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Performance of sodium salts as an inducing phase separation agent on the polyethylene glycol/β-cyclodextrin cloud point extraction for the determination of propylparaben

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ABSTRACT

Propylparaben is a homologous series of parabens that is widely used in cosmetic products. However, this compound is toxic, and many countries have subsequently banned its use in cosmetic products. A simple and cost effective cloud point extraction (CPE) system was developed for the extraction and determination of propylparaben in cosmetic samples prior to its spectrophotometric determination. Two types of CPE systems of polyethylene glycol/β-cyclodextrin were developed based on sodium hydroxide and sodium bicarbonate salts as an inducing phase separation agents, represented as CPE-(PEG/β-CD)-NaOH and CPE-(PEG/β-CD)-Na_2CO_3, respectively. The effects of parameters; salts, surfactant, β-CD, pH, and analyte concentrations, temperature, incubation time, and water content were investigated in the context of removing propylparaben in aqueous samples. The optimized CPE-(PEG/β-CD)-NaOH was used to extract propylparaben in cosmetic samples due to its superior performance to the CPE-(PEG/β-CD)-Na_2CO_3. The calibration graph was linear, in the range of 0.04–2.00 mg L^{-1} of propylparaben, with a regression coefficient of 0.9987. The limit of detection was 0.003 mg L^{-1}, while the relative standard deviation (RSD) was 101.02%. Satisfactory recoveries were reported in the range of 80.63–119.71%. The results confirmed that the proposed method is suitable for the determination of propylparaben content in cosmetic samples.

Keywords: Cloud point extraction; Polyethylene glycol/β-cyclodextrin; Sodium hydroxide; Sodium carbonate; Propylparaben

1. Introduction

The utilization of antimicrobial agents in cosmetic products helps protect consumers while maintaining the effectiveness and stability of the products' formulation. It also prevents alteration and degradation of the formulation due to microbial contamination. Parabens, which is also known as *p*-hydroxybenzoic acid esters, are generally used as antimicrobial reagents in cosmetics due to their broad antimicrobial spectrum and excellent stability and non-volatility. Parabens are found in single or combinations of two or more substances in almost all types of cosmetic products. Cosmetics that could contain parabens include moisturizers, makeup, creams, perfumes, and shaving products.

A propylparabenis a homologous series of parabens that include methyl-, ethyl-, butyl-, and benzylparabens. Propylparaben differs slightly from other alkylparabens due to its alkyl chain lengths. Propylparaben is commonly used and is easily found in commercial cosmetic product. Propylparaben (0.02% (w/w)) is usually used together with methylparaben (0.18% (w/w)) due to its synergistic effect [1]. Propylparaben is frequently used in formulations of

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cosmetic products due to the increased chain lengths of the alkyl moiety, which in turn increases antimicrobial activity, making it effective against yeast and molds compared to other parabens. Moreover, propylparaben is less toxic and more soluble in water compared to butyl- and benzylparaben [2].

Although parabens' acute toxicity is very low, these compounds are classified as endocrine disrupting chemicals due to the elongation of the alkyl chain in its ester group [3]. A possible relationship between breast cancer and prolonged dermal expositions to products containing-parabens has been reported [4,5]. This article is vigorously debated and its veracity/quality is repeatedly questioned and criticized. More detailed studies confirmed that parabens do not mimic estrogenic [6,7]. Due to this heated controversy,the European Union's Scientific Committee on Consumer Safety restricted their usage, and only allow 0.4% (w/w) of methyl- and ethylparaben, 0.14% (w/w) of propyl- and benzylparaben, and up to 0.8% (w/w) as maximum concentrations for parabens and its ester, depending on whether a single paraben or a combination of them are being used. This law was ratified by the European Union (EU) Cosmetics Directive (76/768/EEC) [8].

The controversial use of parabens in cosmetics make this compound particularly interesting to analysts. Several methods have been reported for the determination of propylparaben in real samples. These include liquid-liquid extraction [9], solid phase extraction [10], capillary zone electrophoresis [11], high performance liquid chromatography (HPLC) [1], gas chromatography (GC) [12], and HPLC-GC [13]. However, some of these methods are complex, time consuming, and costly. They are also difficult to use for analysing complex matrix samples without pre-treatment. Therefore, the development of a simple and rapid separation or pre-concentration systems for the analysis of parabens in cosmetic stuffs is essential.

The cloud point extraction (CPE) method was proposed in this study. CPE was firstly reported by Watanabe and Tanaka [14], and further developed by Quina and Hinze [15]. Up till now, it has been used for the pre-concentration, separation, and purification of variety of substances, such as organic and inorganic pollutants in real-world samples, including water [16], drug [17], cosmetic [18], food [19], and biological [20] samples. Compared to traditional liquid-liquid extraction, CPE uses a surfactant that is low in cost and provides higher extraction efficiency enrichment of the detected analyte. The heterogeneous extraction at cloud point based on surfactants are simple, rapid, and powerful, which extract the solutes from the homogeneous or pseudo-homogeneous aqueous solution into the water-immiscible phase post phase separation [21]. The surfactants are degradable and protect the activity of the targets [22]. It is also less toxicthan organic solvent. The use of this micellar system is widespread for the past decade due to its "green chemistry" approach [23].

The CPE system explained that at certain temperatures, aqueous solution of a non-ionic surfactant or zwitter ion surfactant are separated into two phases. The first one is a surfactant-rich phase containing a high concentration of surfactant, which has small volume compared to the solution and the second one is the aqueous phase containing a low concentration of surfactant, near to critical micellar concentration (CMC). This separation temperature is known as the cloud point temperature (CPT) of the surfactant [24]. When an sparingly water soluble analyte is put into contact with an aqueous solution of non-ionic surfactant and the system is heated at temperature above the surfactant cloud point temperature, the analyte will distribute itself between the two phases, preferring the preferential mode of the surfactant rich phase [25].

The two basic components that are prerequisites for CPE include a surfactant and a salt solution, which separates into immiscible surfactant-rich and surfactant-poor phases. Surfactants are of particular interest as guest molecules, due to the balance of several intermolecular forces, such as the hydrophobic effect, which tends to protect the tail from the aqueous environment, the requirement of dehydration of tails and head groups during the formation of complexes, as well as effects due to steric hindrances [21]. A surfactant is used to carry out a systematic study on the association (binding) process by changing its structure to balance hydrophilic and hydrophobic contributions. This subsequently changes the physicochemical property of the surfactants [26] which is CMC.

Many surfactants, such as such as DC193C [27], nonionic polyethylene glycol (PEG) [28], PONPE [17], Triton X [29], anionic sodium dodecanesulfonic acid [30], and cationic Aliquat-336 [31] series have been used for CPE. A PEG surfactant (also known as dimethicone copolyols, silicone glycols, or silicone surfactants) was selected in this study. PEGs are one class of amphiphilic materials having water soluble and a silicone soluble portion in one molecule. Among surfactants, PEGs is known to be a suitable alternative for volatile organic compounds (VOCs), due to it being inert, odourless, colourless, non-irritant, and non-evaporating. PEGs are also considered inert, as they do not react to other materials and are soluble in many organic solvents. Due to its biocompatibility and friendly nature, PEGs have been used in the cosmetics, food, and pharmaceuticals [32]. In the presence of salt, long-tailed surfactants self-assemble in aqueous solution at a particular temperature into long, flexible, and worm like micelles, rendering the resulting solution viscoelastic [21]. An analyte interacting with micellar systems can therefore be concentrated into the surfactant-rich phase in small volumes. Sodium hydroxide (NaOH) [33] and sodium carbonate (Na_2CO_3) [34] salts have been reported to be effective for inducing phase agents in the CPE systems.

The influence of *beta*-cyclodextrin (β-CD) on the aggregation of surfactants in aqueous solution has attracted increasing attention in colloid science. β-CD is most frequently used due to its relative ease of synthesis, low prices, and the size of its internal cavity that can accommodate large number of guest molecules [26]. β-CD isa glucose molecule produced from the enzymatic degradation of starch by bacteria. It is cyclic oligosaccharides, consisting of seven (β) units, which are joined together by α-(1,4)-glycosidic linkage bonds, forming a torus-shaped ring structure. It has a primary hydroxyl group on the narrow side, and a secondary hydroxyl group on the inner cavity, as well as a hydrophilic external surface. Due to its unique structure, it acts as a hosts for various molecules (guests), forming "host-guest complexes" in aqueous media [35]. Therefore, β-CD is able to form host-guest complexes with most

surfactants' hydrophobic tails into CDs' cavities. Xu et al. (2012) [36] found that the addition of β-CD to the non-ionic surfactant (TX-114) solutions leads to growth of the aggregates instead of their dissociation. The result indicated that the solutions undergo micellar growth and micelle to vesicle transitions after the addition of β-CD. Moreover, β-CD is also important for controlling the thicknesses of hydrophobically modified polymers, e.g., ethyl(hydroxyl ethyl) cellulose and modified poly(ethylene glycol) in water by decoupling hydrophobic-hydrophobic intermolecular interactions [26,37]. Hence, we believed that the orientation of the β-CD-surfactant complexes in the CPE is suitable for the cooperative binding of the analyte recoveries.

Taking full advantage of the suitability of the CPE approach, this study aims to develop a more efficient, cheap, and simple CPE system to measure the amount of propylparaben in cosmetic samples using spectrophotometry detection. We have successfully optimized a mixed micelles of polyethylene glycol/β-cyclodextrin (PEG/β-CD) complexes using sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) as salt additives, reported as CPE-(PEG/β-CD)-NaOH and CPE-(PEG/β-CD)-Na_2CO_3, respectively. The extraction efficiency of propylparaben via the effect of concentration salts, surfactant, β-cyclodextrin, and analyte were analysed as well. The temperature, incubation time, and effect of water content has also been investigated.

To the best of the author's knowledge, only some studies described the determination of propylparaben by using CPE system [38,39]. This study differ from the one reported previously, and in this work, we pioneered the development of a very simple, rapid, and cheap of CPE system based on PEG and β-CD mixed micellar with NaOH and Na_2CO_3 as salts-induced phase separation to detect propylparaben in cosmetic samples.

2. Materials and methods

2.1. Materials

The commercial surfactant of polyethylene glycol (PEG) (molecular mass 1500), propylparaben and β-cyclodextrin (β-CD) (99%) were purchased from Sigma-Aldrich (Germany). Sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) were purchased from Bendosen chemicals (Malaysia), respectively. Other salts included sodium chloride (NaCl), Potassium chloride (KCl), and Potassium Iodide (KI), purchased from R&M chemicals (Malaysia). Ethanol and hydrochloric acid (HCl) were purchased from HmbG® chemicals (Malaysia). These chemicals were of analytical reagent grade, and were used as is without further purification. Distilled water was used throughout the experiments. Fresh working standard solutions were made by diluting, stock solution, which was then kept stable during the day.

2.2. Instrumentation

Absorption spectra and absorbance measurements were obtained using a T60 UV-Vis Jenway spectrophotometer (model 6715, UK), with 1 cm glass cells. A Metrohm digital pH meter (model 632, Switzerland) with a combined glass electrode was used to measure the pH values. A MPW-350R centrifuge (Behsa, Iran) was used to accelerate the phase separation process. A Clifton thermostatic water bath (Memmert, Germany) was used to maintain temperature in CPE experiments.

2.3. General procedure for extraction of propylparaben using the CPE method

10 mL of micellar solution was obtained in a centrifugal vial by blending the mixture of 70% (w/v) surfactant concentration in aqueous solution, 1.0 mL of stock solution of propylparaben (15 mg L^{-1}), 1.0 mL of β-CD (15 mg L^{-1}), and 1.0% (w/v) of sodium salts solution. The pH of the solution was adjusted in a glass centrifuge tube prior to the extraction process. Then, the centrifugal vial was left in a thermostatic water bath at 50°C for 15 min, and later cooled to room temperature. This resulted in the separation of the phases and increased viscosity. The surfactant-rich phase at the top layer was separated using a syringe to minimize the possibility of cross-contamination of analyte from the corresponding aqueous phase. Then, the volume of surfactant-rich phase was measured. The surfactant-rich phase was isolated before being analysed using UV-vis spectrophotometer. The data reported in this study are the average of three measurements.

2.4. Water content

The water content of the surfactant-rich phase after extraction was measured by drying the surfactant rich phase at 373 K until no mass loss. The water content was obtained by calculating the weight differences of the surfactant rich phase before and after drying. The data reported in this study are average of five measurements.

2.5. Parameters that optimize CPE

The main variables affecting the extraction process, such as the pH, concentration, and amount of surfactant, equilibration temperature and time, concentration of salt and analyte were optimized. The extraction efficiency of the phenol by surfactant from the sample was calculated using:

$$\text{Extraction efficiency } (\%) = \frac{C_s V_s}{C_o V_o} \times 100$$

where C_S represents the phenol concentration in the surfactant rich phase of volume V_S and C_o represents the phenol concentration in the sample-surfactant mixture of volume V_o.

2.6. Preparation of CPE in cosmetic samples

Appropriate amounts of cosmetic samples were dissolved in distilled water. After dissolving in water, samples solutions were filtered using a membrane filter (0.45 μm) to remove the suspended particulate matter. The filtered sample solutions were diluted to a suitable volume in a volumetric flask. Aliquot of solutions was treated under the

recommended procedure (Subsection 2.3) for CPE and the subsequent determination of propylparaben.

3. Results and discussion

3.1. Effect of type and salt concentration on CPE

The phase separation in the cloud point extraction is normally induced by heating the mixture containing the surfactant to a temperature above the cloud point. However, analytes sensitive to this approach due to its inherent volatility and solution heating could actually results in its loss[40]. The salting out effect is adopted as an alternative to induced phase separation in the aqueous solution. The effect of a variety of salt additives of mono and divalent ions, including NaOH, NaCl, Na_2CO_3, KI, and KCl was extensively investigated to improve the capability of CPE for the extracted propylparaben. The result (Fig. 1) shows that NaOH and Na_2CO_3reported higher responses for propylparaben analyte when compared to those obtained from other salts. Both sodium salts of NaOH and Na_2CO_3 are successfully separated into two phases on the CPE systems. Too little or/and non-forming two phases system on CPE use NaCl, KCl, and KI salts. It is well known that the relative salting-out power observed for the different salt additives seems to agree with the ionic strength of each salts. The ionic strength of the solution can alter the cloud point temperature (CPT) [15], thus the addition of salts to the surfactant micellar solution can increase or decrease its CPT, which will facilitate the separation of two phases by altering the density of the bulk aqueous phase [41,42]. Furthermore, it can also be seen that the salts derived from mono and divalent ion pairs such as $2Na^+/CO_3^{2-}$ reported higher extraction efficiency for propylparaben analyte compared to monovalent ions (e.g., Na^+/Cl^-, K^+/I^- and K^+/Cl^-). This is supported by Purkait et al. [43], where it is believed the salting-out effect is more pronounced for divalent salt than its monovalent counterpart. Taking into account NaOH vs. Na_2CO_3, the result shows the ability to enhance the extraction efficiency of propylparaben analyte when NaOH > Na_2CO_3 (~5 times for NaOH, and 4 times for Na_2CO_3). This took place due to the effect of cations on salting-out on CPE system being smaller than anions [44]. However, the capability of salts to enhance the extraction efficiency cannot completely be attributed to ionic strength, because it is also dependent on other parameters, such as experimental conditions and counter ions [45].

The salt concentration plays a vital role in the CPE process, which accelerates the phase separation for some nonionic surfactant systems since it increases the density of the bulk aqueous phase [46]. The concentration of salt increases the size and aggregation number of micelle, which increases the solubility of the analyte in the surfactant-rich phase. The water molecules goes into the dilute phase due to the salting-out effect. The salt acts as "drying agent", causing partial dehydration for both surfactant and propylparaben via the breakage of hydrogen bonds by water molecules. This obviously results in a significant reduction of the cloud point in a way that phase separation already occurs at room temperature [28].

Since NaOH and Na_2CO_3 reported higher extraction efficiency of propylparaben removal compared to other salts, different concentrations of these salts were tested in the range 0.5–3.0% (w/v). It can be seen in Fig. 2 that the extraction efficiency of propylparaben analyte increase with an increase in salt concentration, from 0.5% (w/v) up to 1.0% (w/v), then slowly decrease to exceed 1.0% (w/v). Above 1.0% (w/v), a strong salting-out effect produced a surfactant-rich phase that became cloudier and dominated to surface of the solution, making it difficult to measure or handle. NaOH is more prevalent than Na_2CO_3. NaOH and Na_2CO_3 provide the same cation (Na^+), but the influence of the cation is usually smaller than that of the anion [44]. OH^- is a stronger breaking agent than CO_3^-, which also exhibited stronger interactions with water molecule than the water molecules itself, rendering it able to rupture hydrogen bonds between water-water hydrogen bonds, forming separate phases. NaOH can immediately separate the CPE at room temperature,whereas no separation could be observed on using the carbonate and/or bicarbonate of sodium and potassium, even at their saturated solu-

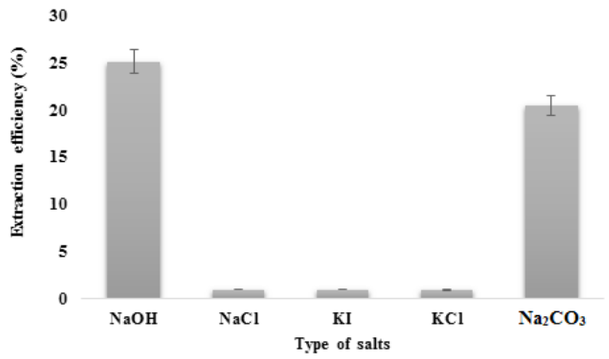

Fig. 1. The effect of the types of salt. PEG concentration (w/v); 1.0%; –CD concentration (v/v): 10 mg L^{-1}; propylparaben concentration (v/v): 10 mg L^{-1}; equilibrium temperature (°C): 50; incubation time (min): 15.

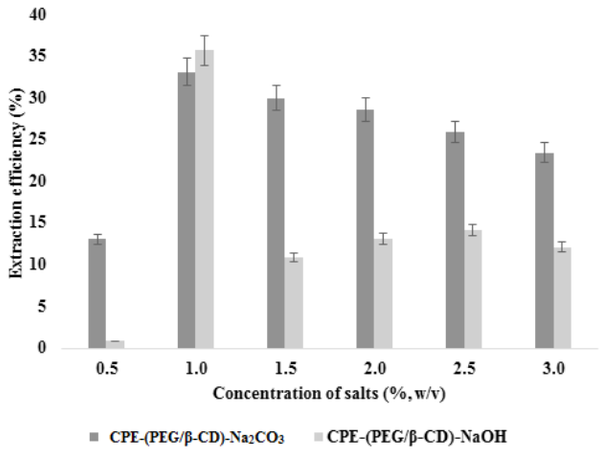

Fig. 2. The effect of the salts concentration. PEG concentration (w/v): 1.0%; β-CD concentration (v/v): 10 mg L^{-1}; propylparaben concentration (v/v): 10 mg L^{-1}; equilibrium temperature (°C): 50; incubation time (min): 15.

tions at room temperature [47]. As reported by Mangels and Bailey [48], within a Hofmeister series of anions, the effect of hydroxyl (OH^-) ion is found to be maximum (at 1.0% (w/v)), meaning it reported the highest viscosity of surfactant suspension among the concentration-viscosity characteristics of surfactant-rich phases. Therefore, 1.0% (w/v) NaOH and 1.0% (w/v) Na_2CO_3 were selected as the optimum satisfied, and the resulting samples of CPE were presented as a CPE-(PEG/β-CD)-NaOH and CPE-(PEG/β-CD)-Na_2CO_3, respectively, for subsequent analyses.

3.2. Effect of surfactant concentration

The theoretical pre-concentration factors depend on the volume of the surfactant-rich phase, which varies with the surfactant concentration in the solution [49]. It is desirable that the minimum amount of surfactant be used for maximum extraction of propylparaben analyte. The amount of PEG not only affect extraction efficiency, it also affect the volume of the surfactant-rich phase [40]. The effect of the non-ionic PEG concentration is analyzed to ensure a successful CPE, due to the maximization of the extraction efficiency via a small phase volume ratio (V_s/V_o), which improves its concentration ability. Fig. 3 shows the effect of PEG surfactant concentration determined at different concentrations: 10% (w/v), 30% (w/v), 50% (w/v), 70% (w/v), and 110% (w/v). The extraction efficiency of propylparaben analyte increases from 10% (w/v) to 70% (w/v) for both CPE-(PEG/β-CD)-NaOH and CPE-(PEG/β-CD)-Na_2CO_3. This is due to the increase in the viscosity of the surfactant-rich phase, where the viscosity of the surfactant PEG will interrupt the CPE phase separation and decrease the volume of the surfactant-rich phase. The addition of more surfactant increases the volume of the micellar phase, which in turn increases the viscosity of the final analysis solution [50]. Therefore, by increasing the PEG surfactant concentration, the number of hydrophobic micelles increased,which in turn increases the extractability of PEG, resulting in increased solubilization of propylparaben in the PEG surfactant. At lower surfactant concentrations, the extraction efficiency is low, which could be attributed to the inadequacy of the assemblies in quantitatively entrapping the hydrophobic complex. Further increase in the concentration of the PEG (concentration exceeding 70% (w/v)) decrease the extraction efficiency due to the increment in the volumes and the viscosity of the surfactant phase. The extract is therefore more diluted when more PEG surfactant is used, resulting in the loss of sensitivity with increasing PEG concentration above 70% (w/v), due to the increased viscosity of the surfactant-rich phase [40]. The more viscous the solution, the slower the mass transport of propylparaben molecules to the PEG-β-CD surfactant during the deposition step, which lead to the un-solubilized excess propylparaben being retained in the aqueous phase, accounting for a decrease in the extraction efficiency of the propylparaben analyte. A concentration of 70% (w/v) was selected as the optimum concentration to affect the highest possible extraction efficiency and pre-concentration factor. It can be seen in this work that the extraction efficiency (%) of propylparaben analyte with CPE-(PEG/β-CD)-NaOH is more successful than CPE-(PEG/β-CD)-Na_2CO_3.

3.3. Effect of β-cyclodextrin (β-CD) concentration

In this study, the β-CD was used as supporter/modifier to enhance the extraction efficiency of the PP. Based on Fig. 4, the extraction efficiency of propylparaben in the absence of β-CD is considered too low. It is evident that the presence of β-CD in the CPE systems enhanced the extraction efficiency of propylparaben from the aqueous solution. A similar study was conducted by Zain et al. [28] and Noorashikin et al. [38] where they used a native β-CD and modified β-CD as a modifier agent in the CPE system with silicon ethylene oxide copolymer (DC193C) as its surfactant agent. The addition of β-CD could enhance the extraction efficiency of propylparaben, due to its hydrophobic inner cavity that interacts with the hydrophobic propylparaben. The binding mechanisms is dominated by hydrogen bonding and hydrophobic interaction between propylparaben and β-CD molecules, forming inclusion complexes.

The effect of the β-CD concentration is investigated between 5 and 25 mg L^{-1} for both CPE-(PEG/β-CD)-NaOH and CPE-(PEG/β-CD)-Na_2CO_3 systems(Fig. 4). It is evident

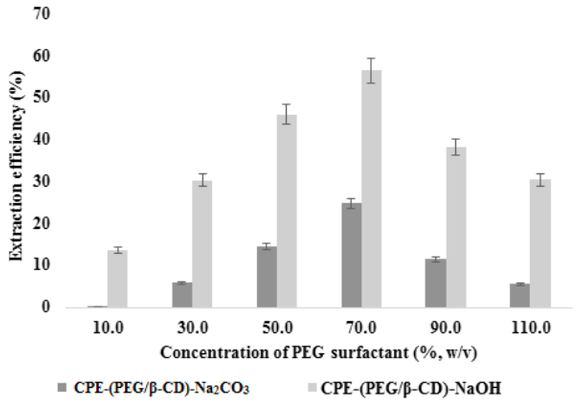

Fig. 3. The effect of PEG concentration. NaOH or Na_2CO_3 concentrations (w/v): 1.0%; β-CD concentration (v/v): 10 mg L^{-1}; propylparaben concentration (v/v): 10 mg L^{-1}; equilibrium temperature (°C) :50; incubation time (min): 15.

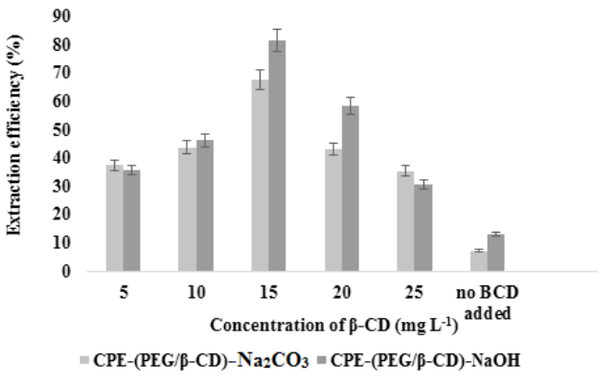

Fig. 4. The effect of β-CD concentration. PEG concentration (w/v): 70.0% with 1.0% (w/v) of NaOH and 90% (w/v) with 1.0% (w/v) of Na_2CO_3; PP concentration (v/v): 10 mg L^{-1}; equilibrium temperature (°C): 50; incubation time (min): 15.

that the extraction efficiency gradually increased initially with the increase of β-CD concentrations from 5 to 15 mg L^{-1} of the propylparaben for both the CPE-(PEG/β-CD)-NaOH and CPE-(PEG/β-CD)-Na_2CO_3 systems. The extraction efficiency of propylparaben is highest at a concentration of 15 mg L^{-1} β-CD, indicating that the inclusion complex possibly occurred between the β-CD with the phenolic ring of the propylparaben due to the hydrophobic species of propylparaben [34]. Moreover, the addition of β-CD in CPE systems lead to a significant aggregate growth in the aqueous PEG surfactant solutions. Xu et al. [36] explained that the β-CD seem can provide a facile and effective approach for controlling the aggregation of non-ionic surfactant, which may in turn change the solution properties, and even lead to analyte recognition. As a surfactant building unit, β-CD can be physically attached to a hydrophobic moiety by host-guest interaction, and the resultant β-CD-surfactant complexes can generally assemble into aggregates in an unconventional and non-amphiphilic manner, driven by CD-CD H bonds. Hence, the aggregation behaviour of the β-CD/surfactant complexes is mainly driven by the H bonds between CD molecules, as the hydrophilic outer surface of the β-CD/surfactant complexes rules out the possibility that the aggregation is driven by a hydrophobic effect. The micelles can come into contact and overlap each other due to local structural reorganization. They fuse with another micelle aggregate, forming larger micelle networks that can transform into vesicles. Beyond 15 mg L^{-1} of β-CD, the extraction efficiency of propylparaben in CPE-(PEG/β-CD)-NaOH and CPE-(PEG/β-CD)-Na_2CO_3 declines. Further increase in the concentration of β-CD leads to excess insolubilized propylparaben due to the insufficient amount of PEG molecules. This could be attributed to the optimal concentration of β-CD (15 mg L^{-1}) being sufficient to control the aggregation of the PEG surfactant (70% (w/v)). It is speculated that if enough β-CD is added to a micellar surfactant solution, all of the surfactant will eventually be complexed, resulting in the total breakdown of the micelles [51]. Thus, excess propylparaben are retained in the aqueous phase, affecting a decrease of extraction efficiency of propylparaben in the CPE-(PEG/β-CD)-NaOH and CPE-(PEG/β-CD)-Na_2CO_3 systems. In addition, the interaction between propylparaben and β-CD could be attributed to the "dynamic equilibrium". The binding of propylparaben molecule within the hydrophobic core of β-CD is not fixed or permanent, which decreases the propylparaben removal efficiency. Furthermore, the binding strength depends on how well the "host-guest" complex fits together and the specific local interactions between the surface atoms [52]. It can therefore be surmised that the β-CD exhibited excellent extraction performance vis-à-vis propylparaben analyte at a β-CD concentration of 15 mg L^{-1}.

3.4. Effect of pH study

pH plays a unique role on the formation of surfactant-analyte complex and the success of the subsequent extraction process. The extraction efficiency depends on the acidity of the solution, as the pH has an impact on the overall charges of the analyte, which affects the generation of the complex between the analyte and the surfactant active functional groups. The variation in the extraction efficiencies can also be explained by accounting for the change in the charge of propylparaben, owing to the pH of the solution. This prompted us to investigate the effect of the different pHs on the extraction efficiency of the propylparaben. Cloud point extraction of propylparaben is carried out within pH of 1–13 on the CPE-(PEG/β-CD)-NaOH and CPE-(PEG/β-CD)-Na_2CO_3 systems (Fig. 5). The extraction recovery for propylparaben increased with increasing pHs from 1 to 9, and is maximized at a pH of 9, where the uncharged form of propylparaben analyte prevailed. At pHs lower than 9, the propylparaben is protonated (less than pKa value = 8.87) [53], which increased the propylparaben ionic characteristics. The electrostatic repulsion between the protonated form of propylparaben and the positive charge of PEG predominates, leading to lower solubilisation of the analyte-surfactant interaction. When the pH of the solution exceeds 9, it could be problematic for the hydrolysis of propylparaben. At pHs higher than 9 (above pKa value), the extraction efficiency for the propylparaben decreases rapidly, due to the formation of phenolate ion of propylparaben. Alkaline hydrolysis of propylparaben takes place, leading to the production of alcohol and hydroxybenzoic acid [53]. Furthermore, the ionic form of a neutral molecule formed upon the deprotonation of a weak acid (or protonation of a weak base) normally does not interact with, or bind, the micellar aggregates as strongly as does in its neutral form due to the non-dissociated type of non-ionic surfactant [54]. The results agreed with the study on the effect of pH toward protonation/deprotonation and the pKa values of parabens. The significant variance of extraction efficiency of extracted propylparaben were clearly higher on CPE-(PEG/β-CD)-NaOH system, at 81.4%, compared to the CPE-(PEG/β-CD)-Na_2CO_3 system, at 40.0%. Taking into account all of these factors, a pH of 9 was the optimal condition set for further study.

3.5. Effect of propylparaben concentration

The influence of the initial concentration of the extraction of propylparabenis investigated in the CPE-(PEG/β-CD)-NaOH and CPE-(PEG/β-CD)-Na_2CO_3 sys-

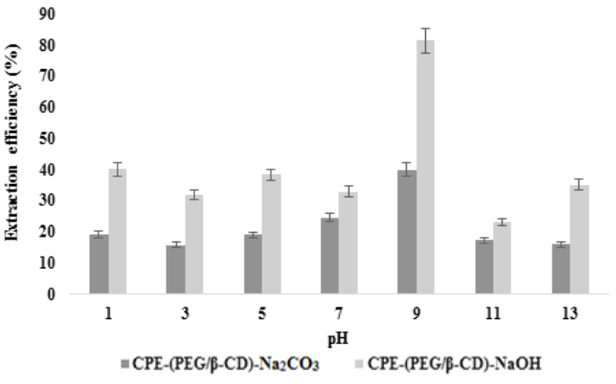

Fig. 5. The effect of the pH solution. PEG concentration (w/v): 70.0% with 1.0% (w/v) of NaOH and 90% (w/v) with 1.0% (w/v) of Na_2CO_3; propylparaben concentration (v/v): 10 mg L^{-1}; equilibrium temperature (°C): 50; incubation time (min): 15; β-CD concentration (v/v): 15 mg L^{-1}.

tems (Fig. 6). The quantity of PEG surfactant, with β-CD as a modifier, was kept constant, while the concentrations of propylparaben were varied between 5 and 25 mg L^{-1} in both CPE systems. The initial concentration delivers an essential driving force between both the solute molecule on the surfactant and in the bulk phase in order to overcome the mass transfer resistance of propylparaben. The result shows that the extraction efficiency slightly increases from 5 mg L^{-1} and up to 15 mg L^{-1} for the CPE-(PEG/β-CD)-NaOH and CPE-(PEG/β-CD)-Na_2CO_3 systems. This phenomenon is due to the large number of vacant surface micelles that are available at the lowest/moderate concentration of solute. Hence, the solubilisation of propylparaben molecules is easily embedded in the micellar core. Later, the extraction efficiency declined gradually with increasing concentration of propylparaben, as the propylparaben concentration exceeded 15 mg L^{-1}, which is probably due to the stability of the analyte-surfactant complex reduction. Further increase in the concentration of the propylparaben leads to excess in solubilized propylparaben due to the insufficient amount of surfactant molecules. Moreover, it is difficult to occupy the remaining vacant surface micelles due to the repulsive forces between the solute molecules on the surfactant and the bulk phase, which decreases the propylparaben removal efficiency [28]. Consequently, the excess propylparaben are retained in the aqueous phase, which accounted for the decreasing extraction efficiency of the propylparaben in the CPE systems. Owing to the optimum propylparaben concentration at 15 mg L^{-1} indicates that the propylparaben removal is higher for the CPE-(PEG/β-CD)-NaOH, ata 93.3% extraction efficiency, compared to the CPE-(PEG/β-CD)-Na_2CO_3 at a 76.4% extraction efficiency.

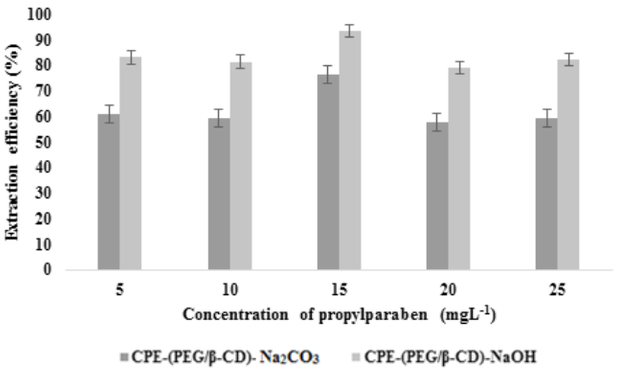

Fig. 6. The effect of propylparaben concentration. β-CD concentration (v/v): 20 mg L^{-1}; PEG concentration (w/v): 70.0% with 1.0% (w/v) of NaOH and 90% (w/v) with 1.0% (w/v) of Na_2CO_3; equilibrium temperature (°C) 50; incubation time (min): 15; sample pH: 9.0.

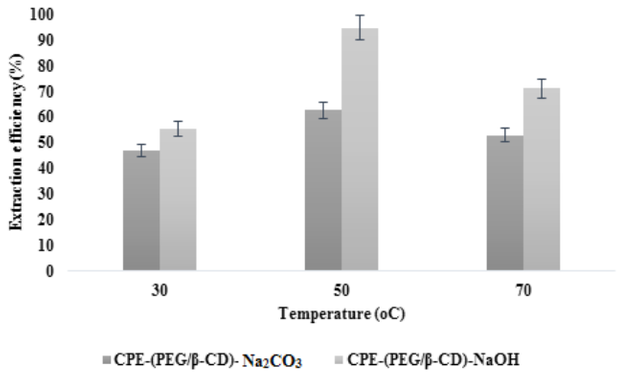

Fig. 7. The effect of equilibrium temperature (°C). β-CD concentration: 20 mg L^{-1}; PEG concentration: 70.0% with 1.0% (w/v) of NaOH and 90% (w/v) with 1.0% (w/v) of Na_2CO_3; propylparaben concentration (v/v): 15 mg L^{-1}; 15; incubation time (min): 15; sample pH: 9.0.

3.6. Effect of temperature and time incubation

The two factors in CPE, which are optimal equilibration temperature and incubation time, are both necessary to complete the reactions and achieve the easy phase separation and pre-concentration in the most efficient manner. It is desirable to employ the lowest possible equilibration temperature and a rapid rate equilibration time as a compromise between completion of extraction and efficient separation phase. The dependence of extraction efficiency on equilibration temperature and incubation time were studied at a range of 30°C 50°C, and 30°C, and 5–25 min, respectively. Fig. 7 shows the dependence of the extraction efficiency of CPE-(PEG/β-CD)-NaOH and CPE-(PEG/β-CD)-Na_2CO_3on the temperature. The extraction efficiency is found to gradually increase from 30°C and up to 50°C due to the transfer of the propylparaben into the surfactant PEG and the β-CD rich phase, and later decrease slightly to 70°C due to the decomposition of the complexes caused by the migration of the propylparaben from the cavity of the β-CD. As a result of this,a temperature of 50°C accentuated the absorbance of the analyte, and the maximum intensity is achieved at this temperature, while the extraction efficiency of propylparaben reported the highest value, proving that the propylparaben has quantitatively been extracted into the surfactant-rich phase. Based on this study, the temperature effect the interactions in both phases by decreasing the hydration of solutes, for instance, the propylparaben or PEG surfactant in the aqueous phase and surfactant rich phase. Due to the phase change and experimental conditions, temperature increase can increase/decrease the extraction of analyte [55]. It is also known that CMC decrease at higher temperatures. Above the CMC, the surfactant monomers accumulate to form micelles. Moreover, the PEG surfactant becomes relatively more hydrophobic at a higher temperature due to an equilibrium shift that favors the dehydration of ether oxygens [43]. Furthermore, for a polyoxyethylated non-ionic surfactant such as PEG, the cloud point increases with the decreasing length of the hydrocarbon chains or increasing length of oxyethylene moiety. The presence of other surfactants or polymers, acids or bases salts, and/or organic additives can alter the critical temperature of such aqueous solutions, sometimes significantly [15]. Based on these facts, it should be pointed out that the presence of electrolytes decreases the cloud point temperature and increases extraction efficiency [56]. It can be seen that the extraction efficiency (%) of propylparaben analyte with CPE-(PEG/β-CD)-NaOH is twice-more effective than CPE-(PEG/β-CD)-Na_2CO_3. Keeping the temperature at 50°C, the

influence of the extraction time on CPE was investigated, and the results are shown in Fig. 8. The extraction time of 15 min is sufficient for the separation process to complete the quantitative extraction of propylparaben analyte. The extraction efficiency deteriorated as the incubation time exceeded 15 min, which is probably due to the stability of the propylparaben-(PEG/β-CD) complexes decreasing. Hence, an incubation time of 15 min at 50 was optimal for the quantitative extraction of propylparaben analyte.

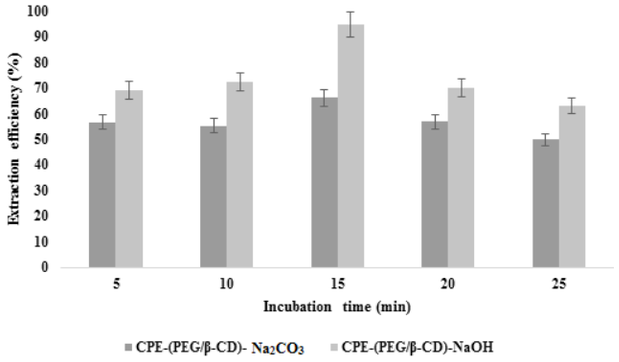

Fig. 8. The effect of incubation time (min). β-CD concentration (v/v): 10 mg L^{-1}; PEG concentration: 70.0% with 1.0% (w/v) of NaOH and 90% (w/v) with 1.0% (w/v) of Na_2CO_3; propylparaben concentration (v/v): 15 mg L^{-1}; equilibrium temperature (°C): 50; sample pH: 9.0

3.7. Effect of water content

Water content is the core part of the surfactant-rich phase post phase separation, which prevents further improvement to the extraction efficiency process. In fact, higher amounts of water in the surfactant-rich phase results in lower concentrations of extracted analyte extracted. The aim of this study is to determine and compare the lowest amount of water in the surfactant rich phase between the CPE-(PEG/β-CD)-NaOH and CPE-(PEG/β-CD)-Na_2CO_3 systems. Fig. 9 shows the comparison of the percentage water content in the surfactant rich phase between the CPE-(PEG/β-CD)-NaOH and CPE-(PEG/β-CD)-Na_2CO_3 systems. Based on the results, the CPE-(PEG/β-CD)-NaOH (27.20%) reported a lower percentage of water content in the surfactant rich phase compared to the CPE-(PEG/β-CD)-Na_2CO_3 (28.27%) after the CPE process. Even though the percentages of CPE-(PEG/β-CD)-NaOH is not significant compared to the CPE-(PEG/β-CD)-Na_2CO_3, the lower percentage of water content reported by the CPE-NaOH showed a significant increment in the extraction efficiency of the propylparaben. The lower water content in the surfactant-rich phase leads to a better performance of the surfactant in the CPE method. Thus, high percentage extraction efficiency of propylparaben will be extracted in the surfactant rich phase. Based on this, the low volume of water contents produced in the surfactant-rich phase is due to the presence of salt. The addition of salts helped the separation of the two phases as it increases the density of the aqueous phase. The presence of salt can increase the incompatibility between the water structures in the hydration shells of the analytes and surfactant macromolecules. This, in turn, reduce the concentration of "free water" in the surfactant-rich phase and reduce the volume of the phase [38]. In this study, the NaOH salt is decreases the water content of the CPE system, which results in increased extraction efficiency of propylparaben analyte. This could be attributed to the increase in the size of the micelle and the aggregation number of surfactant, which promotes non-polar analytes to be more soluble in the surfactant phase. Moreover, a solute-solute interaction between surfactants probably contribute more to the solute-water interaction when the amount of hydrophilic surfactant increases in the solution, resulting in less amount of water being detected in the surfactant phase [38], which means a high percentage of propylparaben extraction recovery. The influence of salts can be defined by the effects of cations and of anions. In this study, the presence of cation (Na^+) favors the dehydration of the polyoxyethylene chain and results in a decreased cloud-point, while the anions (OH^- and CO_3^-) mainly enhances the structure of water in bulk solution by breaking the hydrogen bonds between the water molecules and the polyoxyethylene chains to simplify dehydration and decrease the cloud-point [57]. It has been pointed out

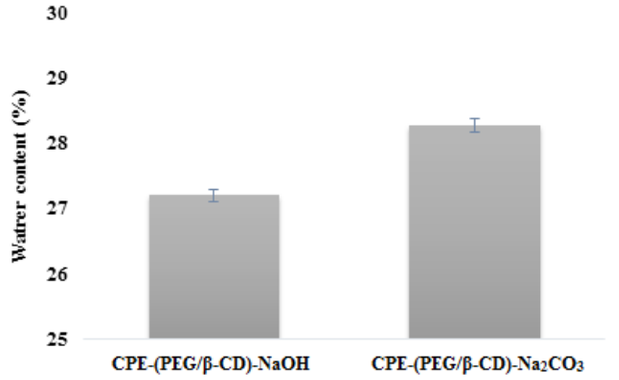

Fig. 9. Water content in the surfactant rich phase obtained by the CPE-(PEG/β-CD)-NaOH and CPE-(PEG/β-CD)-Na_2CO_3 systems.

in Sub-section 3.1 that OH^- reports the highest viscosity of surfactant suspension among the concentration-viscosity characteristics of the surfactant-rich phases, and is a greater breaking agent than CO_3^- based on Hofmeister series of anions. This indicated that the NaOH salt with PEG/β-CD complex surfactant favors the excellent performance of CPE for the extraction efficiency of propylparaben.

3.8. Method validation of CPE-(PEG/β-CD)-NaOH method in cosmetic samples

Table 1 summarizes the experimental variables and optimized conditions for determining and measuring propylparaben analyte in an aqueous solution. The excellent linearity of the calibration curve was achieved in the range of 0.04–2.00 mg L^{-1}. The equation and regression coefficient (R^2) were $A = 0.2661C + 0.0012$ and 0.9987, respectively. The limit of detection (LOD), based on three times the standard deviation of the blank (S/N) = 3, was 0.162 mg L^{-1}. The analytical parameters and optimal conditions of the proposed method have been used to measure the level of propylparaben in different cosmetic matrices.

Table 2 shows the recoveries and concentrations of propylparaben in cosmetic samples with and without being spiked in three types of cosmetic matrices. A spiked propylparaben in the cosmetic samples is 1.0 mg L^{-1} and 2.0 mg L^{-1}. There are six of cosmetic samples randomly selected from the marketplace, and further categorized in three; (1) stated paraben free, (2) stated propylparaben content, and (3) not stated propylparaben and/or any paraben content. A CPE-(PEG/β-CD)-NaOH was approached in this application method due to its excellent performance in extracting propylparaben analyte compared to the CPE-(PEG/β-CD)-Na_2CO_3 system. The reproducibility was evaluated by repeating the proposed approach thrice for each sample. The results indicated that the developed CPE-(PEG/β-CD)-NaOH method for propylparaben performed better at lower detection limits, 0.003 mg L^{-1}, and the relative standard deviation (RSD) was 101.02% (n = 3). Satisfactory results were obtained within the study range in all cosmetic samples and displayed a significant difference in the extraction recoveries between the six cosmetic samples. Satisfactory recoveries were achieved in the range of 80.63–119.71%, with the RSDs of cosmetic samples being between 0.10–0.50%.

As seen in Table 2, the results of the tested cosmetic samples "stated paraben free" label indicated undetected parabens, which means that the product could be trusted. Meanwhile, the tested cosmetic samples "not stated propylparaben and/or paraben contents" indicated that the products contained propylparaben at levels within the current law regulations, even though some of these samples contained propylparaben that were not declared on the labels. Also, the tested cosmetic samples for "stated propylparaben content" label showed that the products still adhere to the regulation of propylparaben usage.

This proposed method is simple, easy, and the analysis time for this method is shorter,and applicable in many laboratories, compared to other methods, especially chromatographic methods. This method also does not need organic solvents. The developed CPE-(PEG/β-CD)-NaOH system proved to be a simple and effective alternative to the liquid-liquid extraction system for the extraction of propylparaben, which means that it could be used to measure the levels of parabens in food and pharmaceuticals products.

Table 1
Studied experimental and optimal conditions

Parameters	Studied range	Optimal conditions
Equilibrium pH	1.0–13.0	9.0
PEG surfactant concentration% (w/v)	10.0–110.0	70.0
β-CD concentration (mg L^{-1})	5.0–25.0	15.0
NaOH concentration % (w/v)	0.5–3.0	1.0
Equilibration time (min)	5.0–25.0	15.0
Equilibrium temperature (°C)	30-70	50

4. Conclusions

Developed countries try to avoid the utilisation of parabens as preservative in the cosmetic industry due to its

Table 2
Determination of PP in real sample of cosmetic products based on CPE-NaOH system

Products		Propylparaben added (mg L^{-1})	Propylparaben found (mg L^{-1}) (% w/w)	Recovery (%)	RSD (%)
Stated paraben free	Gel 1	–	nd	101.02	0.10
		1.0	nd	118.21	0.10
		2.0	nd	110.14	0.10
	Gel 2	–	nd	102.41	0.20
		1.0	nd	119.71	0.10
		2.0	nd	109.43	0.10
Stated propylparaben content	Gel 3	–	0.801 (0.08)	81.54	0.20
		1.0	1.677 (0.17)	90.44	0.30
		2.0	1.592 (0.16)	85.59	0.20
	Gel 4	–	0.182 (0.02)	80.63	0.30
		1.0	0.888 (0.10)	91.15	0.10
		2.0	0.750 (0.08)	85.76	0.10
Not stated propylparaben and/or any paraben content	Gel 5	–	0.010 (> 0.01)	80.95	0.30
		1.0	1.428 (0.14)	91.38	0.10
		2.0	1.375 (0.14)	85.97	0.10
	Gel 6	–	0.003 (>0.003)	98.55	0.30
		1.0	0.203 (0.02)	112.78	0.50
		2.0	0.131 (0.01)	107.48	0.30

nd = not detected.

danger to human health. These issues prompted the development of a simple, rapid, and cheap CPE system to analyse the level of propylparaben in cosmetic samples, prior to its spectrophotometric detection. Two types of CPE systems have been developed, which were CPE-(PEG/β-CD)-NaOH and CPE-(PEG/β-CD)-Na_2CO_3. Under optimized conditions, the CPE-(PEG/β-CD)-NaOH reported superior extractability performance towards propylparaben compared to the CPE-(PEG/β-CD)-Na_2CO_3. Hence, CPE-(PEG/β-CD)-NaOH has been selected to measure the amount of propylparaben in cosmetic samples. The precision and recovery data clearly indicated the reproducibility and accuracy of the CPE-(PEG/β-CD)-NaOH system for propylparaben determination in cosmetic samples. The method is non-toxic and does not require sophisticated instruments such as chromatographic methods.

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