA) was prepared and characterized using different spectroscopic techniques. The protonation constants (pK₁ and pK₂) of the TAA and PTAA were determined by Irving-Rossetti pH titration technique. Also metal-ligand stability constants of their complexes with metal ions (Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+}) have been determined potentiometrically. It appears that PTAA are better complexing agent with metal ions compared to TAA with the order: Mn(II) < Co(II) < Ni(II) < Cu(II). The corresponding thermodynamic parameters (ΔG , ΔH and ΔS) 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.

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