

Full Research Paper

## A Study of Complexation-ability of Neutral Schiff Bases to Some Metal Cations

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**Abstract:** The constants of the extraction equilibrium and the distribution for dichloromethane as an organic solvent having low dielectric constant of metal cations with chiral Schiff bases, benzaldehyde-(S)-2-amino-3-phenylpropanol (**I**), o-hydroxybenzaldehyde-(S)-2-amino-3-phenyl-propanol (**II**), benzaldehyde-(S)-2-amino-3-methylbutanol (**III**) with anionic dyes [4-(2-pyridylazo)-resorcinol mono sodium monohydrate (NaPar), sodium picrat (NaPic) and potassium picrat (KPic)] and some heavy metal chlorides were determined at 25 °C. All the ligands have given strongest complexation for NaPar. In contrast, similar behaviour for both alkali metal picrates is not apparent in the complexation of corresponding ligands.

**Keywords:** Chiral Schiff bases, Extraction, Alkali metal picrates, Anionic dyes, Spectroscopy.

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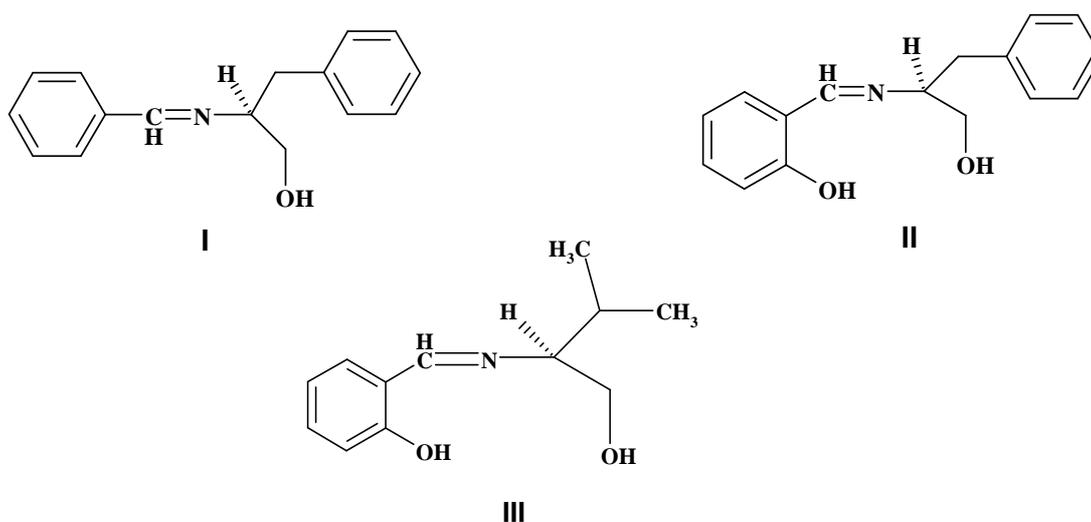
### 1. Introduction

In ion-pair extractive separation of metal cations using a neutral chelation reagent and a counter anion, selection of the chelation reagent is one of most important factors to realize preferable separation. Especially, investigation of effect of steric structure around electron donor atoms in the reagent on the separation ability is very important for the development of novel reagents having high separation performance.

Schiff bases derived from the reaction of salicylaldehyde with primary amines (salen type Schiff base) represent a versatile series of ligand. In attention to importance of these compounds many literatures have been published in this field [1,2]. Symmetric and asymmetric transition metal complexes of these bases have been developed and used as ligands/catalysts in many reactions such as epoxidation [3], asymmetric synthesis [4], asymmetric sulfoxidation [5], asymmetric silylcyanation [6] and many other applications [7]. Schiff bases and the relevant transition metal complexes are still found to be of great interest in inorganic chemistry, although this subject has been studied extensively [8,9]. Schiff bases play a central role as chelating ligands in main group and transition metal coordination chemistry [8,10].

The determination of ion-pair formation constants of organic ligands-metal ion complexes in water can be examined with different methods by following the extraction of metals to the varied organic solvents with organic ligands [11-14]. The solvent extraction of metal cations which contains dye ligands is preferred to use for its easy determination by spectrophotometric methods [15-17].

This paper describes extractive-spectrophotometric determination of sodium and potassium ions as ion-pairs and describes extractive-spectroscopic determination of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$  ions using some chiral Schiff bases as complexing agents.



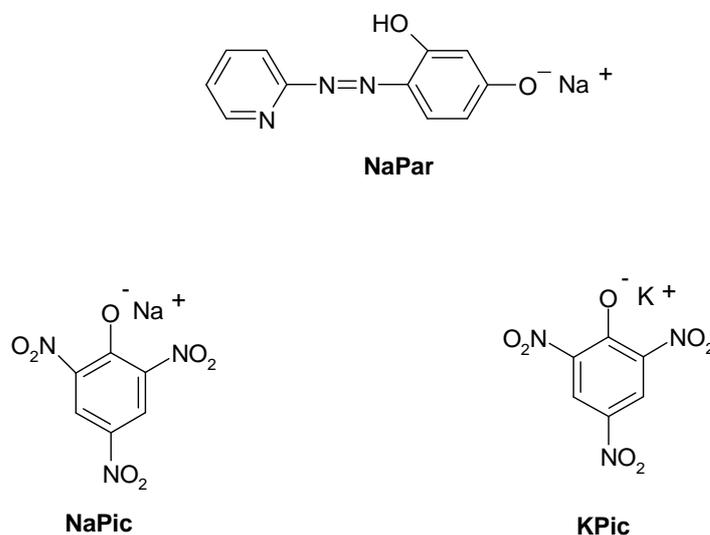
**Figure 1.** Studied Schiff bases.

An anionic color compounds of 4-(2-pyridylazo)-resorcinol mono sodium monohydrate (NaPar), sodium picrat (NaPic) and potassium picrat (KPic) salts which showed in Figure 2, were used to follow the cation transport process using UV-VIS spectrometry [11a,18-20]. The large and strong chromophore anion of the guest metal,  $\text{Na}^+$  was readily mobilized by the organic ligands [21] in  $\text{CH}_2\text{Cl}_2$ /water membranes.

## 2. Results and Discussion

Anionic dyes were examined with various chiral Schiff bases. The selection of the optimum counter anion and chiral Schiff bases were made with regard to phase separation efficiency, determination sensitivity and accuracy of complexation constants ( $K_{ext}$ ). The results of ion-pair extractions obtained in our experimental conditions of identical cation/ligand concentrations of monovalent NaPar, NaPic and KPic salts are summarised in Table 1.

Solvent media effects, and the anion in a salt-ligand system, play a fundamental role on both the stability of the ion-pair complexes, their solubilization and the resulting charge separation in solution [24,25]. Since in real extraction systems some amount of dye salts is soluble in organic solvent without Schiff base, the values of the solubility in organic solvents are also given in the first lines of Table 1.



**Figure 2.** An anionic color compounds of 4-(2-pyridylazo)-resorcinol mono sodium monohydrate (NaPar), sodium picrat (NaPic) and potassium picrat (KPic).

When the used NaPar, NaPic and KPic anionic dyes are extracted as 1:1 complexes with chiral Schiff bases, the cation-complexing ability of the Schiff bases under experimental conditions show that, selectivity was observed only NaPar. It is interesting to note that, all of the ligands display higher extracting ability toward NaPar than do both NaPic and KPic. We suggest that the presence of the Par as the counter ion was increased extraction avidity toward alkali metal salt according to the alkali picrat salts. The organic anion of Par is well hydrogen bonded to the Schiff base by the O-H hydrogen on the anionic dye counter ion.

From the discussion above it was found that NaPar is much more associated with Schiff base and the best extracted organic sodium dye as the ion pair complexes (49-83%) than other dyes.

**Table 1.** Equilibrium constants for extractions of NaPar, NaPic and KPic with chiral Schiff bases in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C.

	K' <sub>D</sub>	VALUE	Chiral Schiff Bases		
			I	II	III
NaPar	1.12*	Log K <sub>ext</sub>	9.38	10.54	11.02
		% Ext	49.62	76.00	83.01
		K <sub>D,L</sub> <sup>(a)</sup>	0.98	3.17	4.88
NaPic	0.02*	Log K <sub>ext</sub>	—	—	—
		% Ext	—	—	—
		K <sub>D,L</sub> <sup>(a)</sup>	—	—	—
KPic	0.09*	Log K <sub>ext</sub>	—	—	—
		% Ext	—	—	—
		K <sub>D,L</sub> <sup>(a)</sup>	—	—	—

(\*) Without Schiff base

(a) K<sub>D,L</sub> ≈ K<sub>D</sub>

**Table 2.** Equilibrium constants for extractions of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cr<sup>2+</sup>, Fe<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup> with chiral Schiff bases in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C.

Cation	I		II		III	
	K <sub>D</sub>	logK <sub>ext</sub>	K <sub>D</sub>	logK <sub>ext</sub>	K <sub>D</sub>	logK <sub>ext</sub>
Ca <sup>2+</sup>	0,20	8,24	-	-	0,04	7,44
Mg <sup>2+</sup>	-	-	-	-	-	-
Cr <sup>2+</sup>	0,08	7,79	0,03	7,37	0,20	8,24
Fe <sup>2+</sup>	0,36	8,62	0,23	8,35	0,40	8,68
Zn <sup>2+</sup>	12,48	12,15	15,15	12,39	14,76	12,36
Cd <sup>2+</sup>	-	-	-	-	0,04	7,44
Ni <sup>2+</sup>	0,82	9,23	0,73	9,13	0,88	9,29
Mn <sup>2+</sup>	-	-	-	-	-	-
Co <sup>2+</sup>	0,35	8,60	0,29	8,48	0,41	8,71

The logK<sub>ext</sub> values of I, II and III for the transition metal cations in dichloromethane have been decreased in order Zn<sup>2+</sup> > Ni<sup>2+</sup> > Co<sup>2+</sup> > Fe<sup>2+</sup> > Cr<sup>2+</sup> Cd<sup>2+</sup>; > Zn<sup>2+</sup> > Ni<sup>2+</sup> > Fe<sup>2+</sup> > Co<sup>2+</sup> > Cr<sup>2+</sup> and Zn<sup>2+</sup> > Ni<sup>2+</sup> > Co<sup>2+</sup> > Fe<sup>2+</sup> > Cr<sup>2+</sup> respectively. Zn<sup>2+</sup> is found to be the best extracted metal cation for the studied chiral Schiff bases and shown to form more stable complex than other divalent cations.

### 3. Experimental

Chiral Schiff bases which studied in this paper, were synthesized according our early study [22]. Sodium dye, 4-(2-pyridylazo)-resorcinol monosodium salt monohydrate (NaPar) was commercial product from Aldrich dried over P<sub>2</sub>O<sub>5</sub> for 48 hours at 0.1 torr. Sodium and potassium picrates (NaPic and KPic) were prepared by adding an alkali metal hydroxyde solution to an aqueous solution of picric acid; the resulting precipitate of sodium picrate mono hydrate and potassium picrate were recrystallized from water-ethanol (1:3) mixture and water, respectively. The picrate salts were dried at 100 °C for 24 hours. CaCl<sub>2</sub>, MgCl<sub>2</sub>.6H<sub>2</sub>O, CrCl<sub>3</sub>.6H<sub>2</sub>O, FeCl<sub>3</sub>.6H<sub>2</sub>O, ZnCl<sub>2</sub>, CdCl<sub>2</sub>, NiCl<sub>2</sub>, MnCl<sub>2</sub>, CoCl<sub>2</sub> are analytical grade reagents from Fluka dried over P<sub>2</sub>O<sub>5</sub> for 48 h at 0.1 torr. The CH<sub>2</sub>Cl<sub>2</sub> used was of analytical reagent grade.

The concentrations of NaPar, NaPic and KPic in the aqueous phases were determined by UV-visible spectroscopy (Varian Cary model 1E UV-visible spectrophotometer) at 407.0, 356.6 and 356.0 nm, respectively, with appropriate quartz cells 2-50 mm in length. The concentrations of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cr<sup>2+</sup>, Fe<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup> metal ions in the aqueous phases have been determined spectroscopically: ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectroscopy : Perkin Elmer Optima 3100 XL).

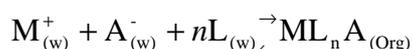
#### 3.1 Extraction Procedure

The extraction measurements were done in a 100 mL glass thermostated cell compartment with a mechanical stirrer where a 25 mL solution of an any aqueous salt (4x10<sup>-5</sup> M) and chiral Schiff bases in CH<sub>2</sub>Cl<sub>2</sub> organic solvent in appropriate concentration were placed and stirred for 120 minutes at 25 ± 0.1 °C and subsequently allowed to stand for 30 min. to complete the phase separation. The optimum concentration of chiral Schiff bases were determined by extracting the alkali salts with 10 mL of various concentrations of Schiff bases (4x10<sup>-5</sup> M). All the extractions were carried out at the natural pH of the aqueous organic salt solution which were about 6.1 - 6.7.

After extraction, NaPar, NaPic and KPic concentrations in the aqueous phase were determined using UV-visible spectrophotometer and the Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cr<sup>2+</sup>, Fe<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup> concentrations in the aqueous phase were determined using ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectroscopy). Each value was the average of three subsequent measurements. Complexation and distribution constants are summarized in Table 1. and Table 2.

#### 3.2 Extraction Equilibria

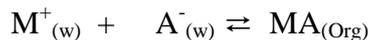
In the present work we made use of a common formalism of equations (1-15) [11,17,23]. The equilibrium processes taking place during the extraction between an aqueous solution containing the alkali metal cation, M<sup>+</sup><sub>(w)</sub>, and organic anion, A<sup>-</sup><sub>(w)</sub>, and an organic solution containing Schiff base L<sub>(org)</sub>, can be written as :



$$K_{\text{ext}} = \frac{[\text{ML}_n\text{A}]_{\text{Org}}}{[\text{M}^+]_{\text{w}} [\text{A}^-]_{\text{w}} \{[\text{L}]_{\text{w}}\}^n}$$

$$\text{and } K_{\text{D}} = [\text{ML}_n\text{A}]_{\text{Org}} / [\text{M}^+]_{\text{w}} \quad (1)$$

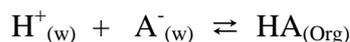
$$\text{L}_{(\text{w})} \rightleftharpoons \text{L}_{(\text{Org})} , \quad K_{\text{D,L}} = [\text{L}]_{\text{Org}} / [\text{L}]_{\text{w}} \quad (2)$$



$$K_{\text{MA}} = [\text{MA}]_{\text{Org}} / [\text{M}^+]_{\text{w}} [\text{A}^-]_{\text{w}}$$

$$\text{and } K_{\text{D}'} = [\text{MA}]_{\text{Org}} / [\text{M}^+]_{\text{w}} \quad (3)$$

and



$$K_{\text{HA}} = [\text{HA}]_{\text{Org}} / [\text{H}^+]_{\text{w}} [\text{A}^-]_{\text{w}} \quad (4)$$

for the extraction process of an acid, HA, with the organic anion in the equations above,  $[\text{M}^+]_{\text{w}}$ ,  $[\text{A}^-]_{\text{w}}$  and  $[\text{ML}_n\text{A}]_{\text{Org}}$  denote the concentrations of uncomplexed cation and anion in aqueous phase and the complex ion-pair extracted in the organic phase, respectively. Mass balances for these processes are expressed as :

$$[\text{L}_0] = [\text{L}]_{\text{w}} + [\text{ML}_n\text{A}]_{\text{Org}} + [\text{L}]_{\text{Org}} \quad (5)$$

$$[\text{M}^+_0] = [\text{M}^+]_{\text{w}} + [\text{ML}_n\text{A}]_{\text{Org}} + [\text{MA}]_{\text{Org}} \quad (6)$$

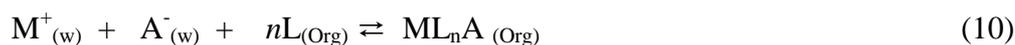
$$\text{and } [\text{A}^-_0] = [\text{M}^+_0] = [\text{ML}_n\text{A}]_{\text{Org}} + [\text{MA}]_{\text{Org}} + [\text{HA}]_{\text{Org}} + [\text{A}^-]_{\text{w}} \quad (7)$$

where the subscript (0) designates the initial concentrations. As can be seen from the results of blank experiments without the Schiff base in Table 1

$$[\text{ML}_n\text{A}]_{\text{Org}} \gg [\text{MA}]_{\text{Org}} + [\text{HA}]_{\text{Org}} \quad (8)$$

$$\text{then, } [\text{ML}_n\text{A}]_{\text{Org}} \cong [\text{A}^-_0] - [\text{A}^-]_{\text{w}} \quad (9)$$

Therefore, for the overall extraction process, the following equation can be written by adding the Eq.(1) to the reverse of Eq.(2) ,



the equilibrium constant of the extraction process can be written as :

$$K_{ext} = \frac{[ML_nA]_{Org}}{[M^+]_w [A^-]_w \{[L]_{Org}\}^n} \quad (11)$$

and hence ,

$$K_{ext} = \frac{[A^-]_0 - [A^-]_w}{\{[A^-]_w\}^2 [L]_{Org}} \quad (12)$$

at  $n = 1$  , where refers to a stoichiometric coefficient for the reaction .

$$\begin{aligned} [L_0] &= [MLA]_{Org} + [L]_{Org} \\ &\cong [L]_{Org} \quad (\text{if } [L]_{Org} \gg [MLA]_{Org} \text{ holds}) \end{aligned} \quad (13)$$

here  $K_{D,L}$  denotes a distribution constant of a Schiff base between water and organic solvent and is defined as ,

$$K_{D,L} = [L]_{Org} / [L]_w \quad (14)$$

hence the Eq.(12) at  $n = 1$  is rewritten as,

$$K_{ext} = \frac{[A^-]_0 - [A^-]_w}{\{[A^-]_w\}^2 [L_0]} \quad (15)$$

According to the Eq.(15),  $K_{ext}$  values were obtained by determining  $[A^-]_w$  spectrophotometrically. The results obtained for chiral Schiff bases are shown in Table 1 and Table 2.

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