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Extraction of β-carotene from organic phase using ammonium based ionic liquids

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ABSTRACT

β-carotene, an important biomolecule from the carotenoid family with highly unsaturated heavy structure ($C_{40}H_{56}$) can be found in plenty of sea products, fruits and vegetables. This hydrocarbon with a noticeable anti-oxidant is known to be a valuable compound in food and pharmaceutical industries. The present study aimed to have a detailed probe on the capability of ammonium based Ionic liquids (ILs) to extract β-carotene from its model solvent, *n*-hexane. The work entails the screening of ILs by employing conductor-like screening model for real solvents (COSMO-RS) tool based on the numerical prediction of relationship between ILs structure and its extraction potential. The simulated results were then complemented experimentally. Besides, process conditions for β-carotene extraction from *n*-hexane; including IL water content, two-phase volumetric ratio (aqueous to organic) and extraction time were also optimized using response surface methodology (RSM) based on central composite design (CCD). The results indicate that tetramethylammonium and trimethylethylammonium based ILs with acetate anion exhibited potential extraction efficiency of 63.09% and 37.89% for β-carotene, respectively. Interestingly, 'IL water content' is found to be the most efficacious parameter in the extraction process while 'time' retained a nominal impact. In the promise of these findings, we firmly believe that this newly proposed method would open a new pathway for β-carotene extraction for numerous applications.

1. Introduction

β-carotene is an organic, fat-soluble compound that is naturally present in many fruits, plants, flowers, oils, grains, vegetables, seeds, roots and is usually liable for orange, red and yellow coloration. Actually, the conjugated double-bond scheme of β-carotene is responsible for its chemical reactivity and photochemical properties that devise the basis for most of its functions. It works as an antioxidant due to its ability to scavenge peroxyl radicals, thus restraining lipid peroxidation accordingly, which provoke the guard against illnesses including heart disease and cancer. It is a member of the carotenes, which are well known for their neuroprotective effect, low density lipoprotein (LDL) oxidation inhibition effect and antioxidant activity [1–4]. An upsurge interest in carotenoids and its associated effects on human health has been profound for many decades since the linkages between β-carotene and vitamin A was first established [5]. Recently, the demand for natural colorants has been continuously increasing primarily due to changes in consumer priorities towards more natural food products. β-carotene has potential applications as a colorant in the food industry and of recent; in the manufacturing of "Golden Rice" – a genetically modified crop – which is engineered to cumulate β-carotene [6,7].

Typically, β-carotene is extracted via a pressurized and super critical fluid extraction method which involves the use of hazardous solvents under extreme conditions of pressure and temperatures [8–11]. Also, the demand for extreme heating evokes the serious risk of β-carotene oxidization and isomerization. Furthermore, the aforesaid methods require the use of expensive and environmentally hazardous organic solvents such as methanol, propanol, *n*-hexane and tetrahydrofuran [12,13]. In the past, many attempts have been made to modify this method. For example, Mustafa et al. utilized ethanol under high pressure and temperature and achieved up to 80% carotenoid extract [12]. In another study, Wiyaratn and Watanapa utilized soxhlet extraction method to extract β-carotene from crude palm oil with 80% efficiency [14]. Besides, many other studies utilized supercritical fluids (SCF) as solvents for better efficiency of extraction [15–17]. Talisic et al. extracted β-carotene from *D. salina* algae utilizing solvents such as supercritical ethane and ethylene [18]. They reported that supercritical ethylene and ethane were better solvents than supercritical CO_2 due to their higher polarizabilities for β-carotene. Although supercritical fluid based methods showed higher than 90% extraction efficiency and alleviated the use of toxic organic solvents, one critical drawback of using non-

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polar supercritical fluids is their limited application range and the tediousness of procedure [18–21]. Similarly, organic solvents used in other extraction methods of carotenoids are not environment benign and also require expensive disposal procedures [22].

Liquid-liquid extraction (LLE) is a promising separation method which is based on the chemical distribution between two different liquid phases. The high volatility of the extraction solvents, not only impose an environmental hazard, but also leads to difficulty for the recovery of extractant. Hence, the use of ILs as extractants could provide a prospective solution to these limitations [23]. ILs are often employed as solvents for biochemical reactions and organic synthesis [24]. ILs have been extensively applied in conventional methods including liquid-liquid extraction (LLE), ultrasound-assisted extraction (UAE), high performance liquid chromatography (HPLC) [25,26]. The extraction of bioactive compounds from plants using ILs has great promise which compared to conventional organic solvents, can minimize the environmental pollution and simultaneously improve the selectivity and extraction yields of compounds in pretreatment processes [27]. The reason for their widespread popularity is that they offer unlimited possibilities for various biological applications as critically reviewed by Sivapragasam et al. [28]. ILs are classified as thermally stable solvents with a broad electrochemical window, high ionic conductivity, insignificant volatility with tunable properties [29–39]. As solvents in separation processes, they form a pure extracting phase [40–42]. Therefore, ILs could be an alternative green solvent for the replacement of hazardous volatile solvents in extraction of bio-based molecules. Once such example is Louros et al. who used phosphonium-based ILs to form aqueous biphasic systems (ABS) with K_3PO_4 aqueous solutions for biomolecule extraction [40]. In another study, Freire et al. utilized a water-stable IL in the formation of ABS to extract β-carotene and caffeine [42]. Other methods such as high hydrostatic pressure assisted extraction (HHPE) for β-carotene extraction have also been explored [43].

According to best of the authors' knowledge, no report has been published regarding the IL based extraction of β-carotene from organic phase with *n*-hexane as the model solvent. This study aims to find potential ILs for β-carotene extraction. The work investigates various structures of ammonium based ILs using COSMO-RS based on activity coefficient. Further, RSM was used to optimize the various affecting parameters, namely ILs water content (A), biphasic (aqueous to organic) volumetric ratio (B) and extraction time (C) on β-carotene separation from *n*-hexane. Analysis of variance (ANOVA) was utilized to model the multiple parameter process and to design the optimum operating conditions for this extraction. The response (extraction efficiency) was fitted by a quadratic polynomial regression model using least square analysis in a five level- four-factor central composite design (CCD). The relationship between reaction variables (A, B and C) was also studied.

2. Simulation and experimental description

2.1. Screening of ILs by COSMO-RS tool

It is well known that ILs properties are highly dependent on their structure [29–39]. To find the IL structure effect on its β-carotene extraction ability, different combinations of cations and anions are investigated. Table 1 provides the list of various cations and anions investigated in the present study for β-carotene extraction.

Activity coefficient of each cation-anion combination for β-carotene and *n*-hexane was predicted using COSMO-RS and selectivity index was calculated for each IL. Further, the effect of alkyl chain length on the performance of ammonium cation was also explored.

COSMO-RS is a powerful tool for the prediction of thermodynamic properties for mixtures and pure fluids using the molecular structure information [44]. In the COSMO-RS, a molecule is considered as a collection of surface segments and the chemical potential is calculated by summing the segments contributions. The high capability of COSMO-RS in ILs polarity correlation has been confirmed in several studies [45–47]. The continuum solvation COSMO prediction of molecular geometry and charge of β-carotene was performed with the TURBOMOLE program package with a BP functional, on the level of density functional theory (DFT) applying the triple-z valence polarized basis set (TZVP). The structure was optimized based on the potential energy surface via vibrational frequency analysis. Subsequently, the COSMO file comprising the ideal screening charges on the β-carotene molecular surface was used. COSMOthermX software was used to estimate ILs interaction energies with β-carotene on the basis of BP_TZVP. It was employed to evaluate ILs separation ability based on their activity coefficients at T = 298.15 K. With respect to activity coefficients given by COSMO*thermx*, the solvent capacity (K) and then selectivity (S) were calculated for each model IL. These two indexes were used to find potential combinations in β-carotene separation from *n*-hexane. The calculations were based on the following equations [48]:

$$K_j = 1/\gamma^{\infty}{}_j \quad (1)$$

$$S^{\infty} = K_{\beta-carotene}/K_{n-hexane} = \gamma^{\infty}{}_{n-hexane}/\gamma^{\infty}{}_{\beta-carotene} \quad (2)$$

Where, $\gamma^{\infty}{}_{n\text{-hexane}}$ and $\gamma^{\infty}{}_{\beta\text{-carotene}}$ represent the activity coefficient of *n*-hexane and β-carotene at infinite dilution, respectively. In screening studies, the term "solvent capacity" is a common and almost exact approximation of solubility at infinite dilution. Thus, $K_{n\text{-hexane}}$ and $K_{\beta\text{-carotene}}$, respectively, indicate *n*-hexane and β-carotene solubility in IL. S_{∞} represents the maximum theoretical selectivity which can be predicted by COSMO-RS while the selectivity at finite dilution was achieved experimentally. The selectivity factor was calculated to compare the solubilities. An ideal IL for β-carotene extraction should have high selectivity (S > 1).

Table 1
Investigated cations and anions.

Cations Name	Abbreviation	Anions Name	Abbreviation
Tetramethylammonium	N^+_{1111}	Tetrafluoroborate	BF_4^-
Trimethylethylammonium	N^+_{1112}	Hexafluorophosphate	PF_6^-
Butyltrimethylammonium	N^+_{1114}	Hydrogensulfate	HSO_4^-
Hexyltrimethylammonium	N^+_{1116}	Methyl sulphate	$CH_3SO_4^-$
Heptyltrimethylammonium	N^+_{1117}	Dimethyl phosphate	$DMPO_4^-$
Octyltrimethylammonium	N^+_{1118}	Acetate	OAc^-

2.2. Design of Experiment (DOE)

Parametric study for the optimized β-carotene extraction using *n*-hexane was conducted by employing central composite design (CCD) using Design Expert 8.0 software. The optimization of operating parameters was analyzed by RSM. The experimental arrays are designed by CCD and the reaction variables with their respective ranges shown in Table 2. The independent input process variables were primarily classified in terms of low and high levels. The factors were then distributed into versatile points called axial, central and factorial points. The axial points are coded by CCD with −2 and +2. Low and High level factor points are designated as −1 and +1. Whereas, central points were coded with 0 and repeated experimental arrays designed on central points.

Table 2
Design parameters for extraction process.

Process parameter	−2	−1	0	+1	+2
IL water content (wt%)	24.89	30	37.50	45	50.11
Two-phase volumetric ratio (ml/ml)	0.08	0.25	0.50	0.75	0.92
Time (hr)	0.61	3	6.5	10	12.39