

Ionic Liquid with β -cyclodextrin Based Aqueous Two Phase Extraction of Parabens in Water Samples

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Abstract. Ionic liquid with β -cyclodextrin based aqueous two phase extraction (IL-ATPS) of parabens has been applied on extraction of parabens in water samples. IL-ATPS is an effective green extraction and new separation technology have been used to extract parabens in sea water, treated water, tap water and river water. In this work, a few parameters were evaluated to get the optimum condition for phase separation of parabens which were the temperature, pH and percentage of recovery (%R). Good results were obtained from this study for methylparaben, ethylparaben, propylparaben and benzylparaben with percentage recovery in between 94% to 100% at 3.0 % wt of ionic liquid and process with IL-ATPS offered an obviously lower phase volume ratio. The method detection limits for this study are 0.03-0.50 ppb with the relative standard deviations less than 2.0% respectively. The parabens were well separated on a reversed-phase Chromolith C₁₈ column using High Performance Liquid Chromatography.

Keywords: Ionic liquid (IL) based aqueous two phase systems (ATPS), β -cyclodextrin, Parabens, High performance liquid chromatography (HPLC).

1. Introduction

Aqueous biphasic systems (ABS) also known as aqueous two-phase systems (ATPS) are formed when two mutually incompatible polymer/polymer, polymer/salt, or salt/salt systems are dissolved in water above a certain critical concentration[1-3]. These systems comprise mass fractions of water of (80 to 90) % in equilibrium phases, each phase containing mainly one of the compounds and a small amount of the others[4]. So, ATPS has been widely used in separation science[5-7]. Ionic liquids (ILs) have been gaining great exposure due to their potential use as green solvents and possible replacements for traditional volatile organic compounds (VOCs)[5, 6, 8]. Rogers *et al.*[4] first reported that 1-butyl-3-methylimidazolium chloride added with potassium phosphate and water can be used to form ATPS.

This new type of ATPS has many advantages, such as low viscosity, little emulsion formation, quick phase separation, high extraction efficiency and gentle biocompatible environment[9, 10]. In recent years, room temperature ionic liquids (ILs) as a class of potential green solvents, have found wide application in chemistry and biochemistry including chemical synthesis, analytical and separation processes[11, 12]. Moreover, a proper choice of the cation and/or anion composing the ionic liquid allows their properties to be tuned for specific applications[13]. Gutowski *et al.*[12] were the first reported show that imidazolium-based ionic liquids can also form ATPS in the present of aqueous solutions of K₃PO₄, representing thus a step forward in the replacement of the conventional ATPS based on polymer/polymer and polymer/salt mixture. Our literature search reveals that this is the first attempt to extract and separate parabens in IL-ATPS with β -cyclodextrin in the system utilizing imidazolium as the extractant.

2. Experimental

2.1. Apparatus and Reagents

Ionic liquid (1-ethyl-3-methylimidazolium chloride), [C₂mim]Cl, 99.5%) was purchased from Merck (Germany). Beta cyclodextrin was purchased from Acros Organics (USA), Potassium phosphate tribasic anhydrous, K₃PO₄ and potassium carbonate, K₂CO₃ were purchased from Acros Organics (USA), potassium phosphate dibasic trihydrate, K₂HPO₄ was purchase from Calbiochem (Germany), potassium hydroxide was purchased from Merck (Germany). All salts were prepared in a series of concentration at 0.5 M, 1.0 M, 1.5 M and 2.0 M in deionized water to study the effect of salt concentration on phase separation of ionic liquid.

2.2. Instrumentation

The separation and quantification of the tested parabens were carried out on Shimadzu HPLC system consisting of a pump, degasser, auto injector, column oven, ultraviolet detector, guard column, Chromolith C₁₈ column (100 mm x 4.6 mm, Merck, Germany). HPLC gradient conditions were used to separate the analytes using acetonitrile and deionized water, flow rate of 0.7 mL/min and detection at 254 nm. The gradient elution was performed as follows: 30% acetonitrile (0-8 min), ramped to 50% acetonitrile (8-14 min) and then ramped to 30% acetonitrile (14-16 min).

2.3. Preparation of Aqueous Two-phase Systems

1.0 mL of [C₂mim]Cl solution 5% wt (w/v), 1.0 mL of β -cyclodextrin (10 ppm), salt, pH and the standard solution of parabens were added into a 15 mL centrifugal tube. The mixture was sonicated to ensure the solution was mixed thoroughly, and two-phases were formed after about two minutes. The top layer of the phase was separated to vials and a 20 μ l of top layer was directly injected into the HPLC system for analysis.

3. Results and Discussion

3.1. Effect of pH on the Extraction Recovery of Parabens

Extraction recoveries of parabens were studied as a function of the pH of the extraction buffer, and the results are shown in Figure 1 below. pH range 2-12 was chosen to study the pH dependence of parabens extraction. As shown in Figure 1, the extraction efficiency of parabens was slightly no changes from pH 2-4, and started to increase until the highest recovery obtained at pH 9 and the recovery was markedly decreased from pH 10 until pH 12.

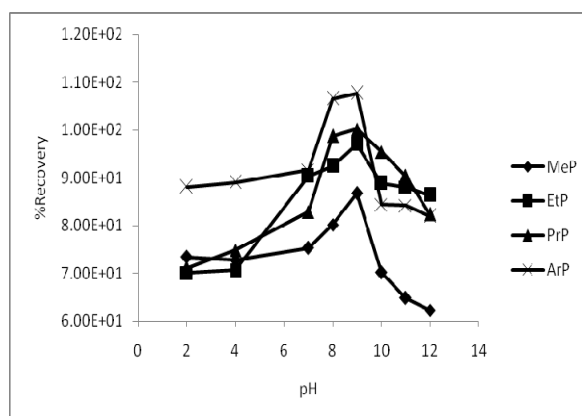


Fig. 1: Effect of pH on percentage recovery of parabens using ATPS

From the pH dependence on the extraction recovery of the parabens was maximum at its pKa value of parabens (Literature pKa values for studied parabens was 8.9-9.2[14]) and decreased as pH values increased[16]. When the pH value was below the pKa value, the parabens become deprotonated form and should be taken into account that this process is called alkaline hydrolysis of paraben take place, leading to the corresponding alcohol and *p*-hydroxybenzoic acid[14]. We can therefore deduce that pH play an important role in determining the optimum condition of paraben extraction.

3.2. Effect of Temperature on the Extraction Recovery of Parabens

The effect of temperature on the extraction recovery of parabens was also investigated as shown in Figure 2. According to previous studies using IL-based ATPS, the temperature was shown to be either a negligible or a significant factor in the extraction of various types of molecules. While He *et al.*[15] indicated that temperature had no significant influence on the distribution behavior of steroids, Pei *et al.*[16] on the other hand, reported that temperature greatly influences the extraction efficiency of proteins. As a result, it can be established that the partition coefficients dependence on temperature will largely depend on the solute and ternary system under study.

The results obtained for study the effect of temperature on the paraben partitioning are depicted in Figure 2. The results indicated that temperature is less pronounced on the paraben extraction using IL-ATPS. Within 25-50°C, the extraction recoveries of parabens fell in the narrow range of 88-94% when 2 ppm of standard parabens were added, indicating that temperature had little influence on the distribution behavior of parabens. Thus, this method provides a relatively wide range of temperature for the study on the extraction behavior of analytes. The following studies were carried out at temperature 30 °C. Similar study had conducted by He *et al.*[15] reported that temperature had little influence on the distribution behavior of steroids with the results obtained fell in the range of 90-97%. While Pei *et al.*[10] studied the effect of temperature on phase separation concluded that the binodal curves are not sensitive to an increase of temperature. This result is not in agreement with the fact that the binodal curves of IL-ATPS are closer to the origin with an increase in temperature. A possible reason is that the hydration of ionic liquid is not sensitive to temperature.

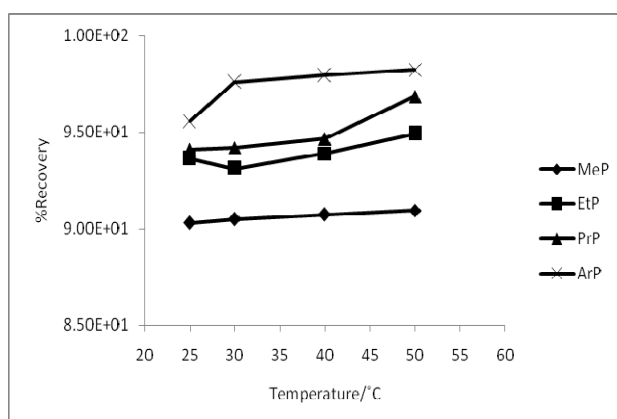


Fig. 2: Effect of temperature on recovery of paraben using ATPS

3.3. Method Validation

The parameters such as linearity and limit of detection and extraction efficiencies of four paraben were determined from spiked solution of analytes under the above optimized condition. The results were listed in Table 1 below. Linear ranges of parabens were obtained from 0.10-10 µg/L respectively. The developed method was applied to the determination of the recoveries of parabens from variety of water samples such as river, treated, sea and tap water. The results were summarized in Table 2. Studies were carried out using sea, river, tap and treated water samples. Recovery rates using IL-ATPS were between 94% and 99% with relative standard deviations (RSD) of less than 4%. The following results show that present method has a satisfactory reproducibility and accuracy for the determination of the analytes in aqueous samples.

Table 1: Linear calibration range, relative standard deviations and limits of detection of parabens.

Chemical name	Linear range (µg/L)	RSD (% n =3)	R ²	LOD (µg/L)
Methyl paraben	0.10-10	1.14	0.994	0.03
Ethyl paraben	0.10-10	1.18	0.995	0.01
Propyl paraben	0.10-10	1.07	0.982	0.07
Benzyl paraben	0.10-10	1.28	0.993	0.52

The present method is compared with other alternative procedures[17-20]. It can be concluded that our proposed method gives good recoveries and almost similar limit of detection as compared to the other procedures. The cost of acquisition, total extraction time and solvent consumption of the present method are however, lower than those methods. Moreover, the complexity of the analytical systems employed[23] and sample pretreatment required [21-22] in those procedures are comparable with the developed IL-ATPS method. These results have shown that the method developed is feasible to be used for monitoring parabens compound in environmental water samples.

Table 2: Recoveries of parabens in water samples (n=3).

Compounds	sea water	river water	tap water	treated water
	IL-ATPS Recovery (%) (RSD)	IL-ATPS Recovery (%) (RSD)	IL-ATPS Recovery (%) (RSD)	IL-ATPS Recovery (%) (RSD)
Me-P	97.4 (1.40)	97.2 (0.60)	94.4 (3.60)	96.1 (0.20)
Et-P	98.5 (2.80)	96.5 (0.40)	97.9 (1.20)	99.9 (0.40)
Pr-P	96.6 (1.90)	95.3 (0.20)	94.8 (2.40)	98.2 (0.50)
Ar-P	96.1 (1.50)	96.3 (0.30)	99.4 (3.50)	98.8 (0.20)

*Me-P = methyl paraben, Et-P = ethyl paraben, Pr-P = Propyl paraben, Ar-P = benzyl paraben

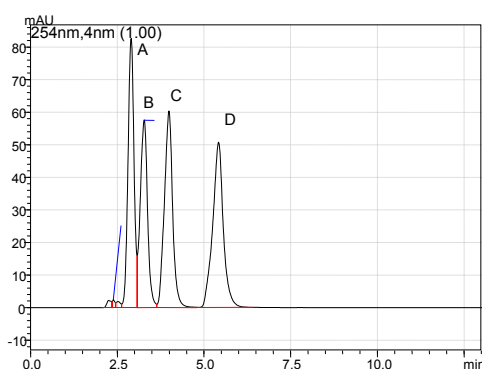


Fig. 3: Chromatogram of sea water spiked with parabens. Amount of spiked at 2 ppm of A=MeP, B=EtP, C=PrP and D=ArP.

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5. References

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