

Study of Complex Formation Constants for Some Cations With O-Phenylenediamine in Binary Systems Using Square Wave Polarography Technique

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Abstract

The formation of metal cation complexes between o-phenylenediamine with metal ions, Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} and Cr^{3+} were studied in the dimethylformamide/water (DMF/ H_2O), acetonitrile/water (AN/ H_2O) and ethanol/water (EtOH/ H_2O) binary systems using square wave polarography (SWP) technique. The stoichiometry and stability of the complexes were determined by monitoring the shifts in half-waves or peak potentials of the polarographic waves of metal ions against the ligand concentration. In the most cases, the formation constants of complexes decreased with increasing amounts of H_2O , DMF and EtOH in AN/ H_2O , DMF/ H_2O and EtOH/ H_2O binary systems, respectively. The stoichiometry of the complexes was found 1:1. The results obtained show that there is an inverse relationship between the formation constant of the complexes and the donor number of the solvents based on the Gattmann donocity scale. Also, the stability constants show a high sensitivity to the composition of the mixed solvent systems. In most of the systems investigated, Cr^{3+} cation forms a more stable complex with o-phenylenediamine than other four cations and the order of selectivity of this ligand for cations in pure water is: $\text{Cr}^{3+} >> \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Pb}^{2+}$.

Keywords: Complex Formation Constant, SWP, Stoichiometry, Cations, Binary System

1. Introduction

Polarographic investigations of chemical substances are not restricted to the measurements in aqueous solution. Some inorganic polarography in non-aqueous solvents has received increasing attention. Polarographic study of metal ions viz. cobalt, lithium, lead, cadmium etc. in various organic solvents have been carried out by many research groups [1,2].

The study of the metal complexes in non-aqueous solvents by polarographic methods has attracted much attention by researchers. Nature of the solvent has a considerable influence on the composition and stability of complexes formed (Turyan and Chebotar, 1959). Lane and co-workers (Lane, 1960) made a polarographic study of the complexes of lead, cadmium and copper with thiourea and its alkyl derivatives. Turyan and his collaborators studied halides and thiocyanate complexes of lead and cadmium ion in various solvents and observed a linear relationship between values of pK for the complex and the inverse of the dielectric constants. Polarographic

studies of complexes in methanol and ethanol by Migal *et al.* and others have shown that there is a sharp increase in the stability of complexes above 20% concentration which they attributed to the solvation effect. Polarographic investigations of lead, cadmium and zinc in dimethylformamide are done by many workers (Fujinaga and Puri, 1974; Sharma *et al.*, 1975; Sharma *et al.*, 1975). Different workers in this field have obtained different results. Thus it is a need for systematic study of the influence of aqueous organic solvent mixtures on complex formation [3]. For the purpose we investigated some cations with o-phenylenediamine complexes in aqueous mixtures of dimethylformamide (DMF), acetonitrile (AN) and ethanol (EtOH). The goal of many studies involving complex formation in mixed solvent systems has been to investigate the effect of solvent composition on the stability and nature of the complex formed [4]. There is well known that the selectivity of the complexation is normally strongly dependent on the solvating ability of the solvent with respect to the cation and the ligand [5-7].

As a result, variations in the nature of the solvent produce significant changes in the binding properties of the ligand [8]. Various physicochemical methods have been used to obtain the stability constants of complexes [9-10]. Of the various techniques polarography has proved to be a useful means for investigation of both the stoichiometry and stability of complexes. Due to the higher speed, higher resolution and also low consumption of mercury in SWP, we preferred to use this technique for the present investigation. In the present work we investigated the effects of the solvent properties on the selectivity and stability of complexes of o-phenylenediamine with Zn^{2+} , Ni^{2+} , Cu^{2+} , Pb^{2+} and Cr^{3+} metal cations in DMF/H₂O, EtOH/H₂O and AN/H₂O binary systems using the square wave polarographic technique.

2. Experimental Section

2.1. Reagents and Solvent

Reagent grade o-phenylenediamine (o-PDA), potassium nitrate(KNO₃), zinc(II)nitrate, copper(II)nitrate, lead (II)nitrate, nickel(II)nitrate, chromium(III)nitrate (all from Merck) and mercury were used without further purification. The organic solvents, dimethylformamide, ethanol and acetonitrile (all from Merck) and also distilled water with the highest purity, were used for the preparation of the desired mixed solvents. The nitrogen gas was purchased from Sabalan Co, Tehran, Iran.

2.2. Apparatus

The polarographic measurements, were carried out on a 797 VA Computrace Polarographic Analyzer (Metrohm) with a hanging mercury drop electrode (HMDE) in a three electrode arrangement. An Ag/AgCl electrode with a bridge containing the base electrolyte as the electrolyzed solution was employed. The auxiliary electrode was a Pt wire. A solution of 0.025 M potassium nitrate was used as the base electrolyte. The distilled water apparatus was local made set.

The instrumental parameters were voltage step, 5 mV; pulse amplitude, 20 mV; equilibration time, 5 s; sweep rate, 251.8 mV/s; frequency, 50 Hz for the SWP technique.

2.3. Procedure

A solution 0.025 M of supporting electrolyte(KNO₃) and 0.1 mM of metal salt in a polarographic cell was de-aerated by a stream of nitrogen gas (99.999%) for 5.0 min; and the half-wave potential of the solution was measured, then the addition of ligand was performed in separate steps to form the desirable concentration of the

ligand in the solution .

3. Results and Discussion

In polarographic investigations, the significant quantity for studying the formation constant of metal ion complexes is the half-wave potential ($E_{1/2}$) or the differential pulse peak potential (E_p) of the complex and the free metal ion. The difference in $E_{1/2}$ or E_p between the complex and the metal ion is used in the calculation of the stability constant of the complexes [11-14]. The reaction between o-PDA with Zn^{2+} , Ni^{2+} , Cu^{2+} , Pb^{2+} and Cr^{3+} was studied in DMF/H₂O, EtOH/H₂O and AN/H₂O binary mixtures of various compositions. We used H₂O as the solvating solvent for the ligand. In general, the addition of ligand to Zn^{2+} , Ni^{2+} , Cu^{2+} , Pb^{2+} and Cr^{3+} solutions in 0.025 M KNO₃ shifts the reduction potential (E_p) of the metal ions toward more negative values. As an example, the square wave polarograms of Zn^{2+} ion in the presence of different concentrations of o-phenylenediamine in one of the DMF/H₂O binary systems is shown in **Figure 1**.

Lingane [13] derived the following relationship between concentrations of ligand (L) and shift in half-wave potential to calculate the formation constants of the cation and ligand :

$$\Delta E_{1/2} = (E_{1/2})_C - (E_{1/2})_M = -(RT/nF) (\ln K_f + p \ln [L]_i) \quad (1)$$

where $(E_{1/2})_M$ and $(E_{1/2})_C$ are the half-wave potentials of free and complexed metal ion, respectively, n is the number of electrons transferred for reduction, $[L]_i$ is the analytical concentration of the ligand, K_f is the complex formation constant and m is the molar ratio of complexing agent to cation. Different experimental techniques such as potentiometric, voltammetric [14], or spectrophotometric [10] techniques are reported in the scientific literature for the measurements of K_f . In this study, the shift of the half-wave potential is measured as mentioned in electrochemistry textbooks. Effect of complexing agent on polarographic half wave potentials at the dropping mercury electrode is applicable whenever the electron transfer is reversible.

The value of K_f and p can be obtained from the intercept and slope of the linear plots of $\Delta E_{1/2}/(RT/nF)$ vs $\log [L]_i$, respectively. In most of the binary mixed solvent systems used in this investigation, addition of the o-PDA ligand to the cation solutions in the presence of KNO₃ shifts the reduction potential of the metal ions towards a more negative value (**Figure 1**).

In **Figure 1** the difference between the half-wave potentials of the free and complexed metal ion is a measure of the complex stability. The more stable the complex between the ligand and a cation the more negative shift of potential is needed for reduction at the surface of the electrode. In the all cases, the cyclic voltametric result

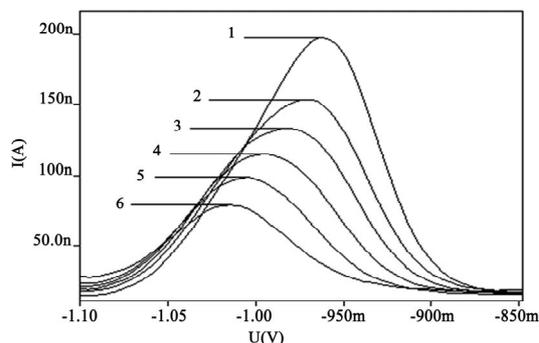


Figure 1. The square wave polarograms of 0.1 mM Zn^{2+} ion in a DMF/ H_2O (60% DMF + 40% H_2O) binary system with different concentration of o-PDA ligand: (1) 0, (2) 0.19, (3) 0.25, (4) 0.3, (5) 0.35 and (6) 0.39 mM.

show that the reductions of Zn^{2+} , Ni^{2+} , Cu^{2+} , Pb^{2+} and Cr^{3+} in the presence of the ligand are reversible. The cyclic voltamogram (CV) of the Zn^{2+} cation ion in the presence of o-PDA in DMF/ H_2O , EtOH/ H_2O and AN/ H_2O binary systems is shown in **Figure 2**. The peak potentials in **Figure 2** shows a reversible polarogram for this study. The Similar polarograms were obtained for the other systems (not shown).

As an example, the variations in $\Delta E_{1/2}/(RT/nF)$ as a function of $\log [o-PDA]_t$ for the complex formation between o-PDA and Cu^{2+} ion in DMF/ H_2O binary systems is shown in **Figure 3**.

The slope of the linear plots in **Figure 3** gave a value of $m = 1$, in agreement with the formation of a 1:1 complex between Zn^{2+} ion and o-PDA in the solution the similar behaviors were observed for the other systems. The formation constants of complexes were obtained by fitting the polarographic data to Equation (1).

From **Table 1**, it is seen that the stability of the complexes of these metal ions with o-PDA decreases in the order of $Cr^{3+} \gg Cu^{2+} > Ni^{2+} > Zn^{2+} > Pb^{2+}$ in pure water system used in this study.

The stability of a complex formed in a solution

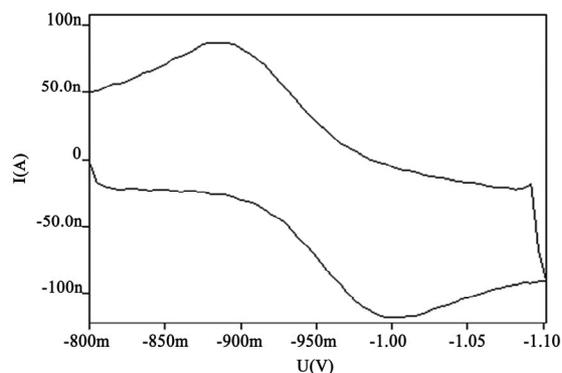


Figure 2. The cyclic voltamogram of the Zn^{2+} in the presence of o-PDA in a DMF- H_2O binary system.

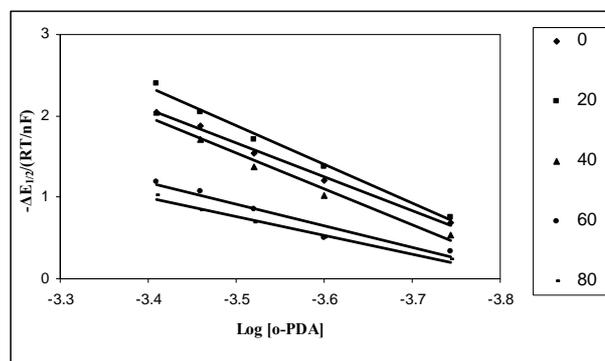


Figure 3. The linear plots of $E_{1/2}/(RT/nF)$ vs. $\log[o-PDA]_t$ for the Cu^{2+} -o-PDA complex in different DMF/ H_2O binary mixtures. The curves show: (♦) 0, (■) 20, (▲) 40, (●) 60 and (○) 80 % (v/v) of the solvents.

strongly depends on the nature of the solvent medium. During the complexation step, the ligand should be able to replace the solvent molecules as completely as possible in the first solvation shell of cation, or the cation should be able to replace the solvent molecule with the ligand [15]. Therefore, the variation of the solvent produces a significant change in the binding properties and selectivity of the ligand for a certain cation over the others. As is evident from **Table 1**, in the most cases there is an inverse relationship between the formation constant of the complexes and the donor number of solvents based on a Gattmann donocity scale. The variation of the formation constants of the o-PDA complexes with Zn^{2+} , Ni^{2+} , Cu^{2+} , Pb^{2+} and Cr^{3+} cations as a function of solvent composition in a AN/ H_2O binary systems is shown in **Figure 4**.

As is evident from **Table 1**, in general the stability of all complexes decreases with an increasing concentration of DMF in a DMF/ H_2O and H_2O in a AN/ H_2O binary systems. Also in the most complexes formation constants decreases with an increasing concentration of EtOH in a EtOH/ H_2O binary system (**Table 1**). The solvating ability

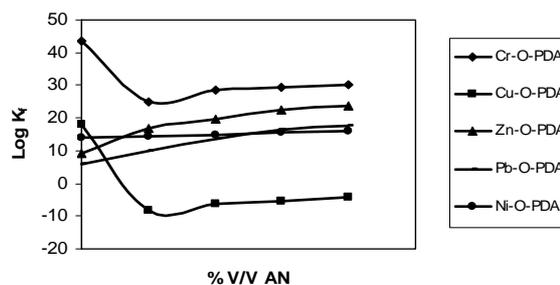


Figure 4. The variation of stability constants of different metal ion complexes of o-PDA in AN/ H_2O binary systems. The curves show: (♦) Cr^{3+} -o-PDA; (■) Cu^{2+} -o-PDA; (▲) Zn^{2+} -o-PDA; (○) Pb^{2+} -o-PDA and (●) Ni^{2+} -o-PDA, complexes.

Table 1. The Log K_f Values of Zn^{2+} , Ni^{2+} , Cu^{2+} , Pb^{2+} and Cr^{3+} complexes with o-PDA in the binary solvent mixtures.

Medium	Solvent Composition		Log $K_f \pm RSD^a$				
	V/VH ₂ O%		Ni ²⁺	Cr ³⁺	Zn ²⁺	Cu ²⁺	Pb ²⁺
EtOH/H ₂ O	100		13.9±0.02	43.50±0.03	9.00±0.03	17.98±0.07	6.00±0.01
	80		12.70±0.01	35.70±0.02	12.00±0.04	21.80±0.06	7.10±0.07
	60		8.27±0.02	11.00±0.03	10.91±0.02	21.00±0.05	7.10±0.03
	40		6.20±0.03	4.30±0.05	10.40±0.80	20.70±0.03	9.25±0.03
	20		7.60±0.07	-21.27±0.02	3.22±0.05	20.20±0.00	13.90±0.04
AN/H ₂ O	100		13.90±0.02	43.50±0.03	9.00±0.03	17.98±0.07	6.00±0.01
	80		14.50±0.02	24.78±0.04	17.00±0.02	-8.17±0.02	9.80±0.02
	60		14.96±0.01	28.41±0.02	19.70±0.05	-6.07±0.02	13.39±0.01
	40		15.51±0.03	29.24±0.09	22.40±0.04	-5.45±0.02	16.40±0.02
	20		16.80±0.02	30.24±0.06	23.50±0.03	4.15±0.02	17.50±0.02
DMF/H ₂ O	100		13.9±0.02	43.50±0.03	9.00±0.03	17.98±0.07	6.00±0.01
	80		6.30±0.03	24.40±0.03	9.40±0.01	20.93±0.05	0.00±0.00
	60		-7.02±0.08	17.00±0.05	20.00±0.02	18.20±0.01	-4.90±0.05
	40		-4.45±0.05	12.00±0.02	17.49±0.04	11.00±0.02	-17.44±0.02
	20		-26.00±0.04	4.80±0.1	7.30±0.1	8.20±0.03	-24.00±0.05

^aRelative standard derivation (n = 3)

of the solvent, as expressed by the Guttmann donicity scale, plays a fundamental role in the complexation reactions [14]. The donor number is nearly a molecular property of the solvent, which is easily determined by experiment. It expresses the total amount of interaction with an acceptor molecule, including contribution both by dipole-dipole or dipole-ion interactions and by the binding effect caused by the availability of the free electron pair; to some extent steric properties of the solvent molecules may be contained in it. Thus the donor number is considered a semi quantitative measure of solute solvent interactions. It is recognized that no allowance has been made for specific interactions between certain individual donor-accepter species. Such refinements are currently impossible owing to a lack of knowledge, and indeed of experimental data, as to the precise nature of such specific interactions. In a weak solvating solvent such as AN, which has a low Guttmann donicity (DN = 14), the solvation of the metal cations and possibly of the ligand should be weaker than in solvents with a strong solvating ability such as for DMF (DN = 26.6), EtOH (DN = 19) and H₂O (DN = 18). Therefore, less energy is necessary for the desolvation step of the Zn²⁺, Ni²⁺, Cu²⁺, Pb²⁺ and Cr³⁺ cations and probably of the ligand during the complex formation in the case of AN than in H₂O. Also, the low formation constants can be explained by hydrogen bonding between water and the ligand in the organic/water binary mixtures, where the ligand is not free to form the complex with the cations.

It is interesting to note that a non-linear behavior is observed for variation of the stability constant (log K_f) of complexes versus the composition of AN/H₂O binary systems. As it is evident from **Figure 4**, when the con-

centration of AN increases, the stability constants of complexes first decrease suddenly, and then increase gradually after about 20% of AN. This behavior may be due to some kind of solvent-solvent interactions between these protic and aprotic solvents when they are mixed with one another or it may be due to preferential solvation of the cations in these binary systems. In some cases, as seen from **Table 1** the value of K_f decreases and irreversibility increases in acetonitrile in comparison to water. Since the value of dielectric constant of solvent is very low and again viscosity also decreases regularly, the shifts of $E_{1/2}$ to more positive values and the change of i_d can be best explained on the basis of solvation and viscosity [15-17].

4. Conclusions

The results obtained show that there is an inverse relationship between the formation constant of the complexes and the donor number of the solvents based on the Guttmann donicity scale. The results show that, the stability of all complexes decreases with an increasing concentration of DMF in DMF/H₂O, water in AN/H₂O and EtOH in EtOH/H₂O binary systems. The stoichiometry of the complexes was found 1:1. As it is seen from the results, in the mixed solvent systems used in this study, the stability of complexes of the metal cations with o-phenylenediamine decreases in the order of Cr³⁺ >> Cu²⁺ > Ni²⁺ > Zn²⁺ > Pb²⁺. Also, a non-linear behavior is observed for variation of the stability constant (log K_f) of some complexes versus the composition of AN/H₂O binary systems. This behavior may be due to some kind of solvent-solvent interactions between these protic and

aprotic solvents when they are mixed with one another or it may be due to preferential solvation of the cations in these binary systems

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