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# Extraction of caffeine using ionic liquids from *Camellia sinensis*

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## ABSTRACT

Dichloromethane is the solvent of choice for extracting caffeine from *Camellia sinensis (tea leaves)*. High volatility of dichloromethane makes it a potential inhalation hazard. Green solvents such as ionic liquids (ILs) are known for their low volatility and tailorable solvent characteristics. Substitution of conventional solvent with ionic liquids is need of the day. In this paper dichloromethane has been replaced with three different ILs for the extraction of caffeine. 1-Ethyl-3-methyl imidazolium dibutylphosphate, Triethylmethylammonium dibutylphosphate and 2-Hydroxyethyl-trimethyl ammonium L+ lactate have been used for the study. These extractions have been carried out by thermal as well as microwave techniques Positive results have been obtained by replacing dichloromethane with ionic liquids. 1- Ethyl-3-methyl imidazolium dibutylphosphate has shown best results and it has been possible to replace 50-80% of dichloromethane. The purity of caffeine has been proven by using different analytical techniques HPLC, NMR, IR and TLC. The feasibility of using ILs for the extraction of caffeine has been established.

Keywords: Caffeine, *Camellia sinensis*, dichloromethane, green solvent, ILs, microwave and thermal extractions.

## INTRODUCTION

Solvent systems have been in use since long. They have found various applications as diluents in the paint industry, as solvents for chemical synthesis, for dissolution, for separation technology in the manufacture of drugs to mention a few. These solvent systems are obtained from petroleum fractions. The major disadvantage of these is their volatility and inflammability. These are highly volatile and are classified into the category of volatile organic carbon or VOC's. These thus pose environmental as well as health hazard. Use of organic solvents at the undergraduate level throughout the

University for carrying out experiments in the area of analysis, synthesis and separation causes exposure to the upcoming generations. Steps should be taken to minimize the exposure to VOC's. Control measures would include elimination/ substitution with less toxic solvents. Are we really thinking in this direction? Efforts are needed to explore & devise methodologies in reducing these levels. Industries are working in developing in plant control measures and we as R& D scientist can work in direction of controlling these levels by developing newer substituents or work in the direction of minimizing use of organic solvent systems. One such effort has been carried by students at the undergraduate level for the extraction caffeine from *Camellia sinensis.*

*Camellia sinensis* is used for extraction of caffeine. Caffeine is a heterocyclic (i.e., has atoms other than carbon in a ring) amine found in many plant materials including tealeaves, coffee beans, kola nuts, cocoa beans, and guarana seeds. Compounds found in nature are referred to as “natural products” and amine natural products are called alkaloids [1]. Hence, caffeine is an alkaloid. The structure of caffeine is given in Figure-I below

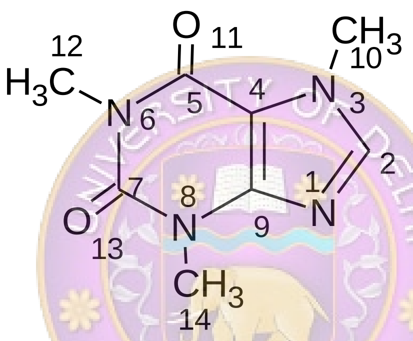



Figure-I: Structure of Caffeine (1,3,7-Trimethylpurine-2,6-dione)

Many alkaloids, including caffeine, have pharmacological effects. In medicine, caffeine is used to stimulate the central nervous system and to increase flow of urine. Because of its stimulating effects, it has been used to relieve fatigue. Caffeine is also used in analgesic tablets, as it is believed to be a pain reliever. It is also beneficial in migraines. Caffeine also finds applications as a protective agent against some diseases like Parkinson disease, heart disease and certain types of cancer. The extraction of caffeine from leaves of *Camellia sinensis* is carried by taking care of difference in the solubility of caffeine in water and dichloromethane [2].

It is important to work on developing solvents which have low volatility and flammability. The ionic liquids have low volatility & flammability, thus efforts have been made to evaluate these for extraction [3, 4]. Further, the extraction has also been carried to minimize energy requirements and time saving in operations using microwave energy [5]. The feasibility of using ionic liquids along with microwave extractions has been studied. The results of the study are presented in this paper. This study has been a step towards sustainability both from environmental and societal point of view.

## METHODOLOGY

**Materials:** Three different brands of *Camellia sinensis* (Figure-II) have been procured from the market. The composition of tea leaves varies from place to place. The general composition of tea is given in Table–I below.

Table-I Composition of Tea

| Composition of Tea | | | | | |
|---|---|---|---|---|---|
| **Substance soluble in water** | **% by weight** | **Substance insoluble in water** | **% by weight** | **Substance partially soluble in water** | **% by weight** |
| Phenolics | 25-35 | Cellulose | 7 | Polysaccharides | 13 |
| Caffeine | 3-4 | Lignin | 6 | Proteins | 15 |
| Amino acids | 4 | Lipids | 3 | Ash | 5 |
| Simple carbohydrates | 4 | Pigments | 0.5 | | |

The caffeine content of tea leaves depends on the variety and where they were grown; most of the tea varieties have caffeine 3-5% by weight.
Ionic liquids have been used as received from Sigma-Aldrich. All other chemical and reagents used are of analytical grade. HPLC is done on Shimadzu C-18 reversed-phase column (250×4.6mm, 5 µm, 1 mL/min) at Dr. B. R. Ambedkar Center for Biomedical Research, University of Delhi. Infrared (IR) spectra obtained using Perkin-Elmer 2000 FT-IR spectrometer at Department of Chemistry, University of Delhi by the KBr disc method. 1H NMR spectra have been recorded on NMR - JEOL ECX 400 MHz NMR spectrometer at University Science Instrumentation Centre, University of Delhi.

**Extraction of Caffeine**: Difference in the solubility of caffeine in water and dichloromethane has been used to separate it from the leaves of *Camellia sinensis*. The extraction has been carried out in steps. These steps are discussed below:

**Step I**- Extraction of Water Soluble Components

- Took about 100ml of distilled water in 250ml conical flask.
- Added 5gm of *Camellia sinensis* leaves and boiled it for 15 minutes. Then cooled and filtered. Microwave extraction was also carried out for 2 minutes.
- Repeated this process again with 100ml of distilled water and residual tea leaves.
- The filtrate in each case was collected.

**Step II**- Isolation of Caffeine

- Took filtrate obtained in step 1 and extracted caffeine in a separating funnel by

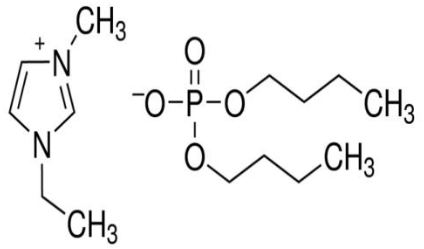
a) adding 100 ml of dichloromethane and
b) mixture of dichloromethane and ionic liquid

and allowing it to stand for 10 minutes.

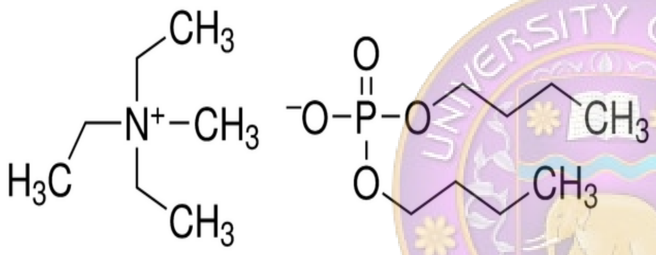
- Again repeated the same procedure as done in (step 1)
- Mixed it with the previous one.
- From this extract, dichloromethane was distilled or evaporated.
- The pale green residue obtained was crude caffeine.

The crude sample of caffeine was recrystallized from ethyl alcohol. The extraction has been carried out with ionic liquids [6]. The dichloromethane used has been replaced by ionic liquids. Three ionic liquids were selected and the structures of these ILs are given below:

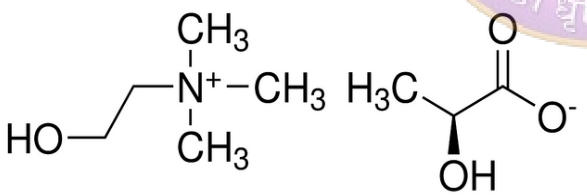
1. 1- Ethyl-3-methyl imidazolium dibutylphosphate



2. Triethylmethylammonium dibutylphosphate



3. 2-Hydroxyethyl-trimethyl ammonium L+ lactate



0.1% (W/W) solution of these ionic liquids was prepared. Dichloromethane was replaced with these ionic liquids in different ratios. The extraction was carried out both under thermal and microwave conditions. The recrystallised caffeine was analyzed for its purity by determining its melting point. Silica gel based TLC plates were run in 5% acetic acid and ethyl acetate mixture. TLC was visualized under UV light. The yield and product quality were compared. This paper covers the observation and results of the study.

## RESULTS

The results of the study have shown that all the three ionic liquids have shown different efficiencies of extraction. Moreover, the brands of tea have also shown different results. Under thermal conditions 1- Ethyl-3-methyl imidazolium dibutyl phosphate proved to be the best IL for extraction of caffeine from all the brands studied. Increasing the

concentration of IL from 50% to 80% resulted in better yields of caffeine in Wagh Bakri Tea. Triethylmethylammoniumdibutyl phosphate can replace up to 20% of dichloromethane depending upon the brand of tea used.
However 2-Hydroxyethyl-trimethyl ammonium L+ lactate, has not shown much promising results in all the brands.
Also microwave assisted extraction with the same IL gave positive results as shown in Figure-III

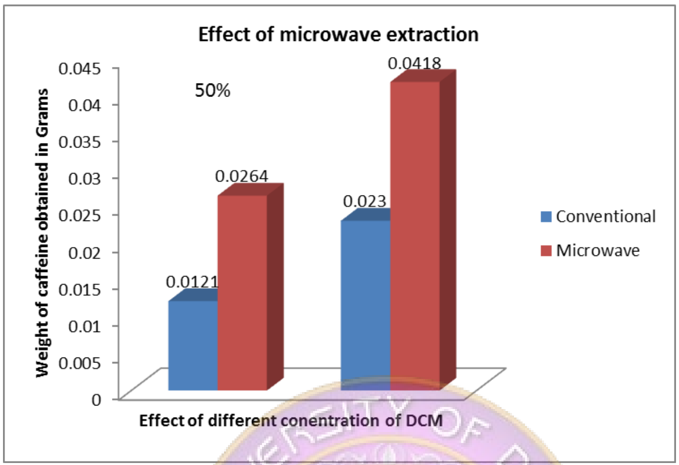



Figure-III

**Melting point**: Melting point of the caffeine thus extracted (Figure IV, recrystallised sample) is within the theoretical range i.e 227-228$^{0}$C. TLC analysis (Figure V) also confirms the purity of the isolated samples as compared to the pure sample.

Figure-IV: Crystals of Caffeine

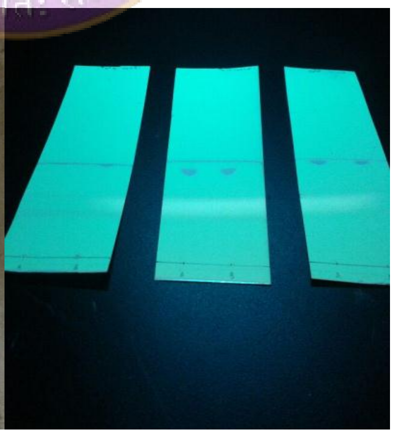


Figure-V: TLC of crystals

**NMR Spectra**: $^{1}$H NMR ($CDCl_3$), Chemical shift, δ in ppm: $C_{12}$ 3.42 ppm (s), $C_{14}$ 3.59 ppm (s), $C_{10}$ 3.99 ppm (s), $C_2$ 7.5 ppm (s). Structure of caffeine is thus confirmed by comparing it with the NMR spectra of the pure sample.
**FTIR Spectra:** Infrared spectra of the extracted sample confirmed the structure with standard FTIR spectra of the pure sample. Sharp C=O stretching peak is observed at 1705 $cm^{-1}$ while C-C stretching and C-H bending are observed at 974 and 1360 $cm^{-1}$

respectively. C-H stretching at 2954 $cm^{-1}$, C-N stretching at 1548 $cm^{-1}$ and N-H stretching frequency at 3111 $cm^{-1}$ confirms the structure of caffeine.

**HPLC:** Structure of the isolated sample of caffeine (Figure-VI) is further supported by HPLC since peak area and the retention time matched with the peak area and retention time of the pure sample (Figure-VII).

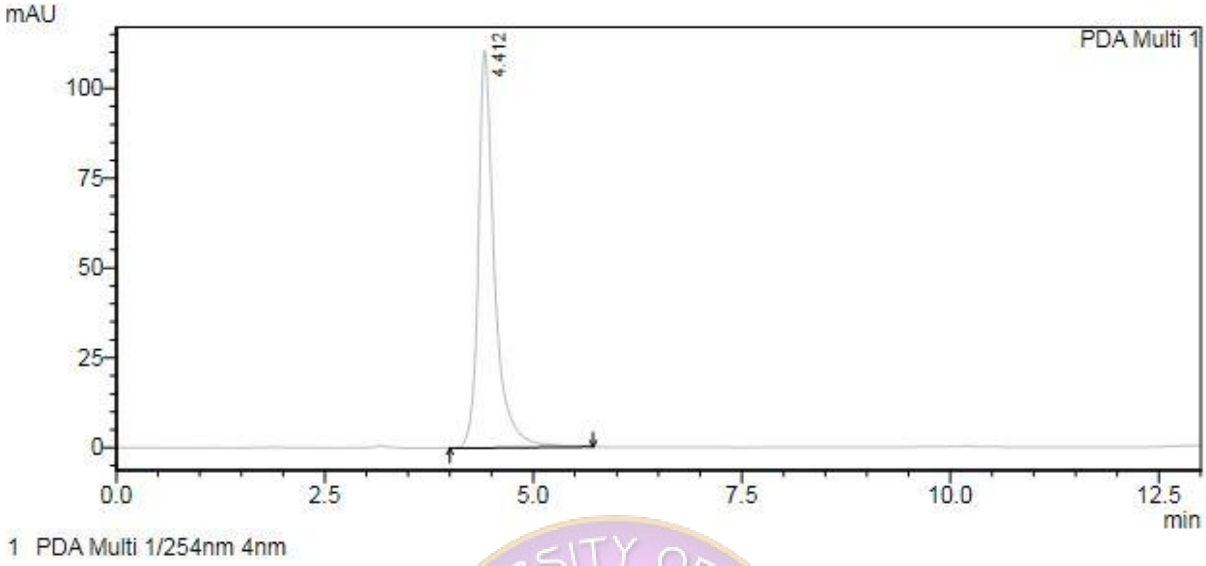



Figure-VI HPLC spectrum of caffeine sample extracted using 1- Ethyl-3-methyl imidazolium dibutyl phosphate for extraction

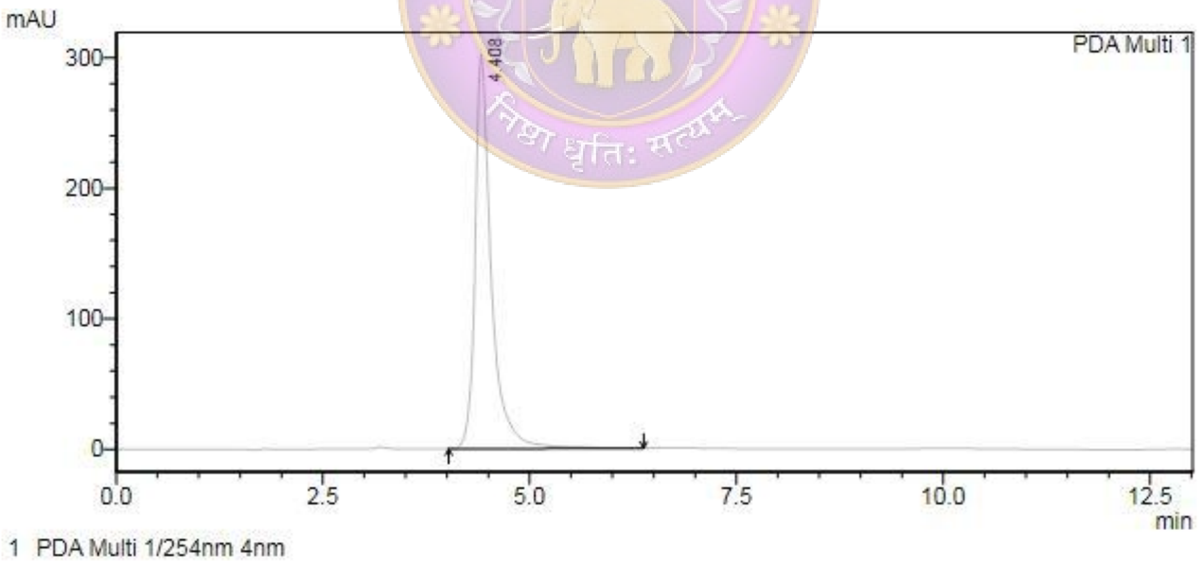



Figure-VII HPLC spectrum of caffeine sample using dichloromethane for extraction

DISCUSSION

The above results have shown that the caffeine extracted is pure. The melting point and TLC further match with that of pure caffeine. The peaks observed matched with that of caffeine. The best result observed with 1-Ethyl-3-methylimidazolium dibutyl phosphate

is due to hydrophobic cation as compared to the other two ionic liquids. In case of 2-hydroxyethyl-trimethylammonium L(+) lactate has a more polar cation. It can thus be commented that the polarity of dichloromethane matches with that if 1-Ethyl-3-methylimidazolium dibutyl phosphate. Due to these reasons it has also been possible to replace it with dichloromethane. As far microwave extractions are concerned it has been reported to carry out extraction with good efficiencies in shorter time. Positive results have thus been obtained with microwave extraction within time duration of 2 min. The microwave heating involves heating through vibration of molecules due to polarity of medium. The diploe moments of the solvents are involved in heating. Since ionic liquids have dipole moments they have also produced positive results.
Further the techniques have been used to match the product obtained with standard caffeine thus proving the feasibility of extraction.

## CONCLUSIONS

The above study concludes that caffeine can be extracted with a mixture of dichloromethane and ionic liquid. Only 0.1% solution of ionic liquid has been able to replace 50-80% dichloromethane. 1-Ethyl-3-methylimidazolium dibutylphosphate has shown to the best ionic liquid out of the three ionic liquids studied.. Microwave extractions have also shown positive results of extraction in case of dichloromethane and mixture of dichloromethane and ionic liquid. The results have been supported with different techniques NMR and IR.

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