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RESEARCH ARTICLE

Complex Formation and Extraction Studies of *N, N′*-Bis (salicylidene)-3,5-diaminobenzoic Acid on Hg(II) and Ag(I)

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Abstract: A novel Schiff base ligand *N, N′*-bis(salicylidene)-3,5-diaminobenzoic acid (H_2B) has been synthesised and characterised by UV, IR, ^{1}H and ^{13}C NMR spectroscopy. The Hg(II) and Ag(I) complexes of H_2B were synthesised and characterised by UV and IR spectroscopy together with ligand to metal mole ratio by Jobs variation method. The IR spectral study of H_2B and its Hg(II) and Ag(I) complexes showed that both metal ions coordinate through the two nitrogen atoms of the azomethine group and the two oxygen atoms of the deprotonated hydroxyl group of the salicyaldehyde moiety. Solvent extraction studies were carried out on Hg(II) and Ag(I) complexes of H_2B using $CHCl_3$ and CCl_4 as organic solvents respectively. Studies were conducted on the effect of time, buffer pH, mineral acids, salting-out agents and complexing agents on the extraction of Hg(II) and Ag(I). Maximum extraction of Hg(II) and Ag(I) using H_2B was observed at pH 8 and pH 8 respectively. At 2.0 M HNO_3 and 1.0 M KNO_3 up to 99.01% of Hg(II) was extracted. At 0.01 M HNO_3 and 1.0 M EDTA, Ag(I) was successfully separated from an aqueous mixture of Hg(II) and Ag(I) using 1% H_2B/CCl_4.

Keywords: *N, N′*-bis(salicylidene)-3,5-diaminobenzoic acid, Complex formation, Extraction, Hg(II) and Ag(I) complexes

Introduction

The use of organic compounds with good ligating ability in the synthesis of metal complexes is replete in literature[1]. This class of organic compounds are also employed in extraction and or separation of heavy poisonous metal ions from different media. Many interests in the later are due mainly to the biological importance of many heavy metals. Other different methods used to remove heavy metals from solutions include complexation[2], precipitation[3], adsorption and ion exchange[4]. However, removal of trace quantities of heavy metals is a limitation imposed by these methods. In this article we report the investigation of complex formation and the extractive ability of *N, N′*-bis(salicylidene)-3,5-diaminobenzoic acid on Hg(II) and Ag(I) from aqueous media under varying conditions.

Experimental

3,5-Diaminobenzoic acid (Fluka), salicylaldehyde (Aldrich), $HgCl_2$ (BDH) and $AgNO_3$ (BDH) were analytical grade and used supplied from commercial sources. Standard solutions of Ag(I) and Hg(II) ions were prepared in a volumetric flask by dissolving appropriate quantity of $AgNO_3$ and $HgCl_2$ in distilled water. All mass and pH measurements were carried out using Metler E-2000 and Fisherband Hydruc 300 pH metre respectively. Melting points were determined using electrothermal melting point apparatus. A micro-elemental analysis was obtained from Microanalytical Laboratory, University of Otago. The UV spectra were obtained using B. Bran 722-2000 spectronic 20D spectrophotometer and UV-2102 PC spectrophotometer. The IR and spectra were recorded using a Schimadzu spectrometer. The ^1H and ^{13}C NMR were recorded in Acetone-D_6 on a mercury-200BB spectrophotometer.

Preparation of N, N′-bis(salicylidene)-3,5-diaminobenzoic acid

A solution of 3,5-diaminobenzoic acid (0.01 M, 1.52 g) in absolute ethanol (10 mL) and 0.01 M NaOH (10 mL) was slowly added to a solution of salicyaldehyde (0.02 M, 2.44 g) in absolute ethanol (20 mL). The reaction mixture was refluxed for 4 hours at 60-65 ºC. The reaction was allowed cooled and the grey coloured precipitate formed collected by gravity filtration. The precipitate was washed with cold ethanol (3x10 mL) and dried to a constant mass to give 2.95 g, 82% yield.

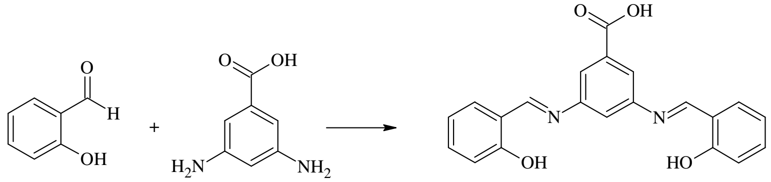
Melting Point: 256 °C, IR (KBr): υ cm^{-1} 795, 1200, 1452, 1617, 1684, 2307 2987 and 3054 ^1H NMR (Acetone-D_6) δ: 9.10 (2H, *s*, Ar-OH); 7.78 (2H, *s*, HC=N); 7.02-7.70 (14H, *m*, Ar-H), ^{13}C NMR ($CDCl_3$) δ: 167, COOH; 166, HC=N; 161, C-OH; 150, C-N; 134.4, HC; 134.0, C-COOH; 133, CCNH; 133-117, Ar. Elemental analysis (%): Calcd for $C_{21}H_{16}N_2O_4$; C 69.99; H 4.48; N 7.77 Found; C 70.15; H 4.66; N 8.10.

Synthesis of Hg(II) and Ag(I) complexes of N, N′-bis(salicylidene)-3,5-diaminobenzoic

Both mercury(II) and silver(I) complexes of the *N,N′*-bis(salicylidene)-3,5-diaminobenzioc acid were synthesized by minor modification of literature procedure[5]. A solution of *N, N′*-bis(salicylidene)-3,5-diaminobenzoic acid (0.001 M) in absolute ethanol (20 mL) and solution of mercuric chloride (0.001 M) or silver nitrate (0.001 M)) in absolute ethanol (20 mL) was stirred under refluxed for 4 hours. This afforded a coloured precipitate {Hg(II) greenish yellow and Ag(I) black} which was filtration under suction followed by repeated washing with cold ethanol (3x20 mL).

Results and Discussion

The ligand H_2B was prepared by the reaction of 3,5-diaminobenzoic acid with salicyaldehyde (Scheme 1). The reaction of the ligand H_2B with Hg(II) and Ag(I) fragments were done by modification of a literature proceudure[5]. Job's continuous variation method was employed in determining the metal-ligand mole ratio of the metal ion {Hg(II) and Ag(I)} and H_2B for complexes HgB and AgB^-. The Jobs plot shows a metal-ligand ration of 1:1 for both metals.



Scheme 1. Synthesis of *N, N′*-bis(salicylidene)-3,5-diaminobenzoic acid

The summary of results of electronic spectra of H_2B, HgB and AgB^- are presented in Table 1. The UV spectrum of the ligand (H_2B) shows maximum absorption at 342 nm and a shoulder at 221 nm. The complexes HgB and AgB^- showed absorptions peaks at 347 nm and [210 nm and 261 nm] respectively. These absorptions are attributable to intraligand π-π^* transitions. The molar absorptivity of the two complexes is appreciably increased in intensity than for the ligand. At higher wavelength, the extra peaks in both complexes is due to metal–ligand charge transfer (MLCT) band[6] indicating the formation of chelate complex thus creating extra chelate ring[7]. There is no indication of a d ← d electron transitions in both complexes[8].

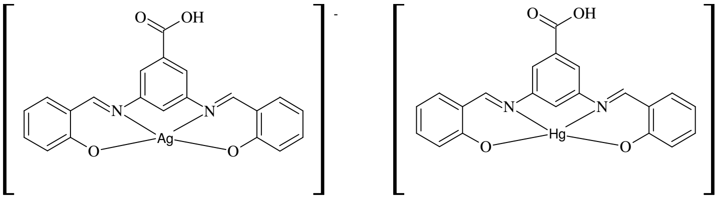
Table 1. Summary of results of electronic spectra of H_2B, HgB and AgB^-

Compound	Wavelength, nm	Absorbance	Molar absorptivity (ε)
H_2B	221	0.475	1710
	342	0.829	2984.4
HgB	347	2.574	14378.1066
	374	2.926	16344.3434
	440	1.713	9568.6467
	455	1.592	8892.7528
AgB^-	210	1.546	72023.502
	261	1.110	51711.57
	336	1.173	54646.551
	348	0.067	3121.329
	355	0.045	2096.415
	373	0.105	4891.635
	436	0.114	5310.918
	444	0.126	5869.962
	454	0.100	4658.7

The IR absorption peaks of H_2B, HgB and AgB^- (Table 2) were expectedly different but showed some similarities due to common functionality of the H_2B moiety. The absorption due to aromatic C-H at 3054.38 cm^{-1} is exactly the same for the ligand and the metal complexes[9]. The -OH stretching vibration of the carboxylic acid group was observed at 2986.87 cm^{-1} for the both ligand and the complexes. These similarities in the IR absorption of -OH and –C=O groups in both the ligand and complexes indicates non-coordination with the metal centres through the carboxylic acid moiety. The absorption at 1617.37 cm^{-1} due to N=C bond[6] of the ligand shifted to lower frequencies and was observed at 1567.21 cm^{-1} and 1595.18 cm^{-1} for the HgB and AgB^- respectively. This evidently suggests the involvement of the azomethine nitrogen in coordinating to the metal centres in the complexes[10,11]. The above evidence thereof rationalised the proposed structures of the neural HgB and the anionic AgB^- complexes Figure 1(a) and (b) respectively.

Table 2. The IR absorption peaks of H_2B, HgB and AgB^-

H_2B, cm^{-1}	HgB, cm^{-1}	AgB^-, cm^{-1}	Functional group
3054.38	3054.38	3054.38	ν(C-H) of aromatic
2986.87	2986.87	2986.87	ν(O-H) stretching of COOH
2306.94	2306.94	2305.01	ν(NC-H)
1684.88	1620.26	1686.81	ν(C=O)
1617.37	1567.21	1595.18	ν(N=C)
1452.45	1510.31, 1421.58, 1383.97,1354.07	1388.79	ν(C=C) of aromatic
1200.73, 1155.4	1002.05	1034.84	ν(C-O) deprotonation of OH
795.66, 737.8	895.96, 735.87, 705.97	953.83, 895.96, 737.8	δ(C-H) of aromatic
464.86	511.15	489.94	Vibration due to entire ring



1 (a) **1 (b)**

Figure 1. Proposed structure of the complexes HgB 1(**a**) and AgB$^-$ 1(**b**)

Dissociation and protonation constants of the ligand

The measured pH of 0.01 M of the Schiff base ligand, *N,N*$'$–bis(salicylidene)-3,5-diaminobenzoic acid (H_2B) is 5.83. The protonation constant pK_b of 4.2 and 4.1 determined through potentiometric titration method[12] with 0.01 M HCl and the Abs-pH curve, by the half-height method[13] respectively indicate a simultaneous protonation of the two azomethine nitrogen atoms;

$$H_2B + 2H^+ \rightleftharpoons H_4B^{2+} \text{ ———— } K_b \tag{1}$$

$$H_2B \rightleftharpoons B^{2-} + 2H^+ \text{ ———— } K_a \tag{2}$$

The acid dissociation constant, pK_a, of 10.1 and 10.2 were also determined by potentiometric titration and half-height methods. These values correspond to pK_a already reported in literature[14,15]. This result indicates that in a basic medium simultaneous loss of two protons of the hydroxyl groups will be expected in accordance with equation (2).

Effect of pH buffer on extraction of Hg(II) and Ag(I)

The extraction of Hg(II) with 1% $H_2B/CHCl_3$ and Ag(I) with 1% H_2B/CCl_4 were studied as a function of pH within buffer range of 1-13 to establish the pH for optimum extraction. A plot of % extraction *vs.* pH (Figure 2) show that extraction generally decrease with an increase in the H^+ concentration (*i.e.* as the pH decrease from 7 to 1). This is obviously due to the competition between H^+ and Hg^{2+} for the azomethine ligation sites. Highest extraction of 98% and 94% were observed for Hg(II) and Ag(I) at pH 8 and 8 respectively.

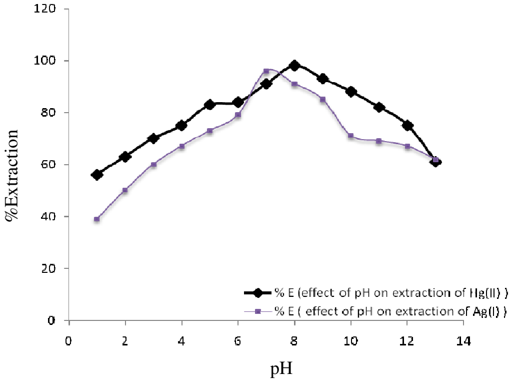


Figure 2. Plot of % extraction *vs.* buffer pH

The extraction at these pH values were enhanced by the formation of a neutral chelate complex which is completely transferable into the organic phase. Deprotonation of the ligand at higher pH enhanced the formation of the chelate complex with the metal ions.

Generally, as the pH increased to 13, the percentage extraction decreased. This may be due to hydrolysis of the metal ion thereby decreasing the amount available for bonding. The masking effect of the base component of the buffer may also contribute to the decrease. Further investigation of the extraction of Hg(II) in 1% $H_2B/CHCl_3$ was studied in different mineral acids (HCl, H_2SO_4, HNO_3 and $HClO_4$) within concentration range 10^{-3} - 2.0 M. A plot of percentage extraction Hg(II) against different acids concentrations is shown in Figure 3a. The percentage extraction of Hg(II) increased as the acidity decreased from 10^{-1} to 10^{-3} M. This compares reasonably with the effect of pH buffer on the extraction. Thus, this is evidently due to the formation of extractable mercury complexes of at higher pH (low [H^+]) which affords facile dissociation of the ligand, yielding anionic species and enhanced the ligating ability. At higher pH, deprotonation of the ligand was favoured to form B^{2-} (equation 2), thus enhancing the formation of the complex. On further increase of the concentration to 2 M the percentage of Hg(II) extracted decreased due to the competition for the azomethine ligation sites between the H^+ and the Hg^{2+} ions. This trend has also been reported by Sato and Noguchi[16]. At high acid concentration, lower percentage extraction was observed in H_2SO_4 medium than in other acid medium. This likely due to the formation of metal complex ion, $Hg(SO_4)_2^{2-}$, which decreased the amount of extractable Hg(II).

The extraction of Ag(I) with 1% H_2B/CCl_4 was studied in HNO_3, H_2SO_4 and $HClO_4$ at concentrations 10^{-3}-2.0 M. Ag(I) reacts rapidly with HCl to give AgCl as precipitate. HCl was therefore not used in studying the extraction of Ag(I) in acid medium[7]. The extraction pattern of Ag(I) is almost the same as that of Hg(II) (Figure 3b). The amount of Ag(I) extracted decreased as the concentration of the acids increases. This could also be due to the formation of non-extractable $Ag(SO_4)_2^{3-}$ complex ion. Same trend was observed for HNO_3 and $HClO_4$ and collaborated by the reports of Irving and Damodaran[17].

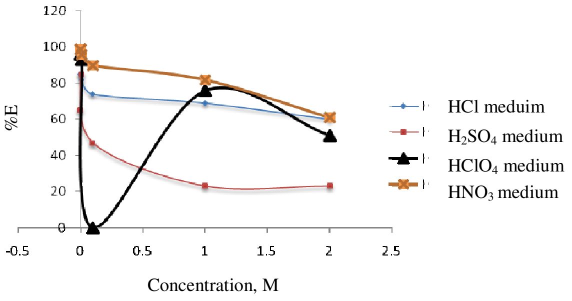


Figure 3a. A profile of extraction of Hg(II) in various acid media

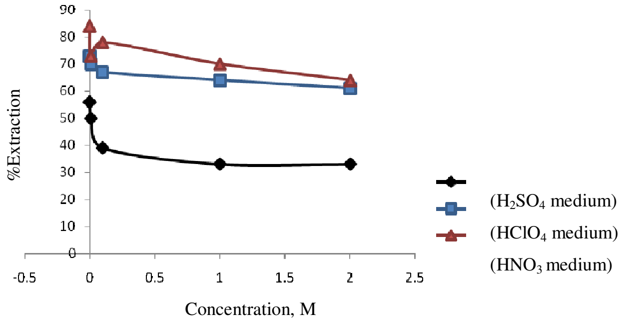


Figure 3b. A profile of extraction of Ag(I) in various acid media

Effect of salting-out agent on extraction

The extraction of Hg(II) with 1% H_2B in $CHCl_3$ and Ag(I) with 1% H_2B/CCl_4 were studied at varying concentrations, 10^{-3} – 1.0 M of the salting out agents (NaCl, Na_2SO_4, $NaClO_4$ and KNO_3) and (Na_2SO_4, $NaClO_4$ and KNO_3) respectively at a constant acid concentrations. In each case, the acid concentration at which there was only partial extraction of the metal ion was selected. The results are graphically shown in Figure 4a and Figure 4b. In general, the amount of Hg(II) and Ag(I) extracted decreased with increased concentration (10^{-2} - 1.0 M) of the salting out agents due to the formation of the corresponding Hg(II) and Ag(I) salts with the acid anion. At 2.0 M HCl, only 58% of Hg(II) was extracted. On addition of small amount (0.5 mL) of 0.001 M NaCl, the percentage extraction was enhanced to 74%. This could be attributed to increase in dielectric constant of the aqueous media in which the complex is less ionic and more soluble in the organic phase[7]. With 0.1 M H_2SO_4, the percentage extraction of Hg(II) was enhanced from 51% to 96% by addition of 0.01 M Na_2SO_4 while the extraction of Ag(I) was enhanced from 56% to 84% in 0.001 M H_2SO_4 with Na_2SO_4 concentration of 0.001 M.

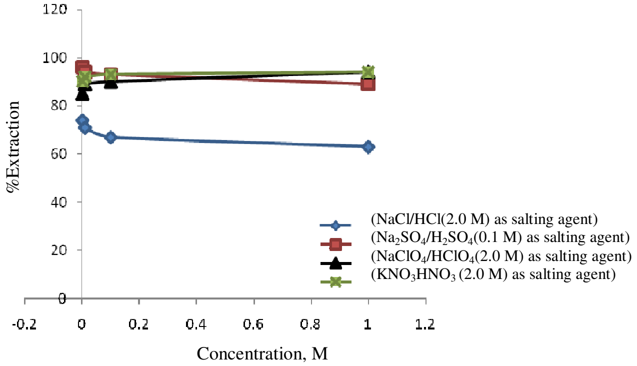


Figure 4a. Effect of salting out agent on extraction of Hg(II)

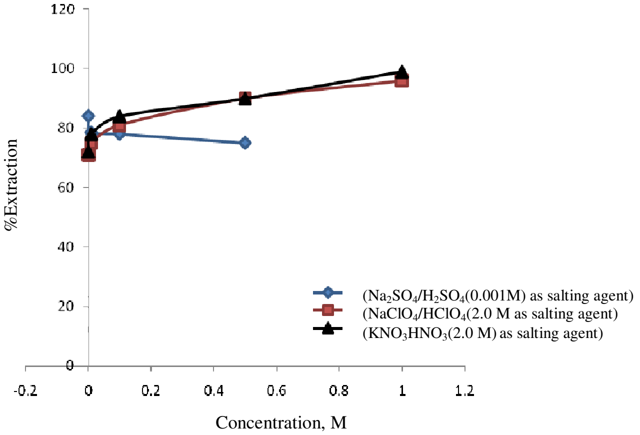


Figure 4b. Effect of salting out agent on extraction of Ag(I)

With 2.0 M $HClO_4$, the percentage extraction of Hg(II) and Ag(I) was enhanced from 52.50% to 85.50% and 61% to 96% respectively by the addition of small quantity of $NaClO_4$ (0.001 M) and 1.0 M $NaClO_4$. Further increase of $NaClO_4$ for Hg(II) increased the percentage extraction to 97%. This is attributable to increased dielectric constant of the aqueous phase which made the complex less ionic. With 2.0 M HNO_3 the salting out effect of KNO_3 is almost the same as that of $NaClO_4$. The amount of Hg(II) and Ag(I) extracted increased with increase in concentration of the salting out agent. For the whole concentration range considered (0.001–1.0 M, KNO_3) more than 90% extraction of Hg(II) was observed. Interestingly, at a concentration 1.0 M KNO_3, up to 99 % of Hg(II) and Ag(I) was extracted. The later observation indicate that 1.0 M KNO_3 and $NaClO_4$ are excellent salting-out agents for the extraction of both Hg(II) and Ag(I) complexes of H_2B.

Effect of complexing agents on extraction

The effect of complexing agents in the concentration range 0.001–1.0 M on the extraction of Hg(II) from 0.001 M $HClO_4$ is shown in Figure 5a. EDTA masked Hg(II) almost completely at a concentration range 0.01–1.0 M. At 1.0 M cyanide ion, up to 94% of Hg(II) was masked. The high masking of Hg(II) in the presence of EDTA and cyanide ions may be due to the formation of very stable non-extractable Hg(II) complexes of EDTA and cyanide as Hg-EDTA and $Hg(CN)_2$ respectively[7]. Thiocyanate had a maximum masking action (90%) at 1.0 M. Hg(II) was masked to about 86% within 0.003–0.01 M oxalate ion concentration, but the interference reduced to 40% at 1.0 M. Phthalate ion showed pronounced masking of up to 82% at 1.0 M but at lower concentration, the effect was reduced. With 0.1M tartrate ion, masking up to 45% was observed.

The effect of complexing agents on the extraction of Ag(I) from 0.001 M $HClO_4$ at the concentration range 0.001–1.0 M is shown in Figure 5b Thiocyanate and cyanide ions greatly influenced the extraction of silver(I). Thiocyanate had the highest interference as up to 96% Ag(I) was masked at 0.1–1.0 M. At a concentration range 0.1–1.0 M, cyanide masked up to 92% silver(I). At 1.0 M oxalate ion, up to 83% of Ag(I) was masked but as the concentration decreased to 0.001 M, the interference reduced to 35%. EDTA masked up to 81% of Ag(I) at 0.05 M. Also as the concentration is reduced to 0.001 M, the effect of EDTA dropped to 59%. At low tartrate concentration, 0.001 M, up to 67% Ag(I) was masked but the interference reduced as the concentration increased to 1.0 M to 47%.

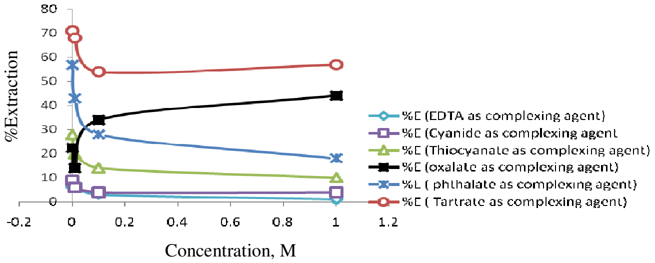


Figure 5a. Effect of complexing agent on the extraction of Hg(II) with $H_2B/CHCl_3$

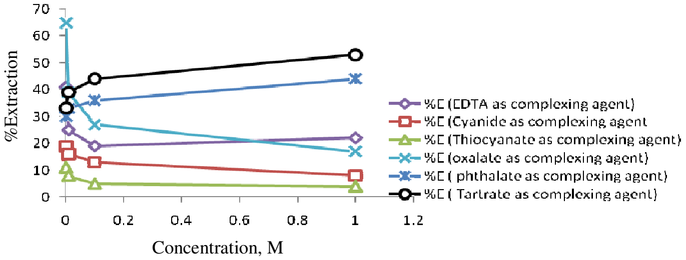


Figure 5b. Effect of complexing agent on the extraction of Ag(I) with $H_2B/CHCl_3$

Conclusion

N,N′-bis(salicylidene)-3,5-diaminobenzioc acid and its Hg(II) and Ag(I) complexes were successfully synthesised and characterised. The extractability of Hg(II) and Ag(I) ions by *N,N*′-bis(salicylidene)-3,5-diaminobenzioc acid at low concentrations and varying conditions was quantitative and thus could potentially be used for removal of heavy metal pollutants from liquid media.

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