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Separation of highly unsaturated fatty acid methyl esters from model bio-oils with ionic liquid-cosolvent as extractants†

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The effective separation and utilization of high value-added unsaturated fatty acid methyl esters from model bio-oils could make full use of the biomass resources and greatly improve the economic feasibility of bio-fuels. Selective separation of unsaturated fatty acid methyl esters was performed by liquid–liquid extraction, using ionic liquids (ILs) as extractants in the presence of cosolvent. The results showed that the mixture of 1-ethyl-3-methylimidazolium dicyanamide ([EMIm][N(CN)$_2$]) and *N*,*N*-dimethylformamide (DMF) demonstrated excellent separation selectivity, reaching up to an outstanding value of 11.7, when the mole ratio of [EMIm][N(CN)$_2$] to DMF was 1 : 9, at least twice the value (5.6) using DMF as the extractant. In addition, the effects of the structure, the mole fraction of ILs, the feedstock concentration and temperature, on extraction equilibrium were studied. By calculating the fractional extraction, the feasibility of liquid–liquid extraction for practical application was confirmed.

1. Introduction

Biodiesel is a renewable and alternative diesel fuel, which is made from a variety of fats and oils[1] including microalgal oils. These oils are always a mixture of acylglycerols of long chain fatty acids which is subjected to a chemical reaction termed transesterification to obtain biodiesel. Thus, biodiesel consists of saturated, monounsaturated and polyunsaturated fatty acid methyl esters (FAMEs). Compared with standard fossil fuels, biodiesel has the merits of enhanced biodegradation, increased flashpoint, reduced toxicity, lower emissions and increased lubricity.[2]

Careful attention should be paid to the presence of unsaturated fatty acid methyl esters (uFAMEs) in the FAMEs derived from microalgae bio-oils. On one hand, while those FAMEs can be used for producing bio-fuels, the widespread use of bio-fuels is limited because of their susceptible nature to oxidation during storage, due to the presence of uFAMEs.[3,4] The removal of uFAMEs from these FAME mixtures would create bio-fuels that would be less sensitive to air oxidation. Both European Standards EN 14214 and EN 14213 require the iodine value, which indicated the extent of total unsaturation of biodiesel, to a maximum of 120 and 130 g iodine/100 g biodiesel, respectively.[5] However, most FAMEs are unlikely to meet European standards due to the high content of uFAMEs in them, which are commonly eliminated by partial catalytic hydrogenation, resulting in a waste of uFAMEs with high commercial value.[6] On the other hand, those uFAMEs are high value-added omega-3 fatty acid ester. There is evidence that uFAMEs play important roles in lowering the risk of heart disease, cancer, cardiovascular disease, disrupted neurological functions, and inflammatory disorders and improvement in cholesterol levels.[7,8] Nowadays, the concept of biorefinery, which is analogous to today's petroleum refinery, has been applied in conversion and utilization of biomass.[9,10] Biorefinery takes advantage of various components in biomass and their intermediates to produce multiple high-value products, therefore maximizing the value of the biomass feedstock, enhancing profitability, and improving the economic feasibility of manufacturing process of bio-fuels.[11–13] Thus, it is necessary for the separation of high value-added uFAMEs from microalgae bio-oils prior to conversion into bio-fuels.

In recent years, a variety of methods have been reported to separate uFAMEs, including urea inclusion complexation,[14,15] low temperature fractional crystallization,[16] molecular distillation,[17] supercritical fluid extraction,[18,19] lipase concentration.[20,21] However, the above mentioned methods still have disadvantages and limitations, such as poor yield, low purity, *etc.* Chromatography[22,23] could get high selectivity, but it is limited to a small throughput and has high solvent consumption and requirement for special apparatuses.

Ionic liquids have been favorable extractants for the development of separation process owing to its high separation capacity and simple manipulations. In addition, ILs have drawn

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much attention due to their unique physical and chemical properties, including negligible vapor pressure, good thermal and chemical stability which lead them to be regarded as green solvents. Besides, they can be considered as designable solvents owing to the feasibility of structural and functional tunability to meet the requirements for specific tasks. On account of the above advantages of IL extraction, it has been explored in many applications and elevated separation selectivity could often be achieved as compared to the traditional organic solvent extraction processes. These studies demonstrate the separation of various compounds, including sulfides[24,25] and nitrides[26] from diesel and gasoline, organic solutes,[27–29] metallic pollutants,[30,31] and bioactive compounds (*e.g.*, amino acids,[32] erythromycin,[33] DNA[34]).

Several works have been done for the separation of polyunsaturated FAMEs with ILs as extractants. Li[35] screened hydrophobic ILs containing silver salts for enrichment of omega-3 polyunsaturated FAMEs and excellent extraction capacity and selectivity was obtained. Cheong[36] extracted and enriched n-3 polyunsaturated fatty acids and ethyl esters through reversible π–π complexation with aromatic rings containing ILs, which increased extraction capabilities and resulted in a higher purity. An interesting paper based on molecular dynamics simulations discusses π–π interactions in three cyano-based imidazolium ionic liquids.[37] Li[38,39] prepared novel π-complexing sorbents by covalently immobilizing ILs onto mesoporous SBA-15 for separating polyunsaturated FAMEs, and prepared π-complexing sorbents by covalently immobilizing ILs onto silica and then coating these silica-supported ILs with silver salts, which had satisfactory extraction capacities and reusability. As we all know, the separation selectivity is crucial in extraction processes, but adding silver salts for improving selectivity has the problems that silver salts are very likely to lose activity and they are costly. In addition, the large viscosity of ILs has negative effect on mass transfer performance in extraction processes. Therefore, IL-cosolvent mixtures instead of pure ILs were used as extraction solvents, which can reduce the viscosity and thus greatly improve the performance of mass transfer, and fine regulate physical and chemical properties of IL phase. It's likely to achieve excellent separation efficiency, and obtain products with high purity and it's capable for industrial application.

In this article, we for the first time reported an IL-cosolvent extraction method for the separation of uFAMEs. The results showed that the mixture of 1-ethyl-3-methylimidazolium dicyanamide ([EMIm][N(CN)$_2$]) and *N*,*N*-dimethylformamide (DMF) demonstrated best separation selectivity, as high as 11.7, at least twice the value (5.6) using DMF as the extractant. The effects of the structure and the mole fraction of ILs, as well as feedstock concentration and temperature, on extraction equilibrium have been evaluated. What's more, fractional extraction simulation was performed and the results show that fractional extraction is promising to separate uFAMEs in industrial applications.

2. Materials and methods

2.1. Materials

The ILs (chemical names and structures shown in the ESI, Table S1†) used in this study were purchased from Lanzhou Green Chemistry and Catalysis, LICP, CAS (China), including [EMIm][(EtO)$_2$PO$_2$], [EMIm][Ac], [EMIm][Ala], [EMIm][CF$_3$SO$_3$], [EMIm][C(CN)$_3$], [EMIm][N(CN)$_2$], [EMIm][SCN], [EMIm][BF$_4$], [EMIm][NO$_3$], [EMIm][CF$_3$COO], [EMIm][NTf$_2$] [Bpy][NTf$_2$], [BMPrr][NTf$_2$], [HOEMIm][NTf$_2$], [MeOEMIm][NTf$_2$], [CNPMIm][NTf$_2$], [HOOCEMIm][NTf$_2$], [BnMIm][NTf$_2$], [AMIm][NTf$_2$], and [C$_{12}$MIm][NTf$_2$]. The compounds, methyl ester of all-*cis*-5,8,11,14,17-eicosapentaenoic acid (C20 : 5, 99%), methyl ester of all-*cis*-4,7,10,13,16,19-docosahexaenoic acid (C22 : 6, 99%), and linolenic acid methyl ester (C18 : 3, 99%) were purchased from Sigma-Aldrich (St. Louis, Missouri, USA), while C22 : 6 + C20 : 5 (80%), linolenic acid methyl ester (C18 : 3, 80%), methyl linoleate (C18 : 2, 99%), methyl oleate (C18 : 1, 96%), methyl stearate (C18 : 0, 95%), and methyl palmitate (C16 : 0, 97%) were procured from Aladdin (Shanghai, China). Organic solvents (Analytical Reagent), *i.e.*, *n*-hexane, *N*,*N*-dimethylformamide (DMF), and ethanol, were commercially obtained, and used without further purification, which was bought from Aladdin (Shanghai, China).

2.2. Methods

2.2.1 Extraction procedure. The extraction experiments were performed as the procedures reported in the literature.[40,41] A known amount of the mixed FAMEs was dissolved in *n*-hexane to form the initial feedstock, and aliquots of the feedstock were mixed with an equal volume of an IL-cosolvent mixture in an Erlenmeyer flask. The flask was shaken for 2 h using a thermostatic rotary shaker with a speed of 200 rpm, and then settled for 2 h at the same temperature. The shaking time was checked to be sufficient for extraction equilibrium. Samples were taken from each of the two phases without disturbing the phase boundary and diluted with ethanol for the HPLC analysis. Several groups of extraction equilibrium experiments were performed in triplicates to evaluate the repeatability of this method. We found that the relative uncertainties of distribution coefficients were within 5%.

The distribution coefficient (D_i) of solute i and selectivity ($S_{i/j}$) of solute i to solute j were calculated according to eqn (1) and (2), respectively:[41,42]

$$D_i = C_i^{\mathrm{e}}/C_i^{\mathrm{r}} \tag{1}$$

$$S_{i/j} = D_i/D_j \tag{2}$$

where C_i^{e} and C_i^{r} stand for the mass fractions of solute i in the extraction phase and in the raffinate phase, respectively.

Methyl stearate (C18 : 0) was used as the reference for the assessment of the selectivity of uFAMEs.

2.2.2 HPLC analysis. The HPLC system included a Waters 717 plus an autosampler, a Waters Atlantis T3 column (5 μm, 4.6 mm × 250 mm), a Waters thermostat, a Waters 1525 binary pump and a Waters 2487 dual λ absorbance detector. The mobile phase was a mixture of acetonitrile and water (90/10, v/v) and the flow rate was 1 mL min^{-1}. The UV detection of FAMEs was performed at 205 nm. The column temperature was 40 °C.

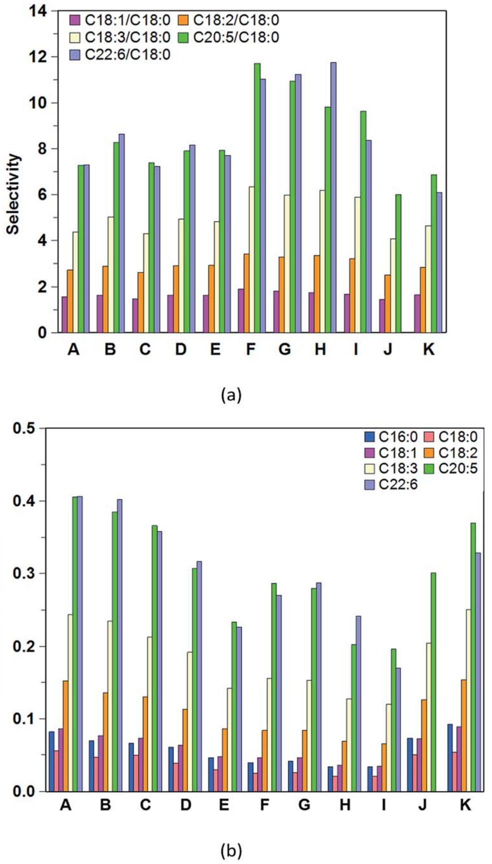
3. Results and discussion

In this work, *n*-hexane was selected as the non-polar phase because it's immiscible with ILs, which can be used in this liquid–liquid biphasic extraction. Moreover it has good solubility for FAMEs and it's one of the most commonly used solvents, which is easy to access and recycle. In addition, it's ok to substitute *n*-heptane for *n*-hexane as *n*-heptane has much lower toxicity than *n*-hexane, while it has similar physicochemical properties and distribution behavior for solutes as *n*-hexane (Fig. S1†). In this work, we applied model bio-oils which had similar components to those in microalgae bio-oils, to evaluate the separation performance of our extraction method for uFAMEs. The initial feedstock contains 10 wt% C22 : 6 + C20 : 5, 15 wt% C18 : 3, 15 wt% C18 : 2, 20 wt% C18 : 1, 20 wt% C18 : 0, and 20 wt% C16 : 0. The initial concentration of FAMEs is 40 mg mL^{-1}. Among seven FAMEs, C18 : 3, C18 : 2, C18 : 1 and C18 : 0 have the same chain length with 18 carbons but have different unsaturation degrees. C20 : 5 has 20 carbons and 5 double bonds while C22 : 6 has 22 carbons and 6 double bonds. Thus it is possible to separate uFAMEs based on their differences in degrees of unsaturation or carbon numbers. The properties of ILs can be fine regulated by designing the structures of anions and cations and introducing functional groups. ILs with aromatic structure or CN group can form π–π interaction with double bonds, enhancing the recognition for double bonds, resulting in the separation of uFAMEs. The reason why DMF was chosen as the cosolvent is that DMF showed high distribution coefficients of FAMEs.[43]

3.1. Effect of the IL's anion on the extraction equilibrium

Various kinds of ILs having the same 1-ethyl-3-methylimidazolium cation ($EMIm^+$) but with different anions, were investigated for the extractive separation of FAMEs. The selectivities and distribution coefficients of FAMEs are presented in Fig. 1. The experimental data showed that the variation of IL's anion had a significant impact on the extraction.

ILs with $N(CN)_2^-$ and SCN^- as anions express the best separation selectivities, and the selectivities of C20 : 5 to C18 : 0 $S_{C20:5/C18:0}$ reached the excellent values as high as 11.7 and 10.9, respectively, significantly larger than those of common IL-containing extractants without CN group, indicating that the anions $N(CN)_2^-$ and SCN^- with CN group can substantially increase selectivities. This was possibly because CN group could form specific π–π interaction with unsaturated double bonds, enhancing the recognition for double bonds. However, when CF_3COO^- and NTf_2^- are utilized as the anions, the selectivities of C20 : 5 to C18 : 0 were as low as 6.0 and 6.9, respectively. Because NTf_2^- anion has strong van der Waals interaction with liposoluble FAMEs, besides, IL with NTf_2^- as anion has weak polarity and thus shows high affinity for liposoluble FAMEs, lowering the recognition for double bonds and carbon chains, resulting in smallest selectivity. Other anions such as $(EtO)_2PO_2^-$ and Ala^- showed appropriate selectivities, between 7 and 8. In terms of the distribution coefficients, the distribution coefficients of FAMEs obtained for $[EMIm][(EtO)_2PO_2]$ and [EMIm][Ac] were relatively high. For example, the distribution coefficient $D_{C20:5}$ of C20 : 5 reached up to about 0.40. Nevertheless, when BF_4^- or NO_3^- is used as anion, $D_{C20:5}$ was lowest, with the value of 0.20.



(a)

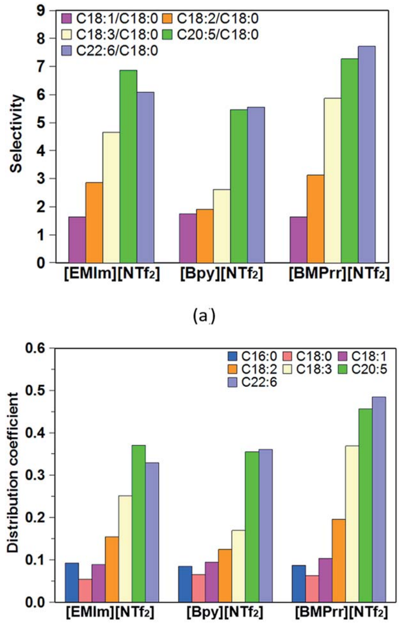
(b)

Fig. 1 Effect of the IL's anion on the selectivities (a) and distribution coefficients (b). The initial concentration of FAMEs in *n*-hexane was 40 mg mL^{-1}. Volume ratio of feed and extraction solvent was 1 : 1. The extraction temperature was 30 °C. The mole ratio of IL to DMF was 1 : 9. A: $[EMIm][(EtO)_2PO_2^-]$; B: [EMIm][Ac]; C: [EMIm][Ala]; D: $[EMIm][CF_3SO_3]$; E: $[EMIm][C(CN)_3]$; F: $[EMIm][N(CN)_2]$; G: [EMIm][SCN]; H: $[EMIm][BF_4]$; I: $[EMIm][NO_3]$; J: $[EMIm][CF_3COO]$; K: $[EMIm][NTf_2^-]$.

3.2. Effect of the IL's cation core structure on the extraction equilibrium

The effects of variation of the IL's cation core structures were examined for the extractive separation of FAMEs, when the given anion was bis((trifluoromethyl)sulfonyl)imide anion (NTf_2^-). The selectivities and distribution coefficients of FAMEs are presented in Fig. 2. The experimental results indicated that the studied cation cores significantly influenced the extraction equilibrium.

The selectivity $S_{C18:3/C18:0}$, $S_{C20:5/C18:0}$ or $S_{C22:6/C18:0}$ followed the order: $[BMPrr][NTf_2]$ > $[EMIm][NTf_2]$ > $[Bpy][NTf_2]$. For instance, $[BMPrr][NTf_2]$ exhibited the highest extraction selectivity $S_{C20:5/C18:0}$, with the value up to 7.3 and the $D_{C20:5}$ value



(a)

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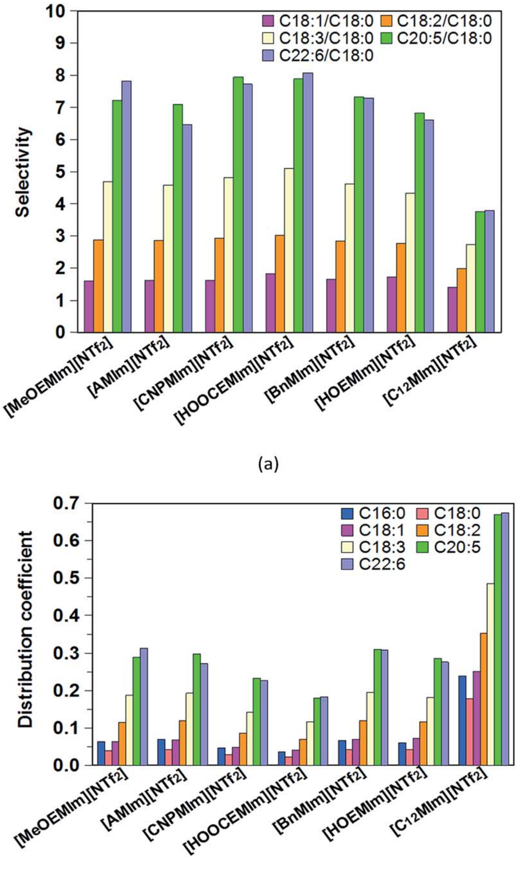
Fig. 2 Effect of the IL's cation core structure on the selectivities (a) and distribution coefficients (b). The initial concentration of FAMEs in *n*-hexane was 40 mg mL^{-1}. Volume ratio of feed and extraction solvent was 1 : 1. The extraction temperature was 30 °C. The mole ratio of IL to DMF was 1 : 9.

was as high as 0.46, indicating that introducing BMPrr$^+$ can enhance selectivities and distribution coefficients in the meantime. In addition, [EMIm][NTf$_2$] and [Bpy][NTf$_2$] showed relatively lower selectivities, with the $S_{\mathrm{C20:5/C18:0}}$ values of 6.9 and 5.5, respectively.

3.3. Effect of the functional group in IL's cation on the extraction equilibrium

Various kinds of ILs with different functional groups were investigated for the extractive separation of FAMEs, when the given anion was bis((trifluoromethyl)sulfonyl)imide anion (NTf$_2^-$) and cation core was 1-ethyl-3-methylimidazolium cation (EMIm$^+$). The selectivities and distribution coefficients of FAMEs are presented in Fig. 3.

The COOH group functional IL [HOOCEMIm][NTf$_2$] exhibited the highest extraction selectivity but the smallest distribution coefficients, indicating that introducing polar COOH group can improve selectivity but decrease distribution coefficients. For example, the $S_{\mathrm{C22:6/C18:0}}$ value reached up to surprising 8.1 and the $D_{\mathrm{C20:5}}$ value was less than 0.20. [CNPMIm][NTf$_2$] with CN group had relatively high selectivities and the $S_{\mathrm{C20:5/C18:0}}$ value was as high as 7.9. It is probably due to the specific π–π interaction between the CN group and the unsaturated double bonds of FAMEs, and thus enhances the molecular recognition ability of ILs for double bonds. Therefore, it is helpful to increase the separation selectivities by introducing CN group. In addition, [MeOEMIm][NTf$_2$] with methoxy group, and [BnMIm][NTf$_2$] with benzyl group had relatively high selectivities, with the $S_{\mathrm{C22:6/C18:0}}$ value between 7.3 and 7.8. Other ILs [HOEMIm][NTf$_2$] and [AMIm][NTf$_2$] expressed proper selectivities. As seen in Fig. 3(b), the D values obtained for [C$_{12}$MIm][NTf$_2$]/DMF-*n*-hexane biphasic system, was significantly larger than other ILs, such as the $D_{\mathrm{C20:5}}$ value of 0.67, while selectivity was the smallest, less than 3.8. Li's work[44] showed the similar trend that distribution coefficient of C18 : 3 increased with an increase in the IL hydrophobicity (*i.e.*, carbon chain length in the cation), when ILs share the same anion. A conclusion was drawn that introducing the dodecyl chain in the cation can significantly increase distribution coefficients, but decrease selectivities. Because the dodecyl chain in the cation greatly increased ILs' affinity for FAMEs, which on one hand decreased ILs' polarity, on the other hand increased ILs' van der Waals interaction with FAMEs.



(a)

(b)

Fig. 3 Effect of the functional group in IL's cation on the selectivities (a) and distribution coefficients (b). The initial concentration of FAMEs in *n*-hexane was 40 mg mL^{-1}. Volume ratio of feed solvent and extractant was 1 : 1. The extraction temperature was 30 °C. The mole ratio of IL to DMF was 1 : 9.

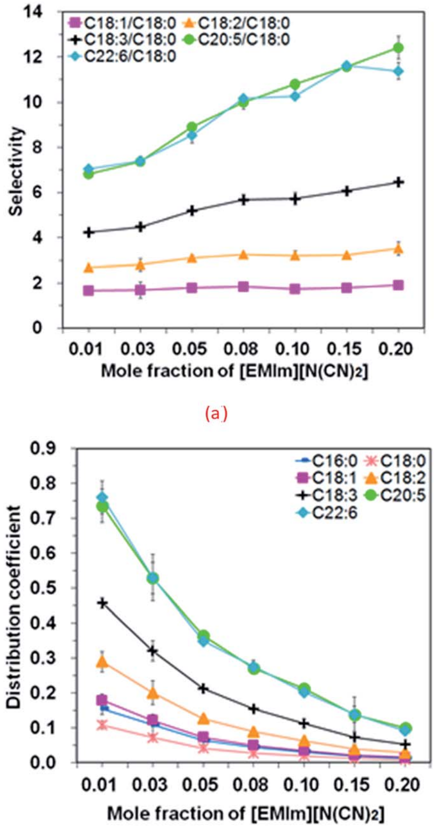
3.4. Effect of the mole fraction of IL in the extraction solvent on the extraction equilibrium

It is worth mentioning that the separation efficiency is closely related to the mole fraction of IL in the extraction solvent, so proper selectivities and distribution coefficients could be obtained by altering the composition ratio of IL-cosolvent.

From Fig. 4, when the mole fraction of IL in the extraction solvent increased from 2.5% to 20%, $S_{\mathrm{C20:5/C18:0}}$ increased remarkably from 6.8 to a surprising value of 12.4, and in contrast the distribution coefficient of C20 : 5 $D_{\mathrm{C20:5}}$ decreased drastically from 0.74 to 0.10. This finding is partially attributed to the fact that the mole fraction of IL affected the polarity of mixed extraction solvents. With the increase of the mole fraction of IL, the polarity of extraction solvents enhanced, and thus greatly decreased ILs' affinity for liposoluble FAMEs, reducing distribution coefficients, besides more and more ILs can form specific π–π interaction with the unsaturated double bonds of FAMEs, and thus enhance the molecular recognition ability of ILs for double bonds, increasing the selectivity.

3.5. Effect of the initial concentration of FAMEs on the extraction equilibrium

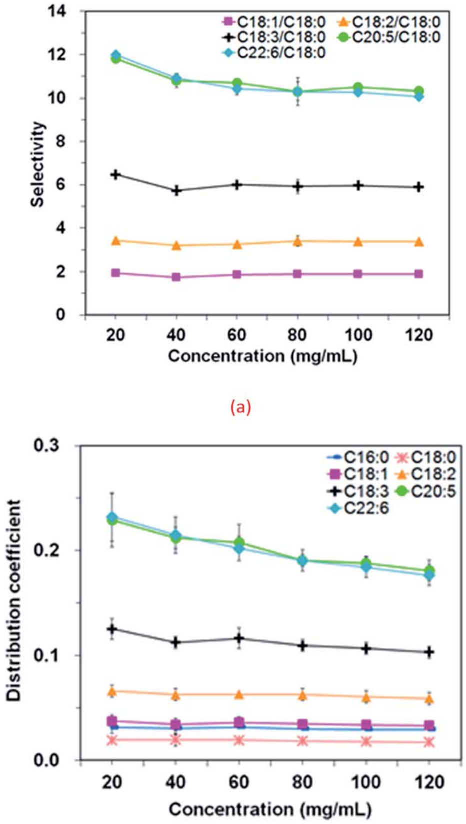
The effects of feedstock concentration of total FAMEs were investigated using [EMIm][N(CN)$_2$]/DMF-*n*-hexane biphasic system as a model system at 30 °C, as shown in Fig. 5. The mole fraction of [EMIm][N(CN)$_2$] in the extraction solvent was 10%. As seen in Fig. 5, the selectivities and distribution coefficients decreased slightly with the increase of the concentration of FAMEs. Manic[45] also found the same trend that, distribution coefficient of linoleic acid and selectivity $S_{\text{linoleic acid/soybean oil}}$ decreased as initial acid content of oil increased. For example, when the initial concentration of FAMEs varied from 20 mg mL^{-1} to 120 mg mL^{-1}, $S_{\mathrm{C22:6/C18:0}}$ decreased gradually from 12.0 to 10.1 and $D_{\mathrm{C20:5}}$ decreased from 0.23 to 0.18. Therefore, the separation efficiency is not notably affected by the variation of feedstock concentration, which is quite beneficial for industrial applications.



(a)

(b)

Fig. 4 Effect of the mole fraction of [EMIm][N(CN)$_2$] in the extraction solvent on the selectivities (a) and distribution coefficients (b). The initial concentration of FAMEs in *n*-hexane was 40 mg mL^{-1}. Volume ratio of feed and extraction solvent was 1 : 1. The extraction temperature was 30 °C. The cosolvent was DMF.



(a)

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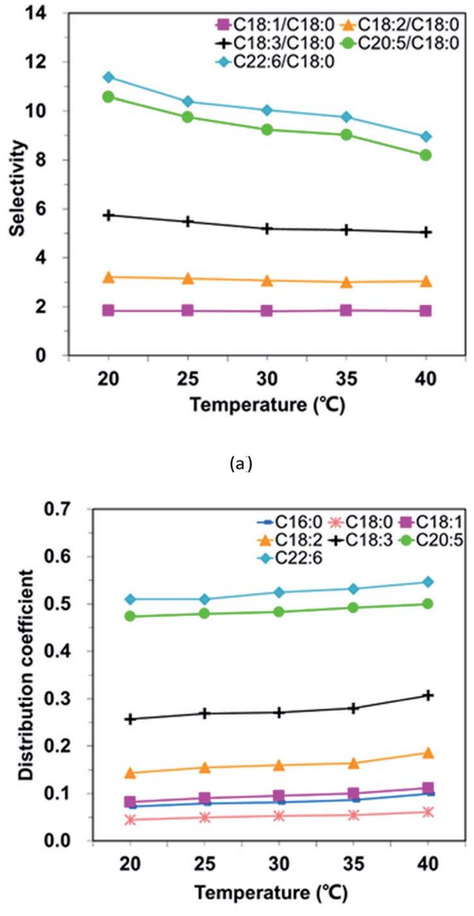
Fig. 5 Effect of the initial concentration of FAMEs on the selectivities (a) and distribution coefficients (b). Volume ratio of feed and extraction solvent was 1 : 1. The extraction temperature was 30 °C. The mole ratio of [EMIm][N(CN)$_2$] to DMF was 1 : 9.

3.6. Effect of temperature on the extraction equilibrium

The selectivities and distribution coefficients of FAMEs in the [EMIm][N(CN)$_2$]/DMF-*n*-hexane biphasic system at different temperatures are presented in Fig. 6. The results demonstrated that temperature had little effect on the extraction. It can be seen that the selectivities of other FAMEs to C18 : 0 declined slightly with the increase of temperature. For example, $S_{\mathrm{C18:3/C18:0}}$ dropped from 5.7 to 5.0, when the



(a)

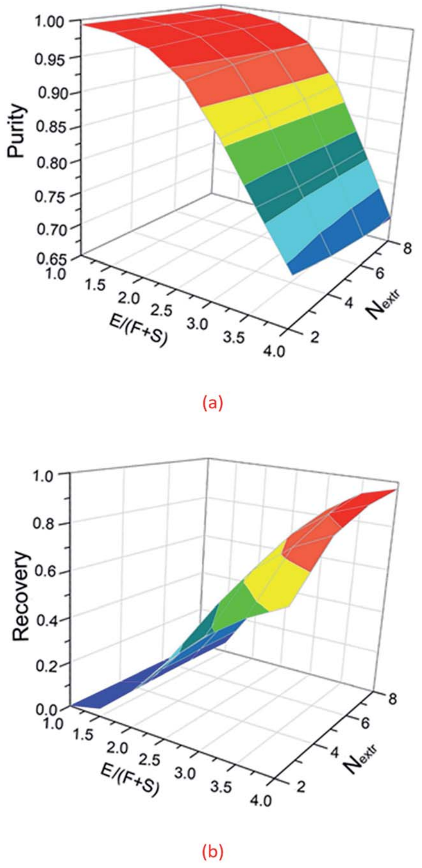
(b)

Fig. 6 Effect of the extraction temperature on the selectivities (a) and distribution coefficients (b). The initial concentration of FAMEs in *n*-hexane was 40 mg mL^{-1}. Volume ratio of feed and extractant was 1 : 1. The mole ratio of [EMIm][N(CN)$_2$] to DMF was 5 : 95.

temperature increased from 20 °C to 40 °C. In contrast, the distribution coefficients of FAMEs increased slightly as the temperature increased. For instance, $D_{\mathrm{C20:5}}$ went up gradually from 0.47 to 0.50 with the temperature increasing from 20 °C to 40 °C.

3.7. Fractional extraction process: design

In order to evaluate the feasibility of separating uFAMEs from bio-oils in continuous extraction processes, fractional extraction was simulated by calculations. The purity and recovery of target products (C20 : 5 + C22 : 6) in the extraction phase were used as the key parameters to evaluate the performance of fraction extraction process. During the calculation, the mass balance and mass transfer of C20 : 5 + C22 : 6 were taken into consideration, other factors such as mutual solubilities of the biphasic systems and heat balance were ignored. The distribution coefficients of FAMEs used for the calculations were under the condition that the mole fraction of [EMIm][N(CN)$_2$] was 5% in the extraction solvent at 30 °C. The calculation results plotted in Fig. 7 reveal the purity and recovery of C20 : 5 + C22 : 6 as a function of extraction stages (N_{extr}) and volume flow ratio ($E/(F + S)$). E, F and S represent the flow rate of extraction, feed and scrubbing solvent, respectively. It is obvious that C20 : 5 + C22 : 6 could be separated from the FAMEs with high purity and recovery under optimized conditions by fractional extraction process.



(a)

(b)

Fig. 7 The purity (a) and recovery (b) of C20 : 5 + C22 : 6. The extraction solvent was the mixture of [EMIm][N(CN)$_2$] and DMF, and the mole fraction of [EMIm][N(CN)$_2$] was 5%. The scrubbing solvents was *n*-hexane. The scrubbing stages were 8. The flow rates of feed and extraction solvents were 1 and 2 mL min^{-1}, respectively.

As the data presented in Fig. 7(a), with constant extraction stages, the purity of C20 : 5 + C22 : 6 declined drastically with the increase of volume flow ratio. With constant volume flow ratio, the purity decreased slightly along with the increase of extraction stages. As the results showed in Fig. 7(b), with constant extraction stages, the recovery of C20 : 5 + C22 : 6 tended to increase sharply with increasing volume flow ratio. Besides, with constant volume flow ratio, the recovery increased along with the increase of extraction stages. This was possibly because the volume flow of extraction solvents increased with the increase of volume flow ratio, which improved extractants' ability to extract C20 : 5 + C22 : 6. In addition, when extraction stages went up, extractants' ability to extract C20 : 5 + C22 : 6 was improved, resulting in the increase of recovery.

4. Conclusions

The separation performance of the ILs/cosolvent-*n*-hexane biphasic systems on the mixture of FAMEs was evaluated. Satisfactory selectivities were obtained with mixed extractants even at high feedstock concentration. The experimental data showed that the structure of ILs had a significant influence on the selectivity and distribution coefficient. The selectivity was mainly affected by ILs' anions. When CN group existed in ILs' anion, ILs/DMF-*n*-hexane biphasic system expressed high separation selectivities. For instance, $[EMIm][N(CN)_2]$/DMF demonstrated excellent separation selectivities, as the selectivity of C20 : 5 to C18 : 0 reached up to an outstanding value of 11.7, when the mole ratio of IL to DMF was 1 : 9, at least twice the value (5.6) using DMF as the extractant.

In order to evaluate the feasibility of liquid–liquid extraction for practical application, the fractional extraction was performed by the process calculation. The results showed that both high purity and high recovery of products could be obtained by adjusting the process parameters, indicating that fractional extraction is promising to separate highly uFAMEs from FAMEs in industrial applications.

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