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Synthesis and Characterization of Arsenic-Catechol Ion-Associates For Determination of Arsenic Contamination

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Abstract:

Arsenic is one of the toxic elements that exhibit harmful effects on human-body. The most common way of arsenic toxification occurs through its contamination in drinking water. Thus, it is important to measure arsenic contamination in water body. A relevant method to determine the quantitative amount of arsenic is by converting the arsenic compounds into its stable complexes and then determination of its amount by spectroscopic technique. Two new ion-associates of arsenic-catechol complex were synthesized and characterized, in this regard.

Introduction:

Arsenic contamination in water is still one of the major concerns in the developing countries and arsenic level can be as high as 0.1µg/ltr in normal drinking water sources[1]. Arsenic determination are generally done by atomic spectroscopy[2-4] or UV-vis spectrophotometry [5] methods. Converting arsenic to a coloured complex followed by spectroscopic measurement is a convenient way for arsenic detection[6]. Hence, ion-associates of arsenic complexes were synthesized for this purpose[7].

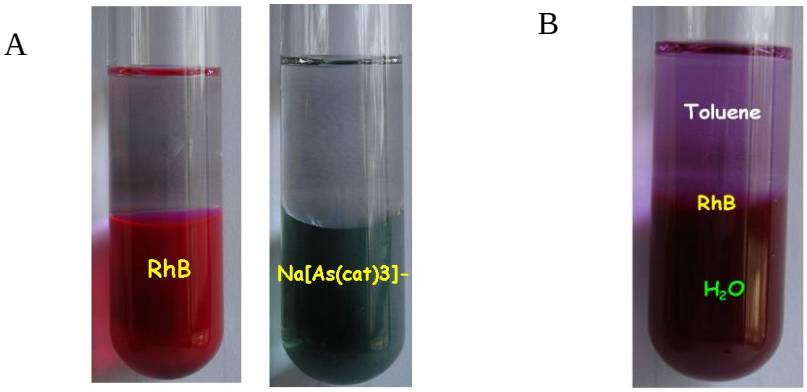
To have a comparative account with PO_4^{3-} and AsO_4^{3-} we found that catechol is unique for arsenic in terms of complexation. It selectively and efficiently bind with arsenic(V) at the elevated temperature. It is interesting to note that As(V) forms an anionic complex with the exact amount of the ligand catechol. Excess amount of added catechol undergo thermal decomposition to quinones and in turn becomes water insoluble. Thus the process becomes a novel technique to quantitatively separate out As(V) leaving aside PO_4^{3-} and even SiO_4^{3-} . Because of the non-availability of the other heavier elements of group VB in water body this findings become useful for arsenic complexation and determination.

Arsenic(v) reacts with catechol (1,2-benzenediol) derivatives in the ratio 1:3 to form a univalent complex anion [As(catechol)3]- [7]. Alkali and alkaline-earth metals do not interfere even in a large amount and phosphate ion does not interfere upto 20 fold molar excess of Arsenic(v). But Sb, Bi and Cr interfered in the same concentration as Arsenic(v)[8].

Result and Discussion:

Synthesis of $Na^+[As(Catechol)_3]^-$ complex and its ion-associates:

We have taken catechol crystals and recrystalised it from ethanol to eliminate the oxidised derivatives of catechol (such as quinone) and obtain highly pure crystals of catechol. Then we have taken sodium hydrogen arsenate heptahydrate and recrystalised catechol crystals in almost 1:3 ratio, taking catechol in a little excess. The crystals were dissolved in water and evaporated to dryness on a water-bath asAs(V) and catechol reacts in solid state[9]. Then the residue was dissolved in 10ml water and placed into a stoppered test-tube. To this 10 ml solution a concentrated aqueous Rhodamine B (RdB) solution was added and kept for 10 min. Zwitterinonic complex of the RdB with the Arsenic catechol complex was supposed to be formed. Finally to this aqueous solution 5ml toluene was added and shaken it thoroughly taking the aim in mind that the formed zwitterionic complex come into the organic layer as because of the neutralization of the charge. After 20 min of vigorous shaking toluene part became red in colour indicating that the zwitterionic complex came into the organic layer as we know that due to the presence of charge RdB won't come to organic phase. Not only RdB but also sodium catechol complex also won't come to the organic layer if shaken well due to the presence of charge (Scheme 1A).



Scheme 1. A) Schematic representation of inability of pure RhB and $Na^+[As(cat)_3]^-$ to be extracted out in toluene layer. B) Schematic representation of the extraction of $RdB^+[As(catechol)_3]^-$ complex in toluene layer

The red coloured organic layer was separated. Then we evaporated toluene to obtain the complex $RdB^+[As(catechol)_3]^-$,which is an ion-associate of the complex $Na^+[As(catechol)_3]^-$. Another ion associate was successfully prepared. $Cs^+[As(catechol)_3]^-$ following the same procedure stated above. All these zwitterionic complexes

$RdB^+[As(catechol)_3]^-$ and $Cs^+[As(catechol)_3]^-$ were collected from organic toluene layer (Scheme 1B).

To replace Na^+ with Cs^+ in simple aqueous medium,we dissolved the residue of $Na^+[As(catechol)_3]^-$ in water and excess $CsNO_3$ was added to it. The solution was kept for sometime. A white amorphous precipitate of $Cs^+[As(catechol)_3]^-$ was obtain and it was separated by filtration. The complexation is qualitativelyconfirmed from the solubility data as the prepared amorphous complex is not soluble in water where as $CsNO_3$ is completely soluble in water.Another strong evidence for the formation of $Cs^+[As(catechol)_3]^-$ complex was the result of back-extraction experiment. 3mL aqueous solution of methylene blue was taken in a clear test tube. 3mL of toluene was poured over that solution and two immiscible liquid layer were formed. Then about 0.5 mg of $Cs^+[As(catechol)_3]^-$ complex was taken in that test tube. After shakingit vigorously for 5 minutes, the clear toluene layer became blue , showing the evidence of formation of$MB^+[As(catechol)_3]^-$ complexin toluene medium by substitution of Cs^+ by MB^+.

Characterizations:

The synthesized arsenic catechol complexes were characterized using different physical methods such as UV-visiblespectroscopy and FTIRspectroscopy.

UV-visible spectroscopy:

We have characterized pure Rhodamine-B dye by taking the UV-visible spectra in aqueous medium as shown in figure 1a. A sharp peak was obtained at 552nm for pure Rhodamine B.

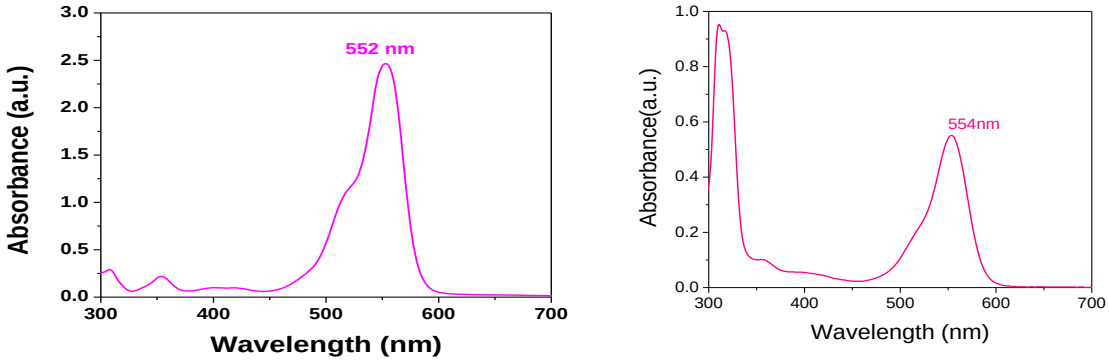


Figure 1: UV-Vis spectra of (a) pure RhB and (b) (b) $RhB^+[As(Cat)_3]^-$

After the synthesis of$RhB^+[As(Cat)_3]^-$ complex we measured its UV-visible spectrum for characterization. Toluene was taken as the medium due to the insolubility of the complexes in

aqueous medium. Figure 2brepresents the UV-visible spectrum of $RhB^{+}[As(Cat)_3]^{-}$ complex in toluene medium and shows a sharp peak at 554nm.

Thereafter, we characterized $Na^{+}[As(catechol)_3]^{-}$complex by UV-visible spectroscopy. Figure 2. represented the UV-visible spectrum of the aqueous solution of $Na^{+}[As(catechol)_3]^{-}$ complex. There was no sharp peak, rather a broad peak having absorbance maxima at 635nm was obtained.

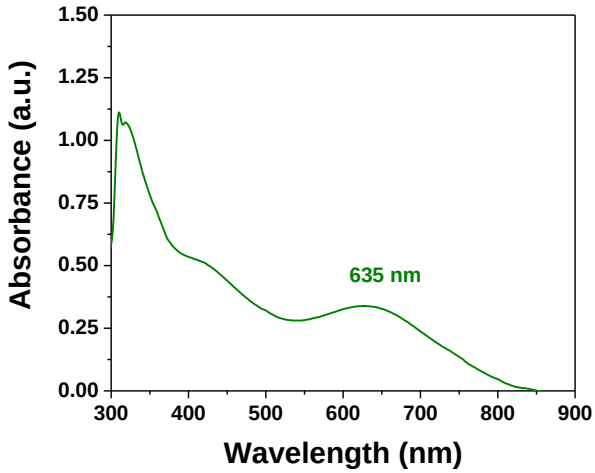


Figure 2: UV-Visible spectra of $Na^{+}[As(Cat)_3]^{-}$

FTIR Spectroscopy:

The $[As(Cat)_3]^{-}$ complex was first characterized using FTIR spectroscopy. The zwitterionic complex formation in organic medium was confirmed from FTIR spectroscopy as well. FTIR spectra of pure sodium hydrogen arsenate, pure Catechol, $Na^{+}[As(Cat)_3]^{-}$ were indicated in figure 3a, 3b and 3c, respectively. The As-O stretching vibration band arises near 800 cm^{-1} [9]. The FT-IR spectrum of the $Na^{+}[As(Cat)_3]^{-}$ complex shows a moderate band at 800 cm^{-1} which indicates the complexation of sodium arsenate and the catechol moiety (figure 3c.).

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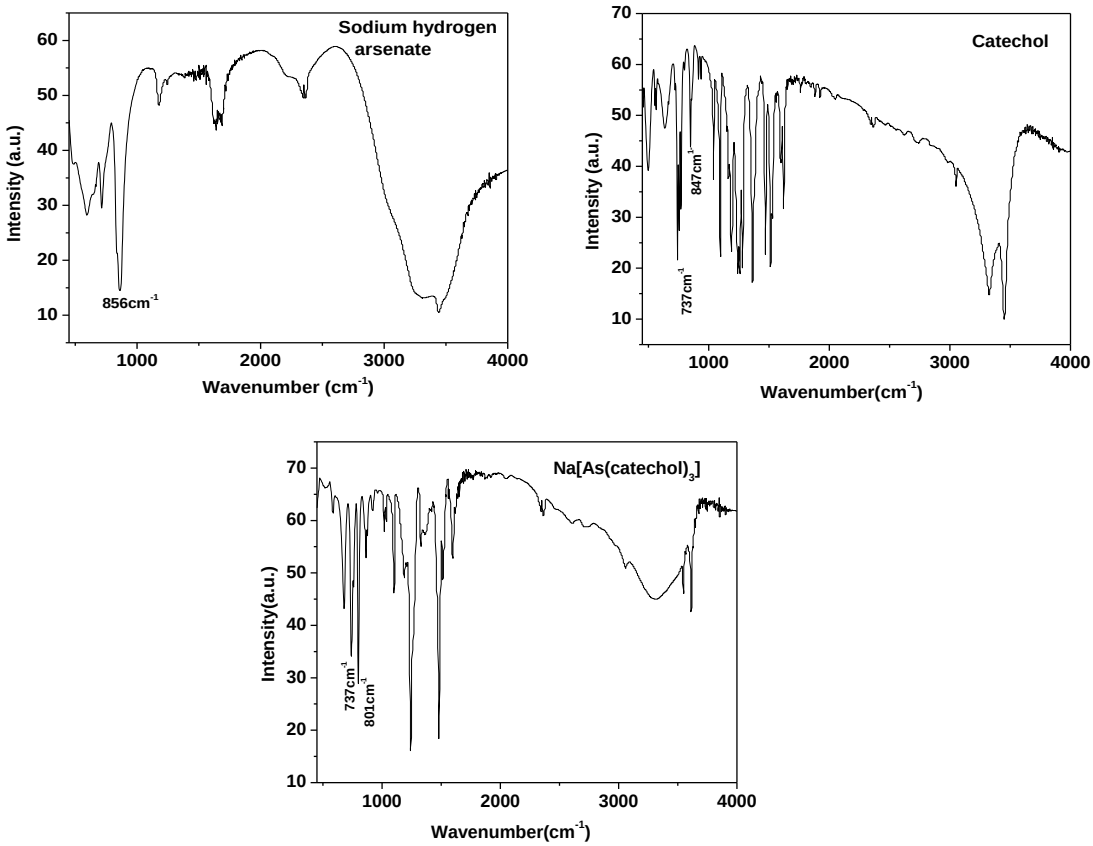

Figure 3: FTIR spectra of (a) sodium hydrogen arsenate, (b) catechol, (c) $Na^{+}[As(Cat)_3]^{-}$ complex

FTIR spectrum of $CsNO_3$ and the synthesised $Cs^{+}[As(Cat)_3]^{-}$ complex were also performed and were presented as figure 4a and 4b, respectively. The peak at $801cm^{-1}$ in the graph of $Cs^{+}[As(Cat)_3]^{-}$ showed evidence of $[As(Cat)_3]^{-}$ moiety again. There is a distinct intense peak at 1384cm-^{1} due to N-O stretching of the NO_3^{-} group in $CsNO_3$ which is completely absent in the FTIR spectrum of the prepared complex.

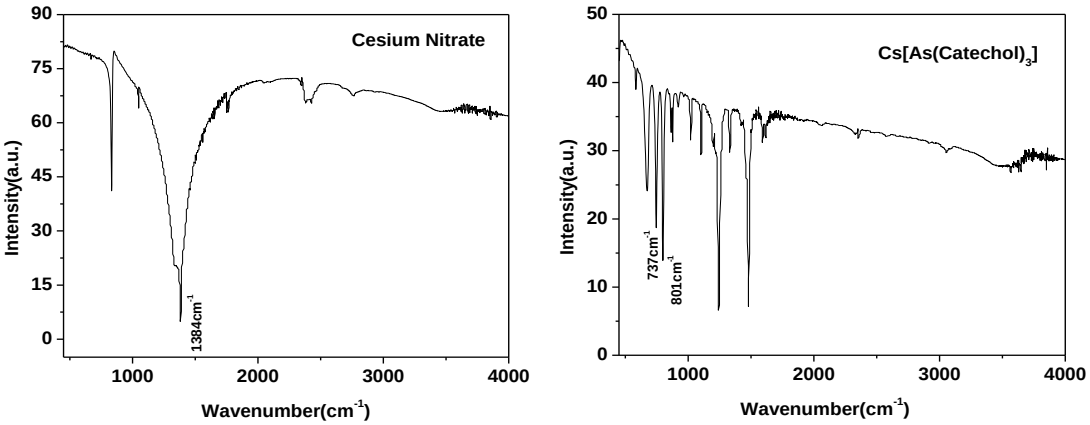

Figure 4: FTIR spectra of (a) pure $CsNO_3$ and (b) $Cs^+[As(Cat)_3]^-$

C,H,N Analysis:

Additional characterization of$Cs^+[As(Cat)_3]^-$ complex was done by C,H,N analysis. Expected percentage of C,H,N and experimental percentage of C,H,N is given in the table below. Nitrogen was may be due to presence of trace amount of $CsNO_3$ as impurity.

Percentage	Carbon	Hydrogen	Nitrogen
Expected from the structure	**40.60**	**2.25**	**0.00**
Experimentally obtained	**39.96**	**1.92**	**0.09**

Experimental:

AR grade reagents were used for all the experiments. Hydrated sodium hydrogenarsenate and 1,2-dihydroxybenzene or Catechol were bought from Nice Chemicals and LOBA CHEMMIE, respectively. CTAB and toluene were bought from SRL.

Shimadzu UV-160 spectrophotometer was used for all the UV-visible spectral measurements. Quartz cuvette of 1 cm path-length was inserted. Nexus 870 Thermo-Nicolet instrument coupled with Thermo- Nicolet Continuum FTIR microscope was used in reflectance mode to record all the FTIR spectrum.

Conclusion:

Two new ion associates of As(V)-catechol complex have been synthesized and characterized using spectroscopic techniques. Detection ofAresenicclevels in water is the novel application of these ion-associates[10]. The exploitation of a fluorescence dye gives a better sensitivity of

the methods through luminescence measurement.The process of As(V) binding with catechol and then simple ion-association of the anionic moiety with cationic dye molecules paves the way for easy and inexpensive arsenic detection. The process has a novelty of testing As in water body without the need of any instrument or whatever giving a 'YES' or "NO' type test for Arsenic without any interference.

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