

Solvent Extraction Properties of Aminophthalic – Anhydride (APA) and Mono-methyl Phthalate-2-Potassium Hydroxamate (MMPPH) Towards Some Metal Ions

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Summary: The aim of this work is to study the extractive ability of hydroxamic acids derived from phthalic acid (an aromatic 1,2-dicarboxylic acid). Thus mono- and di-esters of this acid were synthesized and employed for the preparation of the corresponding hydroxamic acids. Compounds prepared are aminophthalic – anhydride (APA) and mono methyl phthalate 2-potassium hydroxamate (MMPPH) were characterized with different physical and chemical tools. The extractive ability of these compounds towards V(V), Cu(II), Fe(III), Cd(II), Mo(V) and U(VI) were studied under different pH values and the stripping of these metal ions with 2.0M H₂SO₄ is also studied.

Introduction

From the literature data, it has been shown that hydroxamic acids exhibiting an extra complexing capacity towards a very great number of metal-ions. Therefore they should be considered as a very interesting category of newly extracting agents. Since it is well known that aromatic hydroxamic acids are more stable than aliphatic ones, researchers have directed their work towards aromatic ones [1].

Hydroxamic acids were known as the compounds which having the bidentate functional grouping, which fulfill the basic requirements of complex formation [2]. They can be prepared by different methods, but the common used one, is the reaction between an ester and hydroxylamine or an acid anhydride or acid chloride with hydroxylamine [3].

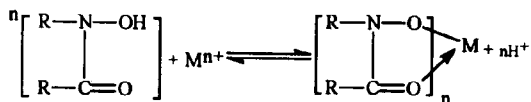
The most important applications of hydroxamic acids as analytical reagents are their uses as complexing agents ions. It is sometimes possible to separate interfering ions by controlling the pH and the use of masking agents [4]. These complexes may be used in medicine [5,6], in electrical conductivity measurements [7,8] etc.

Results and Discussion

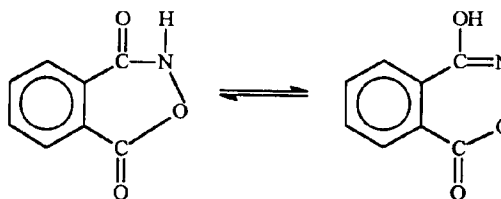
Detection and Complex Formation of Hydroxamic acids

Agarwal [9], described a rapid and simple method for the detection of a small amounts of hydroxamic acids. The chloroform soluble, violet

coloured vanadium complexes formed between vanadium and the hydroxamic acids allows the detection of as little as 10-20 µg of hydroxamic acid. Also alcoholic ferric chloride is used as a detection reagent for hydroxamic acids, the complex of iron (III) hydroxamate is red in colour. The complex formation of hydroxamic usually takes place by the replacement of the hydroxylamine hydrogen by the metal ion and ring closure through the carbon-oxygen. This can be represented as shown below:



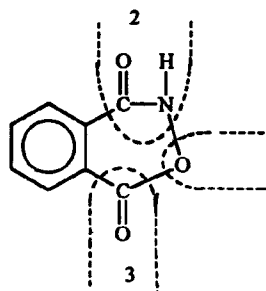
These compounds were characterized by infra red spectroscopy, elemental analysis, mass spectroscopy, nuclear magnetic resonance and melting point. The amount of potassium in MMPPH was determined using X-ray fluorescent and flame photometry. The infra-red spectrum of (APA) showed the expected basic peaks as follows: O-H at 3150, C-O at 1600, C-N at 1380 and N-O at 880 cm⁻¹. The appearance of OH peak in the cyclic structure can be explained by the following tautomeric structures:



The infra-red spectrum of MMPPH shows the same peaks in similar positions: C=O at 1585, C-N at 1375 and N-O at 880 cm^{-1} . The presence of carbonyl and hydroxyl groups in these compounds helps in their stability via an inter- and intramolecular interactions (hydrogen bonding).

Elemental analysis done for the two compounds prepared agreed quite well with the calculated theoretical values. In addition the mass spectrum for APA gave the correct molecular mass (163) and a sequence of fragmentation as : 163, 147, 104 and 76.

This fragments corresponds to the loss of oxygen atom, -CO-NH- group and a carbonyl group as:



163-147=16 corresponds to a loss of oxygen atom
147-104=43 corresponds to a loss of -CO-NH- group
104-76=28 corresponds to carbonyl group. The remaining 76 corresponds to aromatic ring.

Proton nuclear magnetic resonance for APA shows the aromatic protons at a chemical shift of 8.0 ppm and an imide group at a chemical shift of 3.2.

Hydroxamic acids can complexed with metal ions by forming stable five membered ring including the carbonyl group and OH group attached to nitrogen atom. Since the compound APA has no free OH group for this bonding, the only possibility for it to complex is by breaking the cyclic structure in aqueous medium and having the same structural properties of hydroxamic acids.

These compounds are soluble in amyl alcohol, chloroform and forming a faint pink, pale green brown and pale yellow coloured complexes with vanadium, copper, ferric and uranium respectively, while cadmium and molybdenum formed a colourless complexes with the two reagents.

Cu(II), Fe(III) and Cd(II) were determined by atomic absorption spectroscopy, while V(v), Mo(v) and U(vi) were determined colorimetrically.

The results of the extraction and stripping were shown in the following tables 1 to 4.

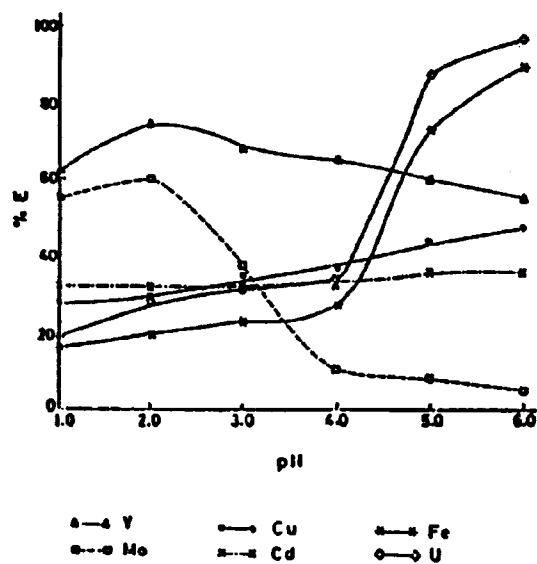


Fig. 1: % Extraction of V(V), Cu(II), Fe(III), Mo(V), Cd(II) and U(VI) with APA

Table-1: % Extraction of V,U, Mo, Fe, Cd and Cu with APA

PH	%E(V)	%E(U)	%E(Mo)	%E(Fe)	%E(Cd)	%E(Cu)
1.0	62.2	18.75	55.0	15.50	32.2	27.50
2.0	75.0	28.13	60.0	19.50	32.2	28.25
3.0	68.2	31.25	37.0	22.00	32.2	34.35
4.0	65.0	34.37	10.0	27.50	32.2	36.50
5.0	60.0	87.50	8.0	73.75	36.0	43.75
6.0	55.2	97.50	5.0	89.42	36.1	47.50

Table-2: % Stripped of metal ions with 2.0 M H_2SO_4

Metal ion	(V)	(U)	(Mo)	(Fe)	(Cd)	(Cu)
% stripped	29.4	94.0	36.0	98.0	99.0	97.0

Table-3: % Extraction of V,U, Mo, Fe, Cd, and Cu, with MMPPH

PH	%E(V)	%E(U)	%E(Mo)	%E(Fe)	%E(Cd)	%E(Cu)
1.0	32.25	25.00	57.50	10.00	36.10	25.00
2.0	51.25	28.13	60.00	13.40	36.10	27.25
3.0	44.00	38.13	30.00	14.50	36.10	40.85
4.0	35.90	43.75	25.00	25.50	42.60	44.25
5.0	30.00	47.20	20.00	56.00	44.00	45.35
6.0	24.00	51.87	22.50	88.40	46.00	45.62

Table-4: % Stripped of metal ions with 2.0 M H_2SO_4

Metal ion	(V)	(U)	(Mo)	(Fe)	(Cd)	(Cu)
% stripped	56.2	85.0	43.0	98.0	99.0	99.0

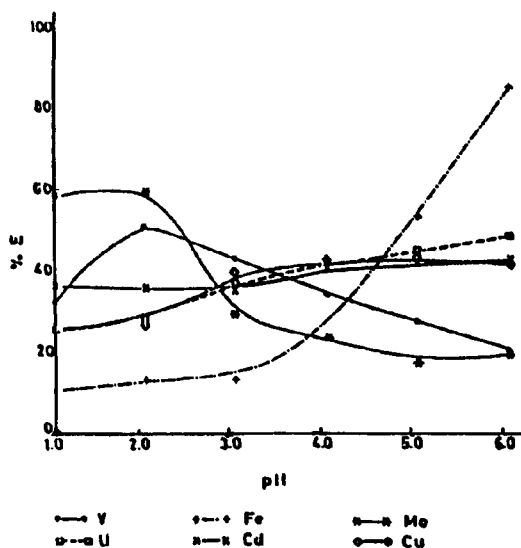


Fig. 2: % Extraction of V(V), Fe(III), Mo(V), U(VI), Cd(II) and Cu(II) with MMPPH

It was found that V(v) and Mo(v) have maximum extraction at pH 2.0 while the other four metal ions at pH 6.0.

The maximum percentage extracted of V(v), Mo(v), Cu(II), Fe(III), Cd(II) and U(vi) are 75.0%, 60.0%, 47.0%, 89.0%, 36.1%, and 97.0% respectively for APA, 51.25%, 60.0%, 26.73%, 45.75%, 28.77%, and 38.86% respectively for MMPPH. V(v) can be stripped upto 55.8%, Cu(II) upto 98.6%, Cd(II) up to 99.1%, Mo(V) upto 43.6% from MMPPH using 2.0 M H₂SO₄. Fe(III) can be stripped upto 97.9%, U(VI) upto 93.7% from APA using the same acid.

The pH_{1/2} which is defined as the pH at which 50% of the solute was extracted is equal to 4.5 for Fe(III), 4.4 for U(VI) and 2.5 for Mo(V) when APA was used as extracting agent.

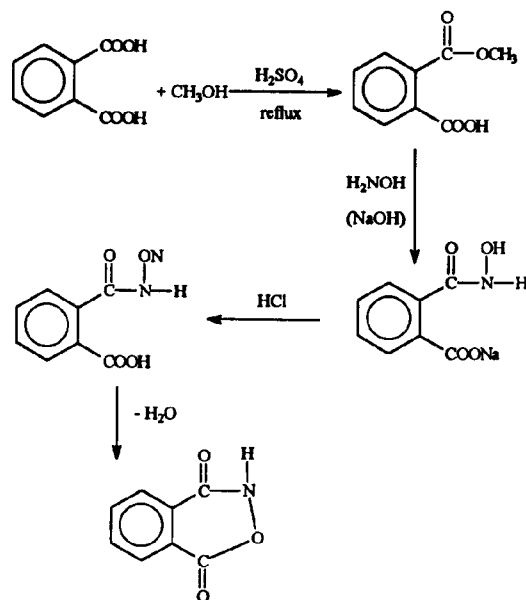
The pH_{1/2} values for V(v), Fe(III) and U(VI) are 2.0, 4.74 and 6.0 when MMPPH was used as extracting agent.

Experimental

The compound (APA) was prepared by refluxing the mono-methyl ester (formed from equimolar quantities of phthalic acid and methanol)

and equal number of moles of hydroxylamine free from hydrochloric acid in methanol for 5-hours in basic media using sodium hydroxide pellets.

The excess methanol was distilled off and the products was acidified with dilute hydrochloric acid and recrystallized from methanol.



(APA)

The compound (APA) was characterized with: (i) Elemental analysis (Table-5) which was carried at the Butterworth Laboratories Limited, Middlesex, U.K. It shows a matching values for the experimental and calculated results.

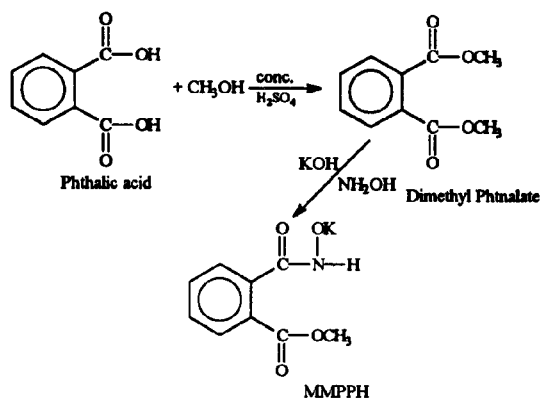
Table-5: Elemental analysis of (APA)

Elemental	%Calculated	%Found
C	58.89	58.42
H	3.07	3.10
N	8.58	8.50

(ii) Infra red spectra which show the expected basic peaks. O-H at 3150, C=O at 1600, C-N at 1380 and N-O at 880 cm⁻¹ (iii) Mass spectroscopy which was done at the Service Center, Columbia, Missouri, U.S.A. It shows a molecular weight of 163 a.m.u. as a base peak which fit quite well with the calculated value. (iv) Proton nmr which shows an aromatic hydrogen at a chemical shift of 8.0 ppm and an imine group at a chemical shift of 3.2 ppm. (sweep frequency range 82-83.2 MHz (Resonance at 82.8 MHz), Magnetic field around 19.7 K Gauss. The

solvent was acetone. (v) Molecular weight determination using the depression in melting point method. The compound was mixed with camphor (melting point of 176°C) and the melting point of the mixture was done. The molecular weight which was found from the depression in melting point (163.2) agreed with the calculated value.

The second compound (MMPPH) were prepared by the same procedure using the diester of the acid instead of the mono-ester.



The compound (MMPPH) was characterized with:

(i) Infrared which shows the main expected peaks. C-O at 1300, C-N at 1375 and N-O at 880 cm⁻¹. The C=O stretching of ester group around 1740 cm⁻¹ and that of amide group around 1685 cm⁻¹. (ii) Elemental analysis (Table 6) in which the calculated and found values are matched.

Table-6

Element	% Calculated	% Found
C	46.35	46.63
H	3.40	3.30
N	6.00	5.56
K	16.74	17.00

(iii) X-Ray Fluorescent:

The amount of potassium in this compound was calculated using X-Ray Fluorescent. It was compared to a known weight of potassium oxalate in phthalic acid matrix. The area under the curve of the unknown was compared with that of the known amount. It was found that about 17.0% of potassium is present in the sample. This value is in a good agreement with the theoretical value (16.74%).

The two compounds were dissolved in chloroform and used for the extraction of different metal ions from aqueous media at different pH values.

The stripping of these metal ions with 2.0 M sulphuric acid from the complexes was also carried out.

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