

Cloud point extraction of Cr(III) and Cr(VI) ions using novel room temperature ionic liquid N-methyl-N,N-trioctyl-1-ammonium-5,7-diiodoquinoline-8-olate followed by FAAS quantification

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Room temperature ionic liquid when coupled with cloud point extraction (CPE) has proven to synergistically enhance the efficiency of an extraction process. In the present work, we report the synthesis of a novel room temperature ionic liquid, N-methyl-N,N-trioctyl-1-ammonium-5,7-diiodoquinoline-8-olate (MTAQO) using Aliquat-336 and 5,7-diiodohydroxyquinoline. Infrared, ¹H and ¹³C NMR have been used for characterization. Viscosity of MTAQO has been found to be 4000 centipoise and thermogravimetric analysis (TGA) of MTAQO showed high thermal stability. Lifetime of MTAQO has been recorded along with fluorophore so as to study the application of fluorescence resonance energy transfer (FRET). Cloud point extraction of Cr(III) and Cr(VI) ions has been carried out using MTAQO. Optimization of pH, concentration of non-ionic surfactant Triton X-100, volume of MTAQO, extraction time, centrifugation speed, centrifugation time and dilution solvent have been carried out in order to get maximum extraction efficiency. The quantification has been carried out by flame atomic absorption spectrophotometer (FAAS). Recovery of 97.8% and 99.4%, LOD of 39 ppb and 18 ppb have been observed in the extraction of Cr(III) and Cr(VI) ions respectively. Enrichment factor of 60 has been observed for both Cr(III) and Cr(VI).

Keywords: Cloud point extraction, Chromium, Ionic liquids, Flame atomic absorption spectrophotometer

Unmanageable use of organic solvents in chemical synthesis and extraction process is a severe problem faced by chemical laboratories and industries, as they have a deleterious impact on human health and environment¹. This is where the environment friendly green solvent ionic liquid gains significance¹⁻⁶. Qualities like non volatility, high thermal stability and non-flammability gives the label of 'greenness' to ionic liquids^{1,2,4,7}. The potential for replacement of organic solvents by ionic liquids is expanded across areas such as synthesis, extraction, catalysis, electrochemistry etc²⁻⁴. Ionic liquids are organic salts which are in the liquid state at or below 100 °C. They have an organic cation and an organic or inorganic anion^{4,6} moiety. Ionic liquids which are in liquid state at room temperature are known as room temperature ionic liquids (RTILs)^{3,8}. RTILs can be used as good solvents for extraction^{2,3,4,10}. Length of the cationic chain of an ionic liquid affects some of its properties like hydrophobicity, viscosity, miscibility, density, surface tension and dielectric constant^{1,2,8,9}. Anionic parts are normally able to control water miscibility of

an ionic liquid⁸. Additionally, ionic liquids also show high thermal stability¹. The flexibility of ionic liquids is promising as they can be designed according to our need by choosing appropriate cation and anion. This is the reason behind the name 'designer solvents' of ionic liquids^{3,11}. As the cationic and anionic part of ionic liquid plays a major role in their physicochemical properties, the choice of the same is very important when it is designed for an extraction process. In the present work, we have designed and synthesized a room temperature ionic liquid, N-methyl-N,N-trioctyl-1-ammonium-5,7-diiodoquinoline-8-olate for the extraction of Cr(III) and Cr(VI) by cloud point extraction method.

Cloud point extraction (CPE) is one of the liquid-liquid extraction techniques which has gained considerable attention in preconcentration and separation of metal ions¹². Non-ionic surfactants play the role of phase transfer agents in cloud point extraction and this method is also considered as an environmental friendly extraction technique since very low volume of non-ionic surfactant is enough for

extraction, instead of using toxic organic solvents as in conventional extraction processes¹²⁻¹⁷. In our work, Triton X-100 is chosen as the non-ionic surfactant due to its low cloud point temperature (66 °C), low toxicity and high density of surfactant rich phase. Simplicity, high extraction efficiency and preconcentration factor, low cost and low extraction time turns cloud point extraction method, a best choice for the extraction of metal ions^{13,14,17-19}.

In the present work, we are combining room temperature ionic liquids and cloud point extraction for the separation of Cr(III) and Cr(VI) ions. Works in room temperature ionic liquid supported cloud point extraction are rare to the best of our knowledge. Advantage of the method is the synergic enhancement effect experienced in the extraction process¹⁰. Extraction efficiency and extraction time show a large difference in value when cloud point extraction is done alone and in presence of room temperature ionic liquid, MTAQO. It is proved that there is a synergic effect when cloud point extraction is carried out in the presence of ionic liquid.

Absorbance and fluorescence behavior of ionic liquids in visible range of the electromagnetic spectrum has been reported. Ionic liquids can be considered as a component in fluorescent functional material²⁰. According to Samanta *et al.*, fluorescence of ionic liquids is due to the different electronic structures of species in the bulk of ionic liquid^{21,22}. It is also reported that molecular aggregates in ionic liquids are responsible for the fluorescence property²³. Identity of an ionic liquid can also be ascertained by applying fluorescence resonance energy transfers (FRET) in them. In FRET, a donor fluorophore absorbs energy due to excitation of incident light and transfers the excitation energy to a nearby chromophore and this energy transfer leads to quenching of donor fluorescence intensity²³⁻²⁷. In the present work, we have examined this property of ionic liquid as a part of characterization. Kadokawa has explained the FRET mechanism of ionic liquids using 1-butyl-3-methylimidazolium chloride (BMIMCl) with Rhodamine 6G²⁰. It is observed that lifetime of donor BMIMCl decreases in presence of acceptor Rhodamine 6G. We have observed the same FRET system in our novel ionic liquid N-methyl-N,N-trioctyl-1-ammonium-5,7-diiodoquinoline-8-olate (MTAQO). Rhodamine 6G is the chromophore selected as the acceptor. Lifetime of MTAQO decreased in presence of Rhodamine 6G.

Developed analytical method of combining RTILs with CPE is validated by extraction of Cr(III) and Cr(VI) ions from food samples and industrial waste. These ions are of different physiological properties²⁸⁻³⁰. Cr(III) is an essential nutrient for plants and animals which coordinates with amino-acids and helps in the metabolism of lipids, proteins and glucose. Cr(VI) is highly toxic and hazardous due to its high oxidizing potential²⁸⁻³³. Since Cr(VI) is carcinogenic, several countries have placed restrictions in use of this ion³³. These properties of Cr(III) and Cr(VI) make it very important to quantify these ions in our surrounding and food.

Herein, the extraction of Cr(III) and Cr(VI) ions is carried out by N-methyl-N,N-trioctyl-1-ammonium-5,7-diiodoquinoline-8-olate (MTAQO) supported cloud point extraction, which is followed by the quantification of the same by flame atomic absorption spectrophotometer (FAAS).

Materials and Methods

Quantification of Chromium ions is carried out using GBC 902 double beam model atomic absorption spectrophotometer. Life time studies of MTAQO and Rhodamine 6G is done using HORIBA Scientific FluoroMax 4P model spectrofluorometer. ¹H NMR, ¹³C NMR (Bruker 500M Hz), and IR (Thermo spectrophotometer system equipped with ZnSe prism) studies are carried out as a part of characterization of MTAQO. EUTECH made Cyberscan pH meter is used to adjust pH of extraction mixture. Phase separation is assisted with Remi make centrifuge (model PR 24).

All the chemicals used for the extraction process were of analytical grade. Milli Q water was used for solution preparation. Stock solutions of Cr(III) and Cr(VI) (1000 ppm) were prepared by dissolving required amount of CrCl₃.6H₂O (Loba Chemie) and K₂Cr₂O₇ (Fisher scientific) respectively in Milli Q water. Standard solutions of the same were prepared by further dilution of stock solution. Room temperature ionic liquid, N-methyl-N,N-trioctyl-1-ammonium-5,7-diiodoquinoline-8-olate is synthesized using Aliquat 336 (N-methyl-N,N,N-trioctyl ammonium chloride) (Sigma Aldrich) and 5,7-diiodo-8-hydroxyquinoline (Sigma Aldrich). Non-ionic surfactant used in this extraction is Triton X-100 (Alfa Aesar) and the buffer used is hexamethylenetetramine (Alfa Aesar). The interference studies were performed by single elemental stock solution of 1000 mg/L NaCl,

(MgNO₃)₂·6H₂O, KCl, CaCl₂, FeSO₄, (CH₃COO)₂ Co and ZnSO₄·7H₂O.

Synthesis of MTAQO

Aliquat 336 (N-methyl-N,N,N-trioctyl ammonium chloride) and 5,7-diiodo-8-hydroxyquinoline were mixed in 5:2 ratio. The reaction mixture was stirred for 48 h at 90 °C to get a viscous dark brownish room temperature ionic liquid, MTAQO^{35,36} (Supplementary Data, Fig. S1).

Cloud point extraction

Even though the cloud point extraction procedure is same for Cr(III) and Cr(VI) ions, both are extracted separately. Chromium solutions are mixed with the required amount of non-ionic surfactant, Triton X-100 and the pH is adjusted using hexamine buffer. It is then mixed with MTAQO and heated to reach cloud point temperature. Soon after, the solution turned cloudy and it is subjected to centrifugation at 3500 rpm for 5 min. The mixture separates into two layers, the upper surfactant rich phase and lower aqueous phase. In case of Cr(III) ions, aqueous phase is removed and surfactant rich phase is diluted with ethanol in order to reduce the viscosity while, 1 M HNO₃ in ethanol is used for Cr(VI) ions. Quantification is done using atomic absorption spectrophotometer (AAS).

To calculate percent recovery (%R), we have adopted the equation proposed by Egorov *et al.*³⁷

$$\%R = 1 - \left(\frac{C_f}{C_i}\right) \times 100 \quad \dots (1)$$

where,

C_f = final volume C_i = initial volume

Results and Discussion

Characterization of MTAQO

¹H NMR of MTAQO yields a chemical shift at 7.3 ppm which indicates quinoline ring protons. The signal between 1–3 ppm indicates methylene protons (Supplementary Data, Fig. S2). The ¹³C NMR signal at 207.06 ppm corresponds to alkyl carbons. The chemical shifts at 148 ppm are due to aliphatic carbons. The chemical shift at 61–62 ppm indicates aliphatic carbons of C-N bond (Supplementary Data, Fig. S3.)

FTIR Spectrum of MTAQO Shows an absorption at around 3000–3500 cm⁻¹ which indicates N-H stretching of amine. Peaks between 2500–3000 cm⁻¹ indicate C-H stretching of alkyl groups. A peak at wave number of 1600 cm⁻¹ corresponds to C=C bending of aromatic

ring. An absorption band between 700–800 cm⁻¹ indicates C-H bending of aromatic ring (Fig. 1).

Viscosity is one of the special properties of ionic liquid^{1,2,8,9}. The viscosity of MTAQO has been calculated by using the following equation.

$$\text{Viscosity} = [2(\rho_s - \rho_l) g a^2] / [9 v] \quad \dots (2)$$

where, ρ_s is density of sphere; ρ_l is density of ionic liquid; g is acceleration due to gravity; a, radius of sphere and v is velocity of sphere.

The determined viscosity of MTAQO is 4337 cP.

Lifetime study of MTAQO

Lifetime of MTAQO, rhodamine 6G and solution of Rhodamine 6G with MTAQO were measured. Here, Rhodamine 6G is the acceptor and MTAQO is the donor. It has already been proved that in presence of an acceptor, the lifetime of donor will get decreased²⁰. In our experiment, we have observed quenching in lifetime value when lifetime of solution of rhodamine 6G with MTAQO is measured. Occurrence of FRET from MTAQO to Rhodamine 6G in the solution is proposed (Supplementary Data, Table S1). Lifetime of MTAQO decreases from 1.37 ns to 0.87 ns. (Supplementary Data, Figs S4 and S5).

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis shows that MTAQO has high thermal stability mass of the sample is measured over time with temperature change. It is observed that decomposition of sample takes place only above 4500 °C (Supplementary Data, Fig. S6).

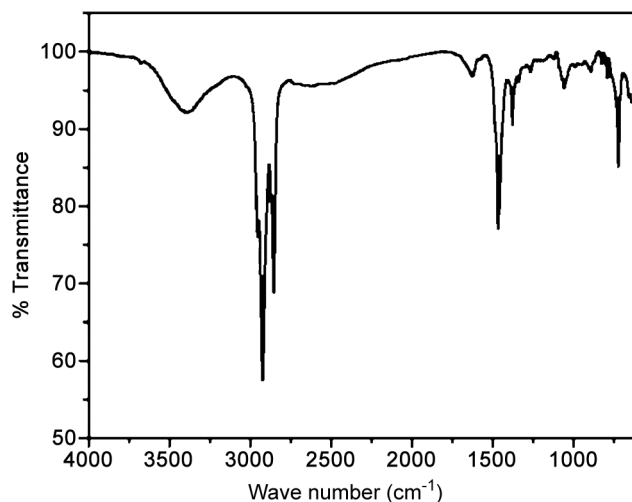


Fig. 1 — FTIR of MTAQO

Mechanism

The highest extraction efficiency of RTIL supported cloud point extraction is due to both cation exchange mechanism and surfactant effect involved in it. Metal transfer occurs from aqueous phase to surfactant rich IL phase. Generally, the mechanisms involved in the process are solvent ion-pair extraction (IP)⁷ and a cation or anion exchange (CE or AE) mechanism^{7,38}. In some cases, cation exchange mechanism and ion pairing mechanism can occur simultaneously⁷. Anion exchange mechanism is observed for the extraction of lanthanides while cation exchange mechanism for metal ions^{7,11,39,40}. In our study, cation exchange mechanism is proposed to happen by exchanging methyltrioctylammonium ion with Chromium ions.

Optimizations of experimental variables

The extraction medium is optimized by varying the pH from 3 to 9. It is observed that recovery percentage (%R) of Cr(III) and Cr(VI) increases up to 7 and is then decreased. Maximum extraction efficiency is observed at pH 7 (Supplementary Data, Fig. S7).

MTAQO supported cloud point extraction of Cr(III) and Cr(VI) ions shows different recovery percentages for different concentrations of Triton X-100. Extraction is carried out at different concentrations of Triton X-100 ranging from 0.1 to 1.1% (v/v). Maximum extraction efficiency is observed at 0.5% for Cr(III) and 1.0% for Cr(VI) which is considered as the optimum concentration for further steps (Supplementary Data, Fig. S8).

Volume of MTAQO is varied from 0.5 mL to 4.0 mL. Recovery percentage increased up to 2.5 mL of MTAQO and then remained same. So, 2.5 mL of MTAQO is considered as optimum and is used for further procedures of cloud point extraction (Supplementary Data, Fig. S9).

Time needed for cloud point extraction at cloud point temperature (75 °C) is considered as extraction time. The extraction time varied from 5 min to 25 min. At 15 min, maximum extraction is observed (Supplementary Data, Fig. S10).

Centrifugation was carried out by varying the centrifugation speed from 1500 rpm to 4500 rpm. At 3500 rpm extraction efficiency was high and did not change thereafter. It is also observed that 5 min. of centrifugation is effective in the range of 1 min to 7 min. So, it is concluded that centrifugation is best performed at 3500 rpm for 5 min (Supplementary Data, Fig. S11)

Different dilution solvents like water, methanol, ethanol, 1 M HNO₃ in methanol were used to dilute the surfactant rich phase. Ethanol is found to be the best solvent for Cr(III) while 1 M HNO₃ in methanol is best for Cr(VI) ions.

Interference study

The effect of various ions in the extraction procedure is studied. The tolerance limits of the coexisting ions are given in Table 1. It can be seen that the major cations in the selected real samples have no obvious influence on the extraction of Cr(III) under the selected conditions. The analytical parameters are given in Table 2.

MTAQO supported cloud point extraction method of Cr(III) and Cr(VI) ions is validated by applying to some real samples for which good recovery was observed. Food samples like orange juice, grape juice and egg white were considered for Cr(III) analysis while leather waste and river water were considered for Cr(VI) analysis. Separation of chromium from leather waste was carried out by urea assisted hydrolysis method⁴¹. All the samples were prepared by employing proper dilution methods. The method

Table 1 — Interference study of foreign ions

Ions	Added as	Tolerance limit (mg/L)
Na ⁺	NaCl	1000
Mg ²⁺	(MgNO ₃) ₂ .6H ₂ O	1000
K ⁺	KCl	1000
Ca ²⁺	CaCl ₂	1000
Fe ²⁺	FeSO ₄	1000
Co ²⁺	(CH ₃ COO) ₂ Co	1000
Zn ²⁺	ZnSO ₄ .7H ₂ O	1000
SO ₄ ²⁻	ZnSO ₄ .7H ₂ O	1000
Cl ⁻	KCl	1000

Table 2 — Analytical parameters

Parameters	After MTAQO supported CPE	
	Cr(III)	Cr(VI)
Calibration Range	1 to 5 ppm	1 to 5 ppm
LOD(3σ)	0.039 mg/L	0.018 mg/L
LOQ(10σ)	0.129 mg/L	0.061 mg/L
Average recovery for three successive determinations	97.77	99.37
RSD % for three successive determinations	0.059	0.058
Enrichment Factor	60	60

Table 3 — Recovery percentage of real samples

Sample	Cr(III) ($\mu\text{g/L}$)		Recovery (%)	Sample	Cr(VI) (mg/L)		Recovery (%)
	Added	Found			Added	Found	
Orange juice	0	60	98.75	Leather waste	0	15	94.28
	100	158			20	33	
Grape Juice	0	30	96.15	River	0	0.016	94.44
	100	125		Water	0.020	0.034	
Egg White	0	80	97.78	-	-	-	-
	100	176					

could effect recovery of Cr(III) and Cr(VI) above 94% (Table 3).

Conclusions

Cloud point extraction has been carried out in presence of newly synthesized room temperature ionic liquid, N-methyl-N,N-trioctyl-1-ammonium-5, 7-diiodoquinoline-8-olate (MTAQO) for the extraction of Cr(III) and Cr(VI) ions. Combination of CPE with MTAQO ion showed a synergistic enhancement effect in the extraction process. Fluorescence resonance energy transfer (FRET) is observed in MTAQO when combined with Rhodamine 6G. It is found that lifetime of MTAQO is reduced in presence of Rhodamine 6G due to FRET. Experimental parameters like pH, concentration of Triton X-100, volume of MTAQO, centrifugation time and extraction time were optimized. Recovery of 97.8% and 99.4% were observed for the extraction of Cr(III) and Cr(VI) ions respectively. Enrichment factor was found to be 60. The method is validated by its application in food samples in case of Cr(III) and leather waste & river water in case of Cr(VI).

Supplementary Data

Supplementary data associated with the article are available in the electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA_57A\(12\)1448-1453_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA_57A(12)1448-1453_SupplData.pdf).

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